

## The Cyclosilylation of Methylcatechols with Dichlorodiorganosilanes

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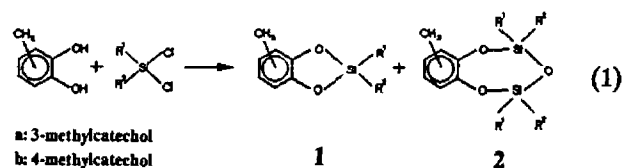
Because the extensive  $\sigma\pi$ - $\pi\sigma$  interaction between silicon and oxygen, the monomeric five-membered ring products, (methyl-1,2-phenylenedioxy)diorganosilanes, rather than dimers were synthesized from methylcatechols and dichlorodiorganosilanes. In addition to the five-membered ring products, the more stable seven-membered-ring cyclodisiloxanes were found. From the X-ray diffraction data of these seven-membered-ring disiloxanes, the latter were found to be free of ring strain and to have better conjugation than the five-membered ring species in the Si-O-C(Ar) moiety of the molecules.

### INTRODUCTION

For many years there have been conflicting reports about the nature and properties of (1,2-phenylenedioxy)silanes.<sup>1-4</sup> It was found that large strain of the five-membered ring caused the instability. According to the literature, (1,2-phenylenedioxy)silanes were obtained more readily as dimers than monomers<sup>1-4</sup> and a reversible dissociation of dimer into monomer might take place at elevated temperatures.<sup>5-8</sup> Catechols with substituents that might increase the stability of the monomeric product were used to obtain the monomeric product without dimer. It is well known that electron-donating groups in substituted phenoxysilanes increase the stability of the Si-O-C bond and prevent hydrolysis.<sup>9,10</sup> As a methyl group is a weak electron donor, it is of interest to use methylcatechols to examine the result of its electron-donating effect. In this work, we have successfully synthesized the monomeric (methyl-1,2-phenylenedioxy)silanes without any dimeric products, a phenomenon which we attribute to the increased  $\sigma\pi$ - $\pi\sigma$  interaction between silicon and oxygen in the methyl substituted monomeric products. However, in our experiments, in addition to the (methyl-1,2-phenylenedioxy)silanes with a five-membered ring, new disiloxanes with a seven-membered ring were found in the reaction products. The structures of seven-membered-ring disiloxanes, 1,5-(methyl-1',2'-phenylenedioxy)-2,2,4,4-tetraphenyldisiloxanes, were determined by single-crystal X-ray diffraction (Figs. 1 and 2). It revealed that there was no ring strain in the seven-membered ring, and the  $\sigma\pi$ - $\pi\sigma$  interaction existing between silicon and oxygen played an important role in the stabilization of such compounds.

### RESULTS AND DISCUSSION

Methylcatechols reacted smoothly with dichlorodiorganosilanes in the presence of pyridine to produce the (methyl-1,2-phenylenedioxy)diorganosilanes with a five-membered ring as we expected. In addition, 1,5-(methyl-1',2'-phenylenedioxy)-2,2,4,4-tetraorganodisiloxanes with a seven-membered ring were also obtained as one of the major products (Eq. 1).



The crude products were not separable into their components by distillation, and one of them, the five-membered-ring silane, decomposed during the isolation process of column chromatography. Thus all these products were identified by GC and GC-MS. Table 1 shows the fragments of major products.

The relative yields of the reactions determined by GC are shown in Table 2. Two seven-membered-ring disiloxanes, 1,5-(3'-methyl-1',2'-phenylenedioxy)-2,2,4,4-tetraphenyldisiloxane and 1,5-(4'-methyl-1',2'-phenylenedioxy)-2,2,4,4-tetraphenyldisiloxane, were isolated by recrystallization. Tables 3 and 4 show the bond angles of the two compounds obtained from the single-crystal analysis by X-ray diffraction.

The significance of different results between pyrocatechol and methylcatechols was concerned to the

Table 1. Mass-spectral Data of Products

Product	R <sup>1</sup> , R <sup>2</sup>	Characteristic Peak					
1a	Me, Me	180 <sup>a</sup>	165 <sup>b</sup>	149	133	119	
1a	Me, Ph	242 <sup>ab</sup>	227	165	149	77	
1a	Ph, Ph	304 <sup>ab</sup>	227	149	77		
1b	Me, Me	180 <sup>a</sup>	165 <sup>b</sup>	149	133	119	
1b	Me, Ph	242 <sup>ab</sup>	227	165	149	77	
1b	Ph, Ph	304 <sup>ab</sup>	227	149	77		
2a	Me, Me	254 <sup>a</sup>	239 <sup>b</sup>	165	133	119	
2a	Me, Ph	378 <sup>ab</sup>	363	301	285	257	242
			227	195	165	77	
2a	Ph, Ph	502 <sup>ab</sup>	425	347	319	227	77
2b	Me, Me	254 <sup>a</sup>	239 <sup>b</sup>	165	133	119	
2b	Me, Ph	378 <sup>ab</sup>	363	301	285	257	195
			165	77			
2b	Ph, Ph	502 <sup>a</sup>	425	347 <sup>b</sup>	319	227	77

<sup>a</sup> Molecular peak. <sup>b</sup> Base peak.

generation of the dimeric species. The former produced dimers as major products whereas the latter produced no dimers except traces in the reaction of 3-methylcatechol with dichloromethylphenylsilane. These results are indeed explained by the effect of the electron-donating ability of the methyl group present in the methylcatechols. Because of this ability, the phenylenedioxy group of methylcatechols has greater electron density than that of pyrocatechol, leading to the increased electron donation to the silicon atom. This enhanced  $p\pi-d\pi$  interaction between silicon and oxygen thus stabilized the products and prevented them

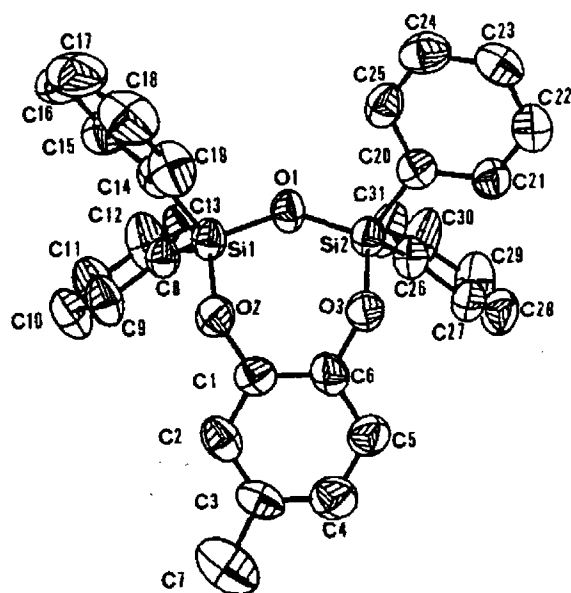


Fig. 1. ORTEP of 1,5-(4'-methyl-1',2'-phenylenedioxy)-2,2,4,4-tetraphenyldisiloxane.

Table 2. The Relative Yields of Products<sup>a</sup>

Starting Material	Silane	Major Products		Residue	
		1(%)	2(%)	Catechol	Others
3-Methylcatechol	Me <sub>2</sub> SiCl <sub>2</sub>	53.42	28.43	14.52	1.10 <sup>b</sup>
	MePhSiCl <sub>2</sub>	60.12	30.84	5.74	1.29 <sup>c</sup>
	Ph <sub>2</sub> SiCl <sub>2</sub>	49.48	26.80	23.71	0.00 <sup>c</sup>
4-Methylcatechol	Me <sub>2</sub> SiCl <sub>2</sub>	13.64	52.64	18.43	9.11 <sup>b</sup>
	MePhSiCl <sub>2</sub>	23.11	50.83	12.54	11.43 <sup>c</sup>
	Ph <sub>2</sub> SiCl <sub>2</sub>	13.69	69.67	10.25	6.15 <sup>c</sup>

<sup>a</sup> Determined by GC. <sup>b</sup> Various siloxanes. <sup>c</sup> D<sub>3</sub> and D<sub>4</sub>.

from polymerizing to dimer or polymer.

The yields of (methyl-1',2'-phenylenedioxy)methylphenylsilanes were the greatest among all products (Table 2). This result arose because the electrons of the phenyl group substituted on silicon were able to delocalize through the silicon atom to the phenylenedioxy group so as to enhance the  $d\pi-p\pi$  interaction and to produce extra stabilization energy. However, such an effect might be cancelled by the steric effect of two phenyl groups substituted on the same silicon atom. The total yields of 1 and 2 obtained from 3-methylcatechol and dichlorodiorganosilanes were greater than those from 4-methylcatechol and dichlorodiorganosilanes. This fact can be explained by the greater solubility of 3-methylcatechol than of 4-methylcatechol in benzene and pyridine.

Furthermore, there were other important products of the reactions. These were the 1,5-(methyl-1',2'-phenylenedioxy)-2,2,4,4-tetraorganodisiloxanes with a seven-membered ring. These compounds were found originally at

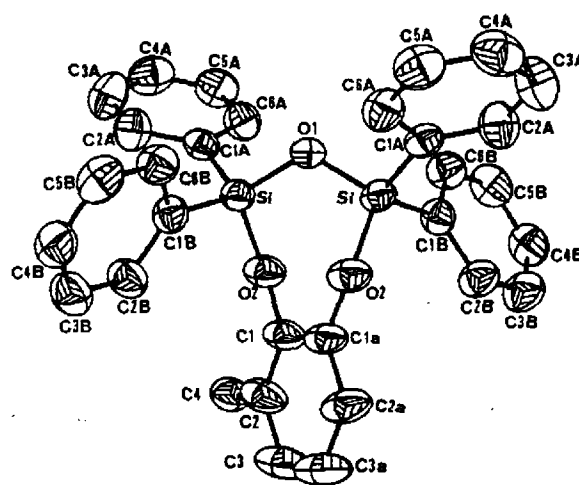


Fig. 2. ORTEP of 1,5-(3'-methyl-1',2'-phenylenedioxy)-2,2,4,4-tetraphenyldisiloxane.

Table 3. Bond Angles/Degrees of 1,5-(4'-Methyl-1',2'-phenylenedioxy)-2,2,4,4-tetraphenyldisiloxane

O(1)-Si(1)-O(2)	107.5(4)	C(8)-C(9)-C(10)	121.7(13)
O(1)-Si(1)-C(8)	110.0(9)	C(9)-C(10)-C(11)	120.2(10)
O(1)-Si(1)-C(20)	111.6(4)	C(10)-C(11)-C(12)	119.8(8)
O(2)-Si(1)-C(8)	110.7(4)	C(11)-C(12)-C(13)	120.3(13)
O(2)-Si(1)-C(20)	104.9(9)	C(8)-C(13)-C(12)	121.1(10)
C(8)-Si(1)-C(20)	111.8(3)	Si(2)-C(14)-C(21)	120.0(4)
O(1)-Si(2)-O(3)	109.3(8)	Si(2)-C(14)-C(25)	123.6(5)
O(1)-Si(2)-C(14)	111.20(24)	C(21)-C(14)-C(25)	116.4(5)
O(1)-Si(2)-C(26)	109.0(7)	C(16)-C(15)-C(20)	122.4(11)
O(3)-Si(2)-C(14)	104.0(6)	C(15)-C(16)-C(17)	118.0(8)
O(3)-Si(2)-C(26)	109.9(5)	C(16)-C(17)-C(18)	121.1(9)
C(14)-Si(2)-C(26)	113.3(8)	C(17)-C(18)-C(19)	121.1(11)
Si(1)-O(1)-Si(2)	135.2(9)	C(18)-C(19)-C(20)	119.2(7)
Si(1)-O(2)-C(1)	126.7(12)	Si(1)-C(20)-C(15)	121.3(9)
Si(2)-O(3)-C(6)	124.2(8)	Si(1)-C(20)-C(19)	120.6(5)
O(2)-C(1)-C(2)	119.5(8)	C(15)-C(20)-C(19)	118.1(8)
O(2)-C(1)-C(6)	120.9(6)	C(14)-C(21)-C(22)	122.1(6)
C(2)-C(1)-C(6)	119.5(6)	C(21)-C(22)-C(23)	119.6(6)
C(1)-C(2)-C(3)	121.0(7)	C(22)-C(23)-C(24)	120.4(5)
C(2)-C(3)-C(4)	119.1(7)	C(23)-C(24)-C(25)	120.0(6)
C(2)-C(3)-C(7)	123.1(8)	C(14)-C(25)-C(24)	121.5(6)
C(4)-C(3)-C(7)	117.8(7)	Si(2)-C(26)-C(27)	121.8(10)
C(3)-C(4)-C(5)	120.8(6)	Si(2)-C(26)-C(31)	120.9(6)
C(4)-C(5)-C(6)	118.9(7)	C(27)-C(26)-C(31)	117.3(12)
O(3)-C(6)-C(1)	120.3(5)	C(26)-C(27)-C(28)	121.4(11)
O(3)-C(6)-C(5)	119.0(7)	C(27)-C(28)-C(29)	119.7(7)
C(1)-C(6)-C(5)	120.6(7)	C(28)-C(29)-C(30)	120.6(12)
Si(1)-C(8)-C(9)	119.6(11)	C(29)-C(30)-C(31)	119.7(11)
Si(1)-C(8)-C(13)	123.4(8)	C(26)-C(31)-C(30)	121.3(7)
C(9)-C(8)-C(13)	116.9(8)		

Table 4. Bond Angles/Degrees of 1,5-(3'-Methyl-1',2'-phenylenedioxy)-2,2,4,4-tetraphenyldisiloxane

O(1)-Si-O(2)	106.69(9)	Si-C(1A)-C(6A)	121.51(17)
O(1)-Si-C(1A)	108.45(9)	C(2A)-C(1A)-C(6A)	116.80(21)
O(1)-Si-C(1B)	112.18(8)	C(1A)-C(2A)-C(3A)	121.18(24)
O(2)-Si-C(1A)	107.64(9)	C(2A)-C(3A)-C(4A)	120.7(3)
O(2)-Si-C(1B)	109.07(9)	C(3A)-C(4A)-C(5A)	119.20(25)
C(1A)-Si-C(1B)	112.55(10)	C(4A)-C(5A)-C(6A)	119.90(24)
Si-O(1)-Si(a)	121.93(12)	C(1A)-C(6A)-C(5A)	122.19(23)
Si-O(2)-C(1)	130.62(14)	Si-C(1B)-C(2B)	120.25(16)
O(2)-C(1)-C(1a)	122.00(19)	Si-C(1B)-C(6B)	122.04(17)
O(2)-C(1)-C(2)	117.08(24)	C(2B)-C(1B)-C(6B)	117.64(19)
C(1a)-C(1)-C(2)	120.91(23)	C(1B)-C(2B)-C(3B)	121.09(21)
C(1)-C(2)-C(3)	117.6(3)	C(2B)-C(3B)-C(4B)	120.32(23)
C(1)-C(2)-C(4)	122.9(3)	C(3B)-C(4B)-C(5B)	119.81(22)
C(3)-C(2)-C(4)	119.5(3)	C(4B)-C(5B)-C(6B)	120.54(22)
C(2)-C(3)-C(3a)	121.47(24)	C(1B)-C(6B)-C(5B)	120.58(22)
Si-C(1A)-C(2A)	121.69(17)		

the beginning of the reaction, and the ratio 1/2 increased as the reaction proceeded. The single-crystal analysis by X-ray diffraction revealed the reason for the stability of these disiloxanes. From Tables 3 and 4, the bond angles of silicon are all in the range 106-112°; all similar to those of octamethyltetrasiloxane ( $D_4^{Me}$ ) ( $O-Si-O = 109^\circ$ ,  $C-Si-C = 109 \pm 4^\circ$ ) lacking ring strain.<sup>11</sup> A stable skeleton was displayed without ring strain and twist or other significant steric effects. In addition, the bond angles at oxygen atoms showed that the bonding type of oxygen was  $sp^2$ . These data indicate that electrons delocalize through the Si-O-Ar bond; thus the  $p\pi-d\pi$  interaction indeed existed. This fact explains that the seven-membered-ring disiloxanes are more stable than the five-membered-ring silanes.

## EXPERIMENTAL SECTION

Melting points were determined on a Buchi 520 in-

strument and are uncorrected. IR spectra were taken of a KBr pellet or the neat oil on a Perkin-Elmer 983G or 1310 Infrared spectrophotometer.  $^1H$  NMR spectra of solutions in  $CCl_4$  with tetramethylsilane as the internal standard were recorded on a Varian EM-390 spectrometer. When the multiplicities of peak are reported, the following abbreviations are used: *s*, singlet; *m*, multiplet. Gas chromatography was carried out on a Hewlett-Packard 5890A instrument using a HP series 530  $\mu$  methylsilicone 10M column. GC-MS was carried out on a Finnigan TSQ46C instrument with a capillary SE-54 20M column. X-ray diffraction measurements were made on an Enraf-Nonius CAD-4 diffractometer using graphite-monochromated radiation with the  $\theta$ - $2\theta$  scan mode. Other relevant experimental data appear in Table 5. Silanes and solvents were obtained commercially and were subjected to distillation. Methylcatechols were obtained from Tokyo Kasei and desiccated under reduced pressure at 40-50°C before use.

## Procedure for the reactions of methylcatechols and dichlorodiorganosilanes

A solution of dichlorodiorganosilane (0.0161 mol) in benzene (30 mL) was added dropwise, with stirring, to a solution of methylcatechol (0.0161 mol) and pyridine (0.0325 mol) in benzene (30 mL). The resulting solution was stirred for 20 h. After reaction, the pyridine salt of hydrochloride was filtered off under reduced pressure. The crude products were analyzed by IR and GC, then were identified by GC-MS. Crystalline solids were found from the reactions of dichlorodiphenylsilane. Recrystallization

Table 5. Crystal Data

Compound	2b	2a
Formula	Si <sub>2</sub> O <sub>3</sub> C <sub>31</sub> H <sub>26</sub>	Si <sub>2</sub> O <sub>3</sub> C <sub>31</sub> H <sub>26</sub>
Cryst. size (mm)	0.1x0.25x0.33	0.3x0.5x0.5
Lattice	Orthorhombic	Monoclinic
Space group	P na <sub>2</sub> 1	C 2/c
a (Å)	20.596(3)	17.838(10)
b (Å)	13.135(2)	9.497(3)
c (Å)	9.922(3)	18.340(11)
β (°)		123.69(3)
Volume (Å <sup>3</sup> )	2684.4(9)	2585.2(23)
Z	4	4
F(000)	1055.87	1055.87
Temperature	300 K	300 K
Fw	502.71	502.71
Dcalc.(g/cm <sup>3</sup> )	1.24	1.29
μ (mm <sup>-1</sup> )	1.43	0.16
2θ <sub>max</sub>	130	50
Octants (h, k, l)	+ 24, 15, 11	-21-17, 11, 21
λ (Å)	1.5418(Cu-Kα)	0.7107(Mo-Kα)
No. of unique reflns	2423	2262
No. of obs. reflns	1832 (> 2.5σ)	1969 (> 2.5σ)
No. of variables	327	169
R(F)	0.040	0.040
Rw(F)	0.046	0.060
S	1.89	3.47

from ethyl acetate, containing minimal benzene, afforded 1,5-(3'(or 4')-methyl-1',2'-phenylenedioxy)-2,2,4,4-tetra-phenyldisiloxanes as colorless crystals.

**1,5-(4'-Methyl-1',2'-phenylenedioxy)-2,2,4,4-tetraphenyl-disiloxane**

mp 102-103°C; IR 1426 (strong, Si-Ph), 1212 (strong, Si-O-Ar), 1119 (strong, Si-Ph), 922 (strong, Si-O-Ph) cm<sup>-1</sup>; <sup>1</sup>H NMR δ 7.28-7.63 (m, 20H), 6.69 (m, 3H), 2.12 (s, 3H); MS m/z 502 (molecular peak), 425 (-C<sub>6</sub>H<sub>5</sub>), 347 (base peak, -2C<sub>6</sub>H<sub>5</sub>), 77 (C<sub>6</sub>H<sub>5</sub>); Crystal analysis (Fig. 1): orthorhombic; space group, P na<sub>2</sub>1; Z = 4; unit-cell dimensions: a = 20.596(3)Å, b = 13.135(2)Å, c = 9.922(3)Å.

**1,5-(3'-Methyl-1',2'-phenylenedioxy)-2,2,4,4-tetraphenyl-disiloxane**

mp 142-142.4°C; IR 1427 (strong, Si-Ph), 1207 (strong, Si-O-Ar), 1117 (strong, Si-Ph), 919 (strong, Si-O-Ar) cm<sup>-1</sup>; <sup>1</sup>H NMR δ 7.35-7.65 (m, 20H), 6.75 (m, 3H), 2.03 (s, 3H); MS m/z 502 (molecular peak and base peak), 425

(-C<sub>6</sub>H<sub>5</sub>), 347 (-2C<sub>6</sub>H<sub>5</sub>), 77 (C<sub>6</sub>H<sub>5</sub>); Crystal analysis (Fig. 2): monoclinic; space group, C 2/c; Z = 4; unit-cell dimensions: a = 17.840(1)Å, b = 9.497(3)Å, c = 18.340(1)Å.

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# Key Words

Cyclosilylation; (Methyl-1,2-phenylenedioxy)dior-ganosilanes.

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