

1,4-Dihydroxyoctaphenyltetrasilane, a stable polysilane- α,ω -diol

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Abstract

1,4-Dihydroxyoctaphenyltetrasilane is obtained in 60% yield by treating a solution of 1,4-dichlorooctaphenyltetrasilane in THF with dilute HCl. Spectroscopic properties of the title compound are reported together with an X-ray structure determination, which shows that there is an intramolecular hydrogen bond between the 2 OH groups. This structural feature accounts for the ease with which the compound loses water to form the heterocyclic siloxane octaphenyloxacyclopentasilane.

Introduction

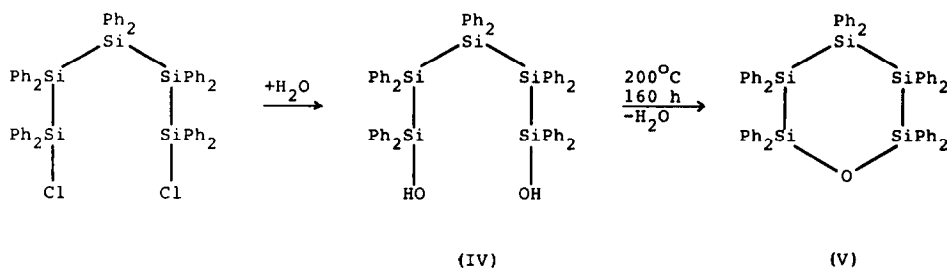
An outstanding characteristic of silanols is the ease with which they usually condense to siloxanes [1]. The stability of organosilanols concerning this condensation increases in the order $\text{RSi(OH)}_3 < \text{R}_2\text{Si(OH)}_2 < \text{R}_3\text{SiOH}$ for a given organic group R, and it also increases with the size of the organic substituents attached to the Si atom.

Few silanols containing Si–Si bonds are known, but the compounds of the series $\text{OH(SiPh}_2)_n\text{OH}$, where members with $n = 2, 3, 5, 6$ have been reported [2–5]. However, attempts to isolate 1,4-dihydroxyoctaphenyltetrasilane (II) failed. The compound is described as being very unstable, readily losing water to yield the heterocyclic siloxane octaphenyloxacyclopentasilane (III). During investigations on heterocyclic silanes and their properties we synthesized decaphenyloxacyclohexasilane (V) [6] and determined its X-ray structure [7]. While trying to do the same for

III we discovered that the title compound II is a stable compound and can easily be isolated, although the outcome of attempts to make it depends strongly on the solvent used. Thus we were able to characterize this compound and to determine its X-ray structure.

Synthesis

Treatment of 1,5-dichlorodecaphenylpentasilane with H_2O in THF gives the stable α,ω -diol 1,5-dihydroxydecaphenylpentasilane (IV) in nearly quantitative yields [6]. To bring about elimination of water to form the heterocycle V requires prolonged heating in vacuum (Scheme 1). After 160 h at 200°C and 10^{-2} Torr the OH signal near δ 1.5 ppm in ^1H NMR has disappeared. The IR spectrum shows new bands at 900 and 640 cm^{-1} , respectively, assigned to ν_s and $\nu_{as}(\text{Si}-\text{O}-\text{Si})$ in place of the bands at 3560 cm^{-1} ($\nu(\text{OH})$) and 800 cm^{-1} ($\nu(\text{Si}-\text{O})$) in the spectrum of the diol. The melting point increases from 170 to 374°C . The structure of V has been determined by X-ray diffraction [7]. The corresponding tetrasilane derivatives behave differently (Scheme 2). Hydrolysis of 1,4-diiodooctaphenyltetrasilane yielded only the heterocycle III and isolation of the α,ω -diol intermediate II was not possible [5]. The outcome of the hydrolysis of the less reactive 1,4-dichlorooctaphenyltetrasilane I, however, strongly depends on the solvent used. In benzene I proved to be remarkably resistant to water (Table 1); even after stirring a benzene solution of I with 1 *M* aqueous HCl for 1 week at room temperature only starting material was recovered. After 4 days at reflux temperature, about 20% of III was present along with 80% of the starting material, and again no open chain α,ω -diol



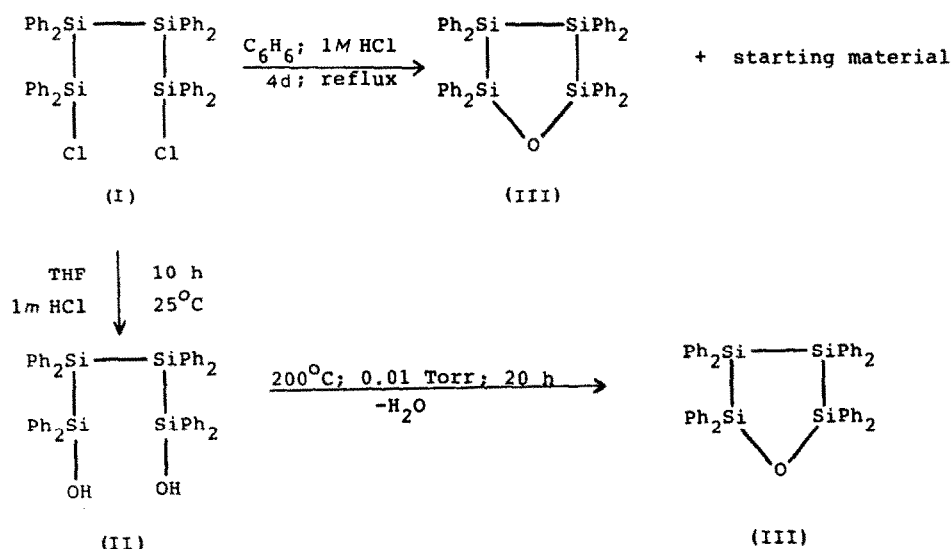
Scheme 1

Table 1
Hydrolysis of α,ω -dihalooctaphenyltetrasilanes

Starting material	Solvent	Reaction ^a conditions	Products
$\text{I}(\text{SiPh}_2)_4\text{I}$	C_6H_6 ^b	2 h/reflux	$\text{Si}_4\text{Ph}_8\text{O}$ (III) 95%
$\text{Cl}(\text{SiPh}_2)_4\text{Cl}$	C_6H_6	1 week/ 25°C	starting material
		4 days/reflux	$\text{Si}_4\text{Ph}_8\text{O}$ (III) 20% ^c + starting material
	THF	10 h/ 25°C	$\text{HO}(\text{SiPh}_2)_4\text{OH}$ (II) 60% ^c + $\text{Si}_4\text{Ph}_8\text{O}$ (III) 40%

^a Reaction mixtures were stirred. ^b Triethylamine was used in stoichiometric amount as HI acceptor.

^c Separation of product mixtures was achieved by recrystallization from benzene/*n*-hexane mixtures.



Scheme 2

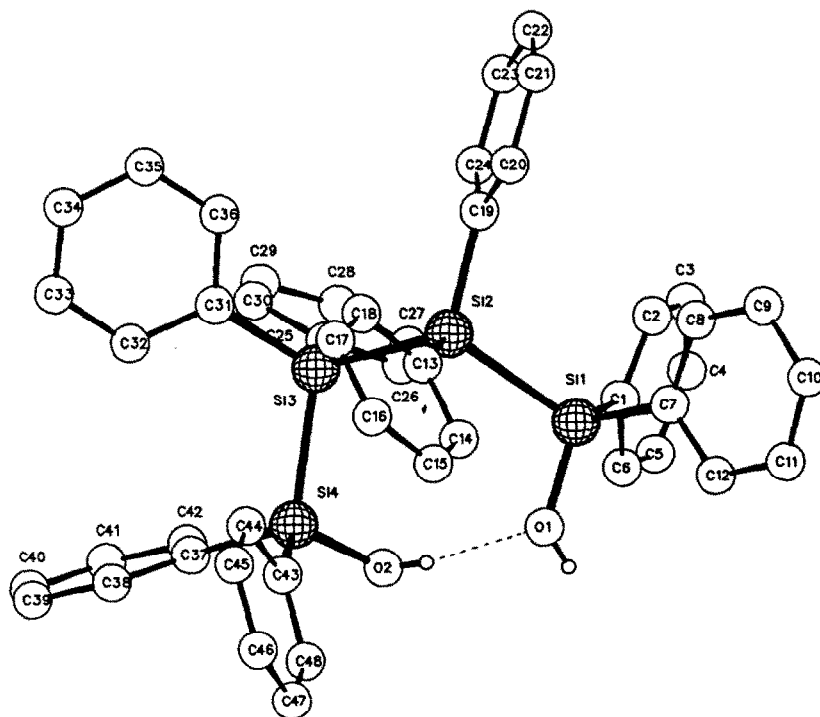


Fig. 1. A molecular diagram showing the numbering of the atoms. Hydrogen atoms (except OH hydrogens) are omitted for clarity.

was observed. When THF was used instead of benzene the outcome was different and stirring of a solution of I in THF with 1 M HCl overnight gave ca. 60% of II along with 40% of III (Scheme 2). Isolation of pure II was achieved by recrystallization from 1/3 benzene/hexane. In addition to absorptions arising from the phenyl rings and the Si skeleton, the IR spectrum of II shows characteristic bands at 3500 and 800 cm^{-1} , which are assigned to $\nu(\text{OH})$ and $\nu(\text{Si}-\text{O})$ vibrations, respectively. The ^1H and ^{29}Si NMR data (see Experimental) are also consistent with the structure proposed. The ring closure on heating proceeds much faster than that of the pentasilane derivative IV. When compound II was kept for 20 h at 200 °C by 10^{-2} Torr the heterocycle III was obtained in quantitative yield. Attempts to determine the melting point of II (a procedure which is easy for IV) also failed because of the lower stability of II. This reduced stability of the tetrasilane diol may arise from steric effects. As can be seen from the X-ray structure of the molecule (Fig. 1), in the solid the ends of the Si chain lie very close together, allowing the formation of a hydrogen bond between the 2 OH groups (see next section), making the elimination of H_2O a very favourable process.

Crystal structure determination

Crystal data. $\text{C}_{48}\text{H}_{42}\text{O}_2\text{Si}_4$, F.W.: 763.2, a 1333.6(1), b 2093.5(2), c 1566.1(2) pm, β 104.93(2)°, monoclinic space group $P2_1/c$, $Z = 4$, $\mu(\text{Cu}-K_{\alpha})$ 154.18 pm 15.9 cm^{-1} , d_x 1.200 g cm^{-3} .

Intensity data, structure solution and refinement. Intensity data were collected on an Enraf-Nonius CAD4 computer controlled four-circle diffractometer using graphite monochromated $\text{Cu}-K_{\alpha}$ radiation. The structure was solved by direct methods [9] and Fourier techniques. The structure was refined by full-matrix least-squares using 6905 observed reflections ($I \geq 5\sigma(I)$). The final R values were 0.0614 (R) and 0.108 (R_w). The hydrogen atoms were placed at calculated positions except for those attached to the oxygen atoms which were located in a difference map. No hydrogen parameters were refined and no absorption correction was applied. The final atomic coordinates are reported in Table 2. Source of atomic scattering factors, and programs used are given in ref. 10.

The description of the crystal structure. The molecular structure is depicted in Fig. 1, the relevant bond lengths, bond angles, and torsion angles are shown in Table 3.

The mean Si-Si, Si-O and Si-C bond distances are 236.9(3), 164.7(4) and 187.6(3) pm. The Si(1)-Si(2) and Si(2)-Si(3) bonds are of equal length but the Si(3)-Si(4) bond is shorter by 0.7 pm. There is a similar difference between the two Si-O bonds (165.1(2) and 164.3(2) pm). These differences are to be attributed to steric effects rather than to the formation of the intramolecular hydrogen bond. The heterocycle V also contains two kinds of Si-Si bonds [6]: two longer ones (mean: 239.1(1) pm) which are adjacent to the oxygen atom, and two shorter ones lying between other Si-Si bonds (mean: 237.3(2) pm). The rather long Si-Si bonds in V are in a crowded part of the molecule which is of a flattened boat conformation.

The intramolecular hydrogen bond (O(1)...H(O2) 212 pm, O...H-O 170.9°) establishes a quasi-ring structure. The presence of the bulky phenyl rings shields the remaining OH hydrogen atom thus no intermolecular hydrogen bonds can be formed.

Table 2. Final fractional atomic coordinates ($\times 10^4$) for the non-hydrogen atoms and the OH hydrogen atoms ($\times 10^3$)

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
Si(1)	6715.4(5)	6051.3(3)	3834.0(4)	C(23)	6134(3)	7367(1)	821(2)
Si(2)	6668.1(4)	5716.7(3)	2376.4(4)	C(24)	6622(2)	6883(1)	1398(2)
Si(3)	8311.6(5)	5402.2(3)	2201.6(4)	C(25)	9270(1)	6081(1)	2364(1)
Si(4)	9062.2(5)	4671.4(3)	3335.6(4)	C(26)	9376(2)	6502(1)	3061(2)
O(1)	7287(1)	5481.5(9)	4507(1)	C(27)	10097(3)	7000(1)	3190(3)
O(2)	9208(1)	5071(1)	4269(1)	C(28)	10721(2)	7074(1)	2615(3)
C(1)	7431(1)	6818(1)	4183(1)	C(29)	10650(2)	6650(1)	1940(2)
C(2)	7140(2)	7393(1)	3749(2)	C(30)	9929(2)	6159(1)	1804(2)
C(3)	7680(2)	7951(1)	4039(2)	C(31)	8199(2)	5062(1)	1066(1)
C(4)	8518(2)	7947(1)	4753(2)	C(32)	8732(3)	4520(2)	923(2)
C(5)	8821(3)	7383(2)	5187(2)	C(33)	8697(4)	4302(2)	81(2)
C(6)	8287(2)	6826(1)	4905(2)	C(34)	8079(3)	4587(2)	-633(2)
C(7)	5352(1)	6130(1)	3938(1)	C(35)	7550(3)	5123(2)	-523(2)
C(8)	4609(2)	6463(1)	3328(1)	C(36)	7597(2)	5353(1)	306(2)
C(9)	3593(2)	6510(1)	3389(2)	C(37)	10378(1)	4427(1)	3240(1)
C(10)	3306(2)	6239(1)	4078(2)	C(38)	10533(2)	3809(1)	2949(2)
C(11)	4032(2)	5928(1)	4715(2)	C(39)	11483(2)	3627(1)	2822(2)
C(12)	5038(2)	5862(1)	4639(2)	C(40)	12288(2)	4063(2)	2962(2)
C(13)	5842(1)	4974(1)	2159(1)	C(41)	12155(2)	4668(1)	3249(2)
C(14)	5586(2)	4639(1)	2837(2)	C(42)	11197(2)	4864(1)	3379(2)
C(15)	5050(2)	4066(1)	2682(2)	C(43)	8301(2)	3932(1)	3377(2)
C(16)	4769(2)	3811(1)	1871(3)	C(44)	7631(2)	3667(1)	2614(2)
C(17)	4985(2)	4130(1)	1172(3)	C(45)	7105(3)	3107(1)	2642(3)
C(18)	5521(2)	4714(1)	1316(2)	C(46)	7224(3)	2802(2)	3423(3)
C(19)	6050(1)	6360(1)	1569(1)	C(47)	7875(4)	3033(2)	4194(2)
C(20)	4991(2)	6342(1)	1150(2)	C(48)	8406(3)	3608(3)	4157(2)
C(21)	4534(2)	6844(1)	570(2)	H(O1)	750	549	500
C(22)	5111(3)	7349(1)	434(2)	H(O2)	875	516	437

Table 3. Relevant bond distances, bond angles and torsion angles

<i>Bond distances (pm)</i>					
Si(1)–Si(2)	237.3(1)	Si(2)–Si(3)	237.1(1)	Si(3)–C(25)	188.5(3)
Si(1)–O(1)	164.3(2)	Si(2)–C(13)	188.5(2)	Si(3)–C(31)	188.5(3)
Si(1)–C(1)	187.4(3)	Si(2)–C(19)	188.5(3)	Si(4)–O(2)	165.1(2)
Si(1)–C(7)	187.5(2)	Si(3)–Si(4)	236.2(1)	Si(4)–C(37)	187.0(2)
				Si(4)–C(43)	186.1(3)
<i>Bond angles (°)</i>					
Si(2)–Si(1)–O(1)	107.2(1)	Si(2)–Si(3)–Si(4)	108.6(1)		
Si(2)–Si(1)–C(1)	114.7(1)	Si(2)–Si(3)–C(25)	113.0(1)		
Si(2)–Si(1)–C(7)	108.9(1)	Si(2)–Si(3)–C(31)	111.2(2)		
O(1)–Si(1)–C(1)	108.5(2)	Si(4)–Si(3)–C(25)	104.2(1)		
O(1)–Si(1)–C(7)	107.9(2)	Si(4)–Si(3)–C(31)	112.3(2)		
C(1)–Si(1)–C(7)	109.4(2)	C(25)–Si(3)–C(31)	107.4(2)		
Si(1)–Si(2)–Si(3)	113.4(1)	Si(3)–Si(4)–O(2)	105.6(1)		
Si(1)–Si(2)–C(13)	106.7(1)	Si(3)–Si(4)–C(37)	110.0(1)		
Si(1)–Si(2)–C(19)	109.5(1)	Si(3)–Si(4)–C(43)	115.8(2)		
Si(3)–Si(2)–C(13)	105.4(1)	O(2)–Si(4)–C(37)	108.1(2)		
Si(3)–Si(2)–C(19)	112.2(1)	O(2)–Si(4)–C(43)	109.3(2)		
C(13)–Si(2)–C(19)	109.5(2)	C(37)–Si(4)–C(43)	107.8(2)		
<i>Torsion angles (°)</i>					
Si(4)–Si(3)–Si(2)–Si(1)	50.0(1)				
O(1)–Si(1)–Si(2)–Si(3)	-52.4(1)				
O(2)–Si(4)–Si(3)–Si(2)	-62.2(1)				

Experimental

1,4-Dichlorooctaphenyltetrasilane (I) was made as described previously [8]. Its identity was confirmed by comparison of its IR and ^{29}Si NMR spectra with those of an authentic sample.

1,4-Dihydroxiocetaphenyltetrasilane (II)

To a solution of 4 g (5 mmol) of 1,4-dichlorooctaphenyltetrasilane in THF (100 ml) was added 30 ml of 1 M HCl. The mixture was stirred overnight at room temperature, 50 ml of ether was added and the organic layer was separated and dried over sodium sulfate. The solvent was removed in vacuum and the oily residue dissolved in 40 ml of benzene. The product was precipitated as a solid by addition of 120 ml of n-hexane, and 2.1 g (55%) of crude 1,4-dihydroxiocetaphenyltetrasilane was isolated. It was purified by repeated recrystallization from ethyl acetate.

M.p.: 160°C decomp.; ^1H NMR (C_6D_6 , TMS, 90 MHz): δ 5.82 (s, 2H, OH), 6.9–7.2, 7.4–7.7 ppm (m, 40 H, C_6H_5); ^{29}Si NMR (C_6D_6 , 17.88 MHz): δ –6.3 ppm (s), δ –40.9 ppm (s); IR (KBr, cm^{-1}): 3520 (m, $\nu(\text{OH})$), 820 (b, vs, $\nu(\text{SiO})$), 555 (m, $\nu(\text{SiSi})$); MS (70 eV): m/e (relative intensity): 762 (2, M^+), 744 (52, $M^+ - \text{H}_2\text{O}$), 580 (29, $M^+ - \text{SiPh}_2$), 398 (16, $M^+ - 2 \text{SiPh}_2$). Anal. found: Si, 14.77; C, 75.64; H, 5.65. $\text{Si}_4\text{C}_{48}\text{H}_{42}\text{O}_2$ calcd.: Si, 14.72; C, 75.54; H, 5.55%.

Ring closure reaction of II

A sample of II (1 g) was heated in a round bottom flask in vacuum (10^{-2} Torr) to 200°C with an oil bath. After 20 h the contents of the flask had solidified. The solid was dissolved in 10 ml of benzene and reprecipitated by addition of n-hexane, to yield 0.8 g of white crystals. Comparison of its ^{29}Si , ^1H NMR and IR spectra with those of octaphenylloxacyclopentasilane (III) showed that ring closure had taken place quantitatively.

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