Improved Synthesis of HOPh₂Si-SiPh₂OH and Crystal Structure Analyses of HOPh₂Si-SiPh₂OH and HOPh₂Si-SiPh₂O-Ph₂Si-SiPh₂OH·1/2C₆H₆

Reinhold Tacke, Joachim Heermann, Martin Penka, Ingo Richter, and Brigitte Wagner

Institut für Anorganische Chemie, Universität Würzburg,

Am Hubland, D-97074 Würzburg, Germany

Reprint requests to Prof. Dr. R. Tacke. E-mail: r.tacke@mail.uni-wuerzburg.de

Z. Naturforsch. 57 b, 731-735 (2002); received March 11, 2002

Disilanes, Silanols, Siloxanes

1,1,2,2-Tetraphenyldisilane-1,2-diol (3) was prepared in a two-step synthesis, starting from 1,2-bis(diethylamino)-1,1,2,2-tetraphenyldisilane (1). Treatment of 1 with acetyl chloride yielded 1,2-dichloro-1,1,2,2-tetraphenyldisilane (2), which upon hydrolysis gave 3 (total yield 83%). Compounds 2 and 3 were characterized by elemental analyses (C, H) and solution NMR experiments (1 H, 13 C, 29 Si; CDCl₃). In addition, compound 1 and its condensation product, 1,5-dihydroxy-1,1,2,2,4,4,5,5-octaphenyl-3-oxa-1,2,4,5-tetrasilapentane (4; studied as the hemibenzene solvate 4 1/2C₆H₆), were structurally characterized by single-crystal X-ray diffraction.

Introduction

1,1,2,2-Tetraphenyldisilane-1,2-diol (3) is a versatile difunctional building block for the synthesis of siloxane systems with Si-Si bonds (for a recent example, see ref. [1]). In 1961 Winkler and Gilman reported on the first synthesis of compound 3, starting from chlorodiphenylsilane and using a coupling reaction with magnesium to form the Si-Si bond $[Ph_2Si(H)Cl \rightarrow HPh_2Si-SiPh_2H \rightarrow ClPh_2Si SiPh_2Cl \rightarrow HOPh_2Si-SiPh_2OH$ [2]. As this synthetic method is characterized by unsatisfactory yields and limited reliability, we have worked out an alternative approach for the synthesis of 3, using a method for the Si-Si bond formation developed by Tamao et al. [3]. We report here on an improved and reliable synthesis of compound 3 and the crystal structure analyses of 3 and its condensation product 1,5-dihydroxy-1,1,2,2,4,4,5,5-octaphenyl-3-oxa-1,2,4,5-tetrasilapentane (4; studied as the hemibenzene solvate $4 \cdot 1/2C_6H_6$).



Results and Discussion

The title compound **3** was prepared according to Scheme 1 in a two-step synthesis, starting



Scheme 1.

from 1,2-bis(diethylamino)-1,1,2,2-tetraphenyldisilane (1) [3, 4]. Thus, treatment of 1 with acetyl chloride in dichloromethane afforded 1,2-dichloro-1,1,2,2-tetraphenyldisilane (2) (yield 89%), which upon hydrolysis in a mixture of dichloromethane, diethyl ether, water, and ammonium carbonate gave the disilanediol **3** (yield 93%; total yield 83%). Compounds 2 and 3 were isolated as crystalline solids, and their identities were established by elemental analyses (C, H) and solution NMR studies (1H, 13C, 29Si; CDCl₃). In addition, 3 and its condensation product 4 (studied as the hemibenzene solvate $4 \frac{1}{2C_6H_6}$ were structurally characterized by single-crystal X-ray diffraction. Compound $4 \cdot 1/2C_6H_6$ [2] was isolated in minor amounts as a by-product in the crystallization of **3**.

0932–0776/02/0700–0731 \$ 06.00 © 2002 Verlag der Zeitschrift für Naturforschung, Tübingen · www.znaturforsch.com K

	3	4 1/2C ₆ H ₆
Empirical formula	$C_{24}H_{22}O_2Si_2$	C51H45O3Si4
Formula mass $[g mol^{-1}]$	398.60	818.23
Collection $T[K]$	173(2)	173(2)
λ (Mo-K _{α}) [Å]	0.71073	0.71073
Crystal system	triclinic	monoclinic
Space group (no.)	P1 (2)	<i>C</i> 2/ <i>c</i> (15)
a[Å]	13.229(3)	23.502(5)
b [Å]	14.664(3)	16.755(3)
<i>c</i> [Å]	19.394(4)	24.508(5)
α [°]	103.96(3)	90
β [°]	100.83(3)	110.99(3)
γ [°].	113.64(3)	90
$V[Å^3]$	3168.9(11)	9011(3)
Ζ	6	8
D (calcd.) [g cm ⁻³]	1.253	1.206
$\mu [\mathrm{mm}^{-1}]$	0.185	0.173
<i>F</i> (000)	1260	3448
Crystal dimensions [mm]	$0.2 \times 0.2 \times 0.2$	$0.4 \times 0.3 \times 0.3$
2θ Range [deg]	5.74-52.86	4.16-46.54
Index ranges	$-16 \le h \le 16,$	$-26 \le h \le 26,$
	$-18 \le k \le 17$,	$-18 \le k \le 18,$
	$-24 \le l \le 24$	$-27 \le l \le 27$
No. of collected reflections	46146	35777
No. of independent reflections	12536	6457
R _{int}	0.0387	0.0759
No. of reflections used	12536	6457
No. of restraints	6	4
No. of parameters	775	536
	0.888	1.009
Weight parameters $a/b^{[0]}$	0.0442/0.0000	0.0554/0.5681
$R1^{[c]}[I > 2\sigma(I)]$	0.0419	0.0360
$wR2^{\iota u_j}$ (all data)	0.0893	0.0934
Max./min. residual electron density [e $Å^{-3}$]	+0.319/-0.290	+0.285/-0.185

Table 1. Crystal data and experimental parameters for the crystal structure analyses of **3** and **4** $1/2C_6H_6$.

^[a] $S = \{\Sigma[w(F_o^2 - F_c^2)^2] / (n-p)\}^{0.5}; n = \text{no.}$ of reflections; $p = \text{no. of parameters;}^{[b]} w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$, with $P = [\max(F_o^2, 0) + 2F_c^2]/3; \ ^{[c]} R1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|;$ $^{[d]} wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma [w(F_o^2)^2]\}^{0.5}.$

Compound **3** crystallizes in the space group $P\overline{1}$, with three molecules in the asymmetric unit (molecules **3***A*, **3***B*, and **3***C*). Compound **4** $1/2C_6H_6$ crystallizes in the space group C2/c, with one half each of molecules **4***A* and **4***B* and one half of a benzene molecule in the asymmetric unit. The crystal data and the experimental parameters used for the crystal structure analyses of **3** and **4** $1/2C_6H_6$ are summarized in Table 1. The structures of molecules **3***A*, **3***B*, **3***C*, **4***A*, and **4***B* are depicted in Figures 1-4.

The Si-Si (Si-O) distances of **3** are in the range 2.3617(9) - 2.3790(11) Å [1.6482(19) - 1.6584(17) Å], and the Si-C bond lengths amount to 1.864(2) - 1.8808(19) Å. All silicon atoms are tetrahedrally coordinated, with bond angles at the silicon atoms in the range $101.42(8) - 117.53(7)^{\circ}$ (for crystal structures of other disilane-1,2-diols, see refs. [5] and [6]). The conformations of the three

crystallographically different molecules are characterized by gauche arrangements, with O-Si-Si-O dihedral angles amounting to $-68.56(10)^{\circ}$ (3*A*), $-70.56(11)^{\circ}$ (3*B*), and $-66.71(11)^{\circ}$ (3*C*). The three conformations differ mainly in the arrangement of their phenyl groups (different degrees of torsion around the respective Si-C bonds).

The crystal structure of **3** is characterized by a complex one-dimensional hydrogen bonding system with six intermolecular $O-H\cdots O$ interactions along the base vector [001] (Table 2, Fig. 5). All six OH groups are involved as donor functions, and the oxygen atoms O1, O2 (2-fold), O3, O4, and O6 act as acceptor atoms. These hydrogen bonds lead to an infinite tube-like arrangement of the molecules in the crystal, with the hydrophilic SiOH groups inside and the hydrophobic phenyl groups outside the tube.



Fig. 1. Structure of molecule **3***A* in the crystal of **3**. Selected distances [Å] and angles $[^{\circ}]$ (standard deviations in parentheses): Si1-Si2 2.3708(10), Si1-O1 1.6584(17), Si1-C1 1.869(3), Si1-C7 1.8808(19), Si2-O2 1.6544(15), Si2-C13 1.871(3), Si2-C19 1.871(2); Si2-Si1-O1 110.64(6), Si2-Si1-C1 111.89(7), Si2-Si1-C7 110.39(7), O1-Si1-C1 106.78(10), O1-Si1-C7 110.49(9), C1-Si1-C7 106.51(10), Si1-Si2-O2 110.56(7), Si1-Si2-C13 112.26(7), Si1-Si2-C19 106.89(7), O2-Si2-C13 109.15(9), O2-Si2-C19 107.73(9), C13-Si2-C19 110.13(10).



Fig. 2. Structure of molecule *3B* in the crystal of *3*. Selected distances [Å] and angles [°] (standard deviations in parentheses): Si3-Si4 2.3790(11), Si3-O3 1.6494(18), Si3-C25 1.877(2), Si3-C31 1.879(2), Si4-O4 1.6526(17), Si4-C37 1.876(2), Si4-C43 1.880(2); Si4-Si3-O3 108.58(7), Si4-Si3-C25 104.61(7), Si4-Si3-C31 117.53(7), O3-Si3-C25 108.57(10), O3-Si3-C31 108.58(9), C25-Si3-C31 108.64(10), Si3-Si4-O4 114.23(6), Si3-Si4-C37 111.57(7), Si3-Si4-C43 106.45(7), O4-Si4-C37 106.23(9), O4-Si4-C43 108.85(10), C37-Si4-C43 109.44(9).

The Si-Si (Si-O) distances of $4 \cdot 1/2C_6H_6$ are in the range 2.3510(9) - 2.3527(9) Å [1.6277(7) -1.6502(15) Å], and the Si-C bond lengths amount to 1.867(2) - 1.873(2) Å. All silicon atoms are tetrahe-



Fig. 3. Structure of molecule **3***C* in the crystal of **3**. Selected distances [Å] and angles [°] (standard deviations in parentheses): Si5-Si6 2.3617(9), Si5-O5 1.6545(15), Si5-C49 1.864(2), Si5-C55 1.869(2), Si6-O6 1.6482(19), Si6-C61 1.877(2), Si6-C67 1.873(2); Si6-Si5-O5 109.64(7), Si6-Si5-C49 117.24(7), Si6-Si5-C55 101.42(8), O5-Si5-C49 108.42(9), O5-Si5-C55 101.42(8), O5-Si5-C55 108.73(10), Si5-Si6-O6 114.80(7), Si5-Si6-C61 107.61(7), Si5-Si6-C67 103.77(7), O6-Si6-C61 108.36(9), O6-Si6-C67 109.15(10), C61-Si6-C67 113.23(10).

drally coordinated, with bond angles at the silicon atoms in the range $103.62(6) - 116.31(7)^{\circ}$ (for the crystal structure of a related cyclic condensation product, see ref. [7]). The conformations of the two crystallographically different molecules can each be described as eight-membered rings, including one of the two OH hydrogen atoms.

Attempts to localize the OH hydrogen atoms in the difference Fourier synthesis failed. Thus, the O-H distances were constrained in the refinement to result in a chemically acceptable hydrogenbonding situation. Due to symmetry requirements of the unit cell, the OH hydrogen atoms are disordered on two equally occupied positions. The hydrogen-bonding system depicted in Fig. 4 represents one of the two possible arrangements (intramolecular O2A-H2OD O2 and O4-H4OB O4A interactions as well as intermolecular O2-H2OA···O4 and O4A-H4OC O2A interactions; second arrangement: intramolecular O2-H2OB O2A and O4A-H4OD O4 interactions as well as intermolecular O2A-H2OC ··· O4A and O4-H4OA ··· O2 interactions). As a result, this hydrogen-bonding system leads to the formation of dimers of 4A and 4B in the crystal of $4 \cdot 1/2C_6H_6$.



Fig. 4. Structures of molecules **4***A* and **4***B* in the crystal of $4 \cdot 1/2C_6H_6$ (phenyl groups represented as stick models for clarity). Selected distances [Å] and angles [°] (standard deviations in parentheses) for **4***A*: Si1-Si2 2.3510(9), Si1-O1 1.6277(7), Si1-C1 1.867(2), Si1-C7 1.871(2), Si2-O2 1.6492(16), Si2-C13 1.869(2), Si2-C19 1.871(2); Si2-Si1-O1 105.03(6), Si2-Si1-C1 116.31(7), Si2-Si1-C7 111.98(7), O1-Si1-C1 105.17(10), O1-Si1-C7 110.09(8), C1-Si1-C7 107.92(9), Si1-Si2-O2 104.23(6), Si1-Si2-C13 111.37(7), Si1-Si2-C19 115.60(7), O2-Si2-C13 109.43(10), O2-Si2-C19 108.96(9), C13-Si2-C19 107.14(9), Si1-O1-Si1A 161.50(14). Data for **4***B*: Si3-Si4 2.3527(9), Si3-O3 1.6307(8), Si3-C25 1.873(2), Si3-C31 1.871(2), Si4-O4 1.6502(15), Si4-C37 1.867(2), Si4-C43 1.871(2); Si4-Si3-O3 108.25(7), Si4-Si3-C25 107.87(6), Si4-Si3-C31 112.40(7), O3-Si3-C25 108.07(7), O3-Si3-C31 108.39(9), C25-Si3-C31 111.71(9), Si3-Si4-O4 103.62(6), Si3-Si4-C37 113.85(7), Si3-Si4-C43 112.79(7), O4-Si4-C37 106.85(9), O4-Si4-C43 109.10(9), C37-Si4-C43 110.17(10), Si3-O3-Si3A 175.70(14).

Table 2. Hydrogen-bonding geometries in the crystal of **3** (distances [Å] and angles $[\circ])^{[a]}$.

D-H…A	D…A	D-H	H···A	D-H···A
01-H1004	2.676(3)	0.83(3)	1.84(3)	179(3)
O2-H2O…O2	2.737(3)	0.80(3)	1.97(3)	163(3)
O3-H3OO6	2.699(2)	0.83(2)	1.92(2)	156(2)
O4-H4O ··· O2	2.764(2)	0.809(18)	1.956(18)	177(3)
05-H50···03	2.736(2)	0.82(3)	1.93(2)	168(3)
O6-H6O…O1	2.735(2)	0.83(3)	1.91(3)	170(3)

^[a] Data calculated by using the program PLATON [8].

Experimental Section

General procedures. All syntheses were carried out under dry nitrogen. The organic solvents used were dried and purified according to standard procedures and stored under nitrogen. Melting points were determined with a Büchi Melting Point B-540 apparatus using samples in sealed capillaries. The ¹H, ¹³C, and ²⁹Si NMR spectra were recorded at 22 °C on a Bruker DRX-300 NMR spectrometer (¹H, 300.1 MHz; ¹³C, 75.5 MHz; ²⁹Si,



Fig. 5. Infinite tube-like arrangement of molecules 3A, 3B, and 3C in the crystal of 3 (projection along [0 0 1]), with the hydrophilic SiOH groups inside and the hydrophobic phenyl groups outside the tube. The phenyl groups are represented as stick models for clarity.

59.6 MHz). CDCl₃ was used as solvent. Chemical shifts (ppm) were determined relative to internal CHCl₃ (¹H, δ = 7.24), internal CDCl₃ (¹³C, δ = 77.0), or external TMS (²⁹Si, δ = 0).

1,2-Bis(diethylamino)-1,1,2,2-tetraphenyldisilane (1)

This compound was synthesized according to ref. [3].

1,2-Dichloro-1,1,2,2-tetraphenyldisilane (2)

Acetyl chloride (1.60 g, 20.4 mmol) was added to a stirred solution of **1** (5.00 g, 9.83 mmol) in dichloromethane (40 ml) at 0 °C and the mixture then stirred for 1 d at r. t. The solvent was removed under reduced pressure and the resulting solid recrystallized from toluene / petroleum ether (40 - 60 °C) [1:1 (v/v)] to give 3.81 g (8.75 mmol) of a colorless crystalline product (yield 89%). – M. p. 106 - 109 °C. – ¹H NMR: δ = 7.26 - 7.69 (m, 20 H, SiPh). – ¹³C{¹H} NMR: δ = 128.2 (C-2/C-6 *or* C-3/C-5, SiPh), 130.8 (C-4, SiPh), 132.2 (C-1, SiPh), 135.0 (C-2/C-6 *or* C-3/C-5, SiPh). – ²⁹Si{¹H} NMR: δ = –4.6. – C₂₄H₂₀Cl₂Si₂ (435.5): calcd. C 66.19, H 4.63; found C 66.2, H 4.7.

1,1,2,2-Tetraphenyldisilane-1,2-diol (3)

A solution of **2** (2.00 g, 4.59 mmol) in dichloromethane (7 ml) was added dropwise at 0 °C to a stirred mixture of water (17 ml), diethyl ether (5 ml), and ammonium carbonate (618 mg, 6.43 mmol). Stirring was continued for 1 h at the same temperature and the aqueous phase then saturated with sodium chloride. The two phases were separated, and the aqueous layer was extracted with diethyl ether (2 × 20 ml). The combined organic phases were dried over anhydrous sodium sulfate, and the solvent was removed under reduced pressure. The resulting crude product was recrystallized from benzene / petroleum ether (60 - 70 °C) [1:1 (v/v); cooling of a boiling saturated solution to room temperature] to give 1.70 g (4.26 mmol) of a colorless crystalline product (yield 93%). – M. p. 138 - 140 °C. – ¹H NMR: $\delta = 2.65$ (br. s, 2 H, SiOH), 7.21 -

- [1] R. Tacke, C. Burschka, J. Heermann, I. Richter, B. Wagner, R. Willeke, Eur. J. Inorg. Chem. 2211 (2001)
- [2] H. J. S. Winkler, H. Gilman, J. Org. Chem. 26, 1265 (1961).
 [3] Synthesis of 1: K. Tamao, A. Kawachi, Y. Nakagawa, Y. Ito,
- J. Organomet. Chem. **473**, 29 (1994). [4] Crystal structure analysis of **1**: F. Huppmann, M. Nolte-
- meyer, A. Meller, J. Organomet. Chem. **483**, 217 (1994).
- [5] Crystal structure analysis of HO(*t*-Bu)₂Si-Si(*t*-Bu)₂OH:
 R. West, E. K. Pham, J. Organomet. Chem. 403, 43 (1991).
- [6] Crystal structure analysis of HOMe₂Si-SiMe₂OH: M. Prasse, H. Reinke, C. Wendler, H. Kelling, J. Organomet. Chem. 577, 342 (1999).

7.40 and 7.45 - 7.54 (m, 20 H, SiPh). $-{}^{13}C{}^{1}H$ NMR: $\delta = 127.8$ (C-2/C-6 or C-3/C-5, SiPh), 129.7 (C-4, SiPh), 134.2 (C-1, SiPh), 136.2 (C-2/C-6 or C-3/C-5, SiPh). $-{}^{29}Si{}^{1}H$ NMR: $\delta = -10.4$. $-C_{24}H_{22}O_2Si_2$ (398.6): calcd. C 72.32, H 5.56; found C 72.2, H 5.6.

1,5-Dihydroxy-1,1,2,2,4,4,5,5-octaphenyl-3-oxa-1,2,4,5-tetrasilapentane-Hemibenzene ($4\cdot 1/2C_6H_6$)

Compound $4 \cdot 1/2C_6H_6$ was formed in minor amounts as a by-product in the crystallization of **3**. A procedure for the synthesis of $4 \cdot 1/2C_6H_6$ has been reported elsewhere [2].

Crystal structure analyses of 3 and 4 1/2C₆H₆

Suitable single crystals of 3 and $4 \cdot 1/2C_6H_6$ were obtained by crystallization of 3 from benzene/petroleum ether (60 - 70 $^{\circ}$ C) (see preparation). The crystals were mounted in inert oil (perfluoroalkyl ether, ABCR) on a glass fiber and then transferred to the cold nitrogen gas stream of the diffractometer (Stoe IPDS; graphite-monochromated Mo-K_{α} radiation, $\lambda = 0.71073$ Å). The structures were solved by direct methods (SHELXS-97) [9] and refined by full-matrix least-squares on F^2 with all unique reflections (SHELXL-97) [10]. For the CH hydrogen atoms of 3 and 4 1/2C₆H₆, a riding model was employed. The OH hydrogen atoms of 3 were localized in the Fourier synthesis and refined freely. The OH hydrogen atoms of 4 $1/2C_6H_6$ were placed on ideal positions and refined using distance restraints. Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no CCDC-181214 (3) and CCDC-181215 $(4 \cdot 1/2C_6H_6)$. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie.

- [7] Crystal structure analysis of the all-*trans*-isomer of 2,3,5, 6-tetramethyl-2,3,5,6-tetraphenyl-1,4-dioxa-2,3,5,6-tetrasilacyclohexane: V. V. Semenov, E. Y. Ladilina, Y. A. Kurskii, S. Y. Khorshev, N. P. Makarenko, G. A. Domrachev, L. N. Zakharov, G. K. Fukin, Y. T. Struchkov, Russ. Chem. Bull. 45, 2420 (1996).
- [8] The hydrogen-bonding system was analyzed by using the program PLATON: A. L. Spek, PLATON, University of Utrecht, The Netherlands (1998).
- [9] G. M. Sheldrick, SHELXS-97, University of Göttingen, Germany (1997); G. M. Sheldrick, Acta Crystallogr. A 46, 467 (1990).
- [10] G. M. Sheldrick, SHELXL-97, University of Göttingen, Germany (1997).