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1,3-Dimethoxy-1,3-dimethyl-1,3-diphenyl- and 1,3-dimethoxy-1,3-tetraphenyldisiloxanes: synthesis and structure

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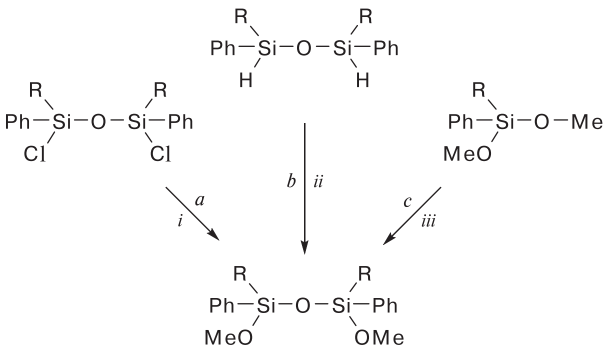
1,3-Dimethoxy-1,3-dimethyl-1,3-diphenyl- and 1,3-dimethoxy-1,3-tetraphenyldisiloxanes were synthesized. Their structures were confirmed by IR and NMR spectroscopy. The structure of 1,3-dimethoxy-1,3-tetraphenyldisiloxane was determined by X-ray diffraction.

Key words: 1,3-dimethoxy-1,3-tetraphenyldisiloxane, 1,3-dimethoxy-1,3-dimethyl-1,3-diphenyldisiloxane, molecular structure, X-ray diffraction.

Siloxanes are among the most important silicon compounds bearing the Si—O—Si group. Their structures and properties, as well as approaches to their synthesis have attracted great attention over several decades.[1—9] Siloxanes are widely used for the preparation of hybrid and composite materials with unique physicochemical properties.[10—20] Due to high hydrophobicity, good biocompatibility, low dielectric permittivity, low glass transition temperatures, and high thermal stability, these materials are widely applied in instrumentation engineering, technology, medicine, aerospace industry, and construction industry. Siloxanes containing functional groups at the silicon atom are convenient starting compounds for the preparation of such materials. In recent years, the chemistry of (alkoxy) organosiloxanes has been rapidly developed. The ability of these compounds to undergo hydrolysis and polycondensation giving rise to new bonds offers considerable opportunities for their use in synthetic organic chemistry and materials chemistry (see, for example, publications[21—27]). (Alkoxy)aryldisiloxanes Ar(AlkO) RSiOSiR(OAlk)Ar are of particular interest. The presence of an aryl group significantly enhances the synthetic potential of these compounds. The aryl group at the silicon atom is a latent functional group,[28—32] and the ease of Si—C_{Ar} bond cleavage allows the synthesis of new organosilicon compounds. However, data on the synthesis and experimental physicochemical properties of the simplest representatives of such siloxanes are absent in the literature. The goal of this study is to develop methods for the synthesis of 1,3-dimethoxy-1,3-dimethyl-1,3-diphenyl- and 1,3-dimethoxy-1,3-tetraphenyldisiloxanes and to investigate their properties.

(Alkoxy)phenyldisiloxanes can be synthesized by methods based on exchange reactions of the Si—X bond in functionally substituted silanes. The reaction of 1,3-dichloro-1,3-dimethyl-1,3-diphenyl- and 1,3-dichloro-1,3-tetraphenyldisiloxanes with methanol affords the corresponding 1,3-dimethoxy-1,3-dimethyl-1,3-diphenyl- (**1**) and 1,3-dimethoxy-1,3-tetraphenyldisiloxanes (**2**) in high yields (Scheme 1, pathway *a*). The reaction proceeds in hexane in the presence of urea as a hydrogen chloride acceptor.

Scheme 1



1, 2

R = Me (**1**), Ph (**2**)

i. MeOH, $(H_2N)_2C=O$, n-C_6H_{14}; *ii*. MeOH, $RhCl(PPh_3)_3$, C_6H_6; *iii*. H_2O, HCl, C_6H_6.

Path	Yield (%)	
	1	**2**
a	93	90
b	78	82
c	59	67

Compounds **1** and **2** were also synthesized by methanolysis of the corresponding 1,3-dimethyl-1,3-diphenyl- and 1,1,3,3-tetraphenyldisiloxanes (see Scheme 1, pathway *b*).

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The reaction proceeds in benzene in the presence of the catalyst $RhCl(PPh_3)_3$ at room temperature and is completed overnight. In this case, the yields are lower (78 and 82% for compounds **1** and **2**, respectively). An increase in the reaction time and a rise of the temperature did not lead to a significant change in the yield of the target products. The reaction gave unidentified oligo- and polysiloxanes as by-products.

We found that siloxanes **1** and **2** are formed in significant amounts in the synthesis of methylphenyldimethoxysilane and diphenyldimethoxysilane from appropriate chlorosilanes (see Scheme 1, pathway *c*). The formation of these compounds can be attributed to the hydrolysis of either the starting chlorosilanes or the already formed methylphenyldimethoxysilane and diphenyldimethoxysilane. The hydrolysis of methylphenyl- and diphenyldichlorosilanes in methanol at room temperature furnished a mixture of di- and oligosiloxanes even when using the reagents in an equimolar ratio. The reaction gave the target products in yields lower than 20%. It is noteworthy that the controlled acid hydrolysis of alkoxysilanes affords siloxanes.[33,34] The reaction of methylphenyldimethoxysilane and diphenyldimethoxysilane with an equimolar amount of water at room temperature in benzene in the presence of catalytic amounts of hydrogen chloride gave siloxanes **1** and **2** in 59 and 67% yields, respectively.

The structures of compounds **1** and **2** were confirmed by IR spectroscopy and multinuclear NMR spectroscopy.

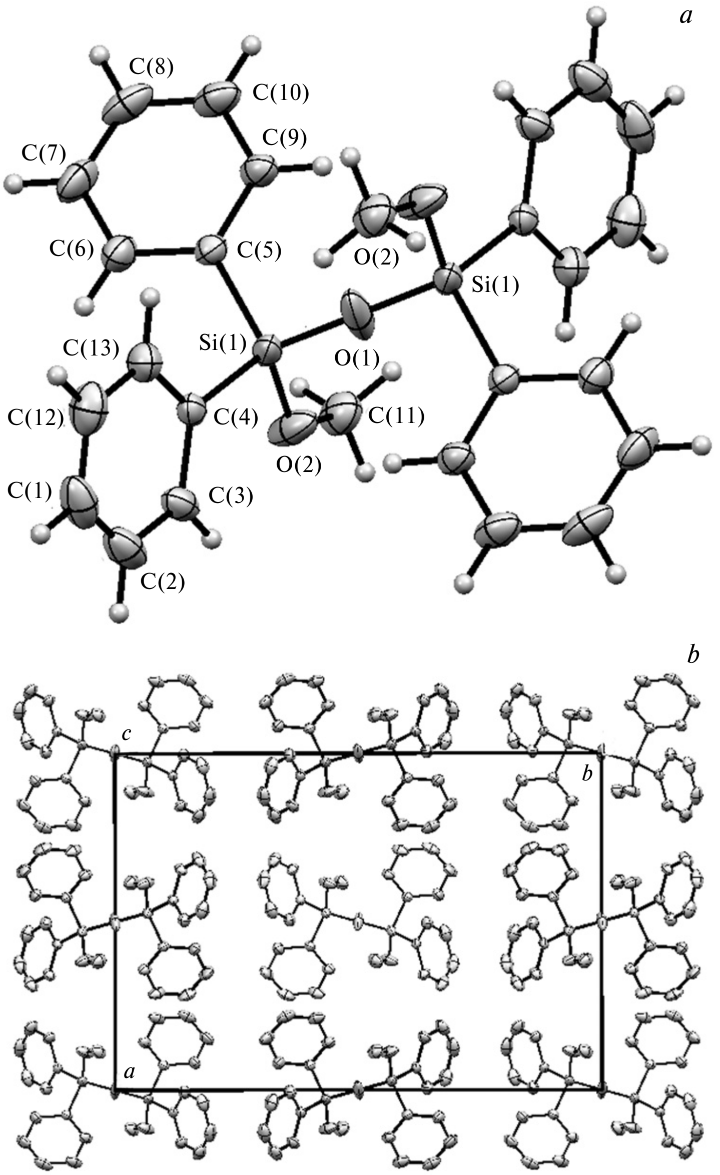

Fig. 1. (*a*) Molecular structure of compound **2** with displacement ellipsoids drawn at the 20% probability level; (*b*) the projection along the *0c* axis (hydrogen atoms are omitted for clarity).

Table 1. Selected geometric parameters of compound **2**

Bond	*d*/Å	Bond angle	φ/deg	Torsion angle	θ/deg
Si(1)—O(1)	1.595(1)	O(1)—Si(1)—O(2)	110.9(1)	O(1)—Si(1)—O(2)—C(11)	68.3(3)
Si(1)—O(2)	1.629(3)	O(1)—Si(1)—C(4)	110.2(1)	C(4)—Si(1)—O(2)—C(11)	−172.8(3)
Si(1)—C(4)	1.841(3)	O(2)—Si(1)—C(4)	104.8(1)	C(5)—Si(1)—O(2)—C(11)	−51.1(4)
Si(1)—C(5)	1.855(3)	O(1)—Si(1)—C(5)	107.6(1)	C(12)—C(1)—C(2)—C(3)	0.9(6)
O(2)—C(11)	1.399(4)	O(2)—Si(1)—C(5)	110.8(1)	C(1)—C(2)—C(3)—C(4)	−0.3(6)
C(1)—C(2)	1.336(6)	C(4)—Si(1)—C(5)	112.6(1)	C(2)—C(3)—C(4)—C(13)	0.0(5)
C(2)—C(3)	1.364(5)	Si(1)—O(1)—Si(1)	180.0(1)	C(2)—C(3)—C(4)—Si(1)	−179.2(3)
C(3)—C(4)	1.387(4)	C1(1)—O(2)—Si(1)	126.5(3)	O(1)—Si(1)—C(4)—C(3)	108.6(2)
C(5)—C(6)	1.380(4)	C(1)—C(2)—C(3)	121.4(4)	O(2)—Si(1)—C(4)—C(3)	−10.8(3)
C(6)—C(7)	1.389(5)	C(2)—C(3)—C(4)	121.4(4)	C(5)—Si(1)—C(4)—C(3)	−131.2(2)
C(7)—C(8)	1.374(6)	C(3)—C(4)—C(13)	116.9(3)	O(1)—Si(1)—C(4)—C(13)	−70.6(3)
C(9)—C(10)	1.375(4)	C(3)—C(4)—Si(1)	121.4(2)	O(2)—Si(1)—C(4)—C(13)	170.1(2)
C(12)—C(13)	1.391(5)	C(13)—C(4)—Si(1)	121.7(2)	C(5)—Si(1)—C(4)—C(13)	49.6(3)

The recrystallization from pentane gave crystals of compound **2**. The structure of **2** was established by X-ray diffraction. The molecular structure and a fragment of the crystal structure are shown in Fig. 1. Selected bond lengths, bond angles, and torsion angles are given in Table 1. The molecule of compound **2** has a plane of symmetry passing through the central oxygen atom O(1). There is one-half of molecule **2** per asymmetric unit. The Si(1)—O(1) and Si(1)—O(2) bond lengths are 1.595 Å and 1.629 Å, respectively. These values differ from the ideal Si—O bond lengths (1.603 Å) in four-coordinate silicon compounds; however, they are similar to those in symmetrical disiloxanes.[35—37] The Si—O—Si angle in compound **2** is 180°, like in other related structures.[35—37]

Experimental

The ^{1}H, ^{13}C, and ^{29}Si NMR spectra of compounds **1** and **2** were recorded on a Bruker DPX 400 spectrometer (400.13, 100.61, and 79.5 MHz, respectively) in $CDCl_3$ with $SiMe_4$ as the internal standard. The IR spectra were measured on a Varian 3100 FT-IR spectrometer.

All experimental procedures were carried out under dry inert gas atmosphere. The solvents were dried by standard procedures prior to use.[38] Commercially available phenylmethyl- and diphenyldichlorosilanes were purified by distillation before use. Phenylmethyl- and diphenyldimethoxysilanes were synthesized by standard procedures.[39,40] 1,3-Dichloro-1,3-dimethyl-1,3-diphenyl- and 1,3-dichloro-1,3-tetraphenyldisiloxanes,[41] as well as 1,3-dimethyl-1,3-diphenyl- and 1,3-tetraphenyldisiloxanes[42] were synthesized by procedures described in the literature.

Reaction of 1,3-dichloro-1,3-dimethyl-1,3-diphenyl- and 1,3-dichloro-1,3-tetraphenyldisiloxanes with methanol. The appropriate siloxane (0.01 mol) was added dropwise to a mixture of anhydrous methanol (0.02 mol) and carbamide (0.02 mol) in hexane (25 mL). The reaction mixture was stirred at room temperature for 60 min. The top layer of liquid was separated using a separatory funnel, and hexane was removed by distillation. 1,3-Dimethoxy-1,3-dimethyl-1,3-diphenyldisiloxane (**1**) was isolated by distillation (93% yield); 1,3-dimethoxy-1,3-tetraphenyldisiloxane (**2**), by recrystallization from pentane (90% yield).

Reaction of 1,3-dimethyl-1,3-diphenyl- and 1,3-tetraphenyldisiloxanes with methanol. The appropriate siloxane (0.01 mol), freshly prepared benzene (30 mL), and methanol (0.44 mL, 11 mmol) were placed in a two-neck round-bottom flask equipped with a Teflon-coated magnetic stirrer. The solution was bubbled with argon for 15 min. Then tris(triphenylphosphine)rhodium(I). chloride (5 mg) was added to the reaction solution. The reaction mixture was stirred at room temperature for 12 h. Benzene was removed *in vacuo*. Compound **1** was isolated by distillation (78%); compound **2**, by recrystallization from pentane (82%).

Hydrolysis of $PhMeSi(OMe)_2$ and $Ph_2Si(OMe)_2$. A mixture of methanol (2 mL), distilled water (0.09 g, 5 mmol), and trimethylchlorosilane (0.01 g) was slowly added dropwise to a vigorosuly stirred solution of the appropriate silane (0.01 mol) in methanol (10 mL). Trimethylchlorosilane was used as a source of hydrogen chloride. The reaction mixture was stirred for 10 h and allowed to stand for 16 h. Excess methanol was removed *in vacuo*. Compound **1** (59%) was isolated by distillation; compound **2** (67%), by recrystallization from pentane.

1,3-Dimethoxy-1,3-dimethyl-1,3-diphenyldisiloxane (1). B.p. 155—158 °C (5 Torr). ^{1}H NMR, δ: 0.26 (s, 6 H, Me—Si); 3.36 (s, 6 H, MeO); 7.23—7.43 (m, 10 H, Ph). ^{13}C NMR, δ: −2.92 (Me—Si); 50.06 (MeO); 127. 57, 129.74, 133.36, 134.90 (Ph). ^{29}Si NMR, δ: −23.22. IR (film), ν/cm^{-1}: 481; 584; 706, 733, 783,808, 1081; 1116; 1311; 1427; 1461; 1591; 1772; 1826; 1895; 1962; 2836; 2968; 3011; 3059. Found (%): C, 59.58; H, 6.92. $C_{16}H_{22}O_3Si_2$. Calculated (%): C, 60.33; H, 6.96.

1,3-Dimethoxy-1,3-tetraphenyldisiloxane (2). M.p. 55 °C. ^{1}H NMR, δ: 3.50 (s, 6 H, MeO); 7.30—7.64 (m, 20 H, Ph). ^{13}C NMR, δ: 50.66 (MeO); 127.71, 130.11, 133.31, 134.46 (Ph). ^{29}Si NMR, δ: −36.83. IR (KBr), ν/cm^{-1}: 421; 490; 520; 700; 719; 739; 787; 1002; 1071; 1125; 1188; 1246; 1310; 1428; 1589; 1836; 1898; 1970; 2360; 2836; 2936; 3006; 3064. Found (%): C, 70.24; H, 5.71. $C_{26}H_{26}O_3Si_2$. Calculated (%): C, 70.54; H, 5.92.

X-ray diffraction study. A single crystal of compound **2** was obtained by recrystallization from pentane. The X-ray diffraction data were collected on a Bruker D8 Venture diffractometer (Mo-Kα radiation, λ = 0.71073 Å) using φ- and ω-scanning technique. An absorption correction was applied with the

Table 2. Crystallographic data for compound **2**

Parameter	**2**
Molecular formula	$C_{26}H_{26}O_3Si_2$
Crystal habit	Colorless prisms
Crystal size/mm	0.170×0.300×0.450
T/K	293
Crystal system	Orthorhombic
Space group	*Pccn*
Molecular weight/g mol^{-1}	442.64
$\theta_{min}/\theta_{max}$	3.10/30.08
a/Å	14.7327(7)
b/Å	21.2727(13)
c/Å	7.8099(5)
α/deg	90
β/deg	90
γ/deg	90
V/Å^3	2447.7(2)
Z	8
d_{calc}/g cm^{-3}	1.201
F(000)	936
Absorption coefficient/mm^{-1}	0.169
Number of reflections	33942
unique	3584
Number of refined parameters	143
R factor (%)	7.42
Rw (based on all reflections)	0.1604
Goodness of fit based on F^2	1.017
Residual electron density (ρ_{max}/ρ_{min})/e Å^{-3}	0.326/–0.278

* The weighting scheme: $w = 1/[\sigma^2(F_o^2) + (0.0815\ P)^2 + 1.2512\ P]$, where $P = (F_o^2 + 2\ F_c^2)/3$.

SADABS program. The structure was solved by direct methods using the SHELX program package.[43] The refinement was performed with anisotropic displacement parameters for all non-hydrogen atoms using the SHELX program package.[43] Crystallographic data and structure refinement statistics are given in Table 2. Complete crystallographic data for compound **2** are available at www.ccdc.cam.ac.uk/data_request/cif (CCDC 1890676).

Results were obtained using analytical equipment of the Baikal Analytical Center for Collective Use of the Siberian Branch of the Russian Academy of Sciences.

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