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Chiral trialkoxysilanols derived from terpene alcohols. Molecular structures of tris([(1*S*)-*endo*]-(−)-bornoxy)silanol and tetrakis((−)-menthoxy)silane

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Abstract

Terpene alcohols (−)-menthol and [(1*S*)-*endo*]-(−)-borneol react with $SiCl_4$ in the presence of base to give $(MenO)_3SiCl$ (**1**) and $(BorO)_3SiCl$ (**2**) in high yields. Hydrolysis of **1** yields $(MenO)_3SiOH$ (**4**) and $(MenO)_4Si$ (**3**). Hydrolysis of **2** yields only $(BorO)_3SiOH$ (**5**). The crystal structures of **3** and **5** are reported. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Trialkoxysilanols; Chiral; Terpenes

1. Introduction

Organosilanols, $R_nSi(OH)_{4-n}$, containing at least one organic substituent and a hydroxyl group represent a well-documented class of compounds [1]. In the solid state, the silanol groups are usually involved in extensive hydrogen bonding giving rise to the formation of supramolecular frameworks with a fascinating diversity of structural motifs [1]. Organosilanols find applications as building blocks for the preparation of metallasiloxanes, which hold potential as soluble model compounds for heterogeneous silica-supported metal catalysts [2]. In general, the catalytic activity of the metallasiloxanes increases with the number of oxygen atoms surrounding the silicon atoms proximate to the metal center [3].

Alkoxysilanols, $(RO)_nSi(OH)_{4-n}$, containing no silicon-bound organic substituents have received much less attention presumably due to their greater tendency to undergo self-condensation. Although a number of these species has been described previously [4–14], only few compounds have been characterized by state-of-the-art methodologies, such as ^{29}Si-NMR spectroscopy or X-ray diffraction [15].

Organosilanols, $R_nSi(OH)_{4-n}$, and alkoxysilanols, $(RO)_nSi(OH)_{4-n}$, can be regarded as organically modified derivatives and partial esters, respectively, of orthosilicic acid, $Si(OH)_4$. The latter is only stable in highly diluted solution and immediately undergoes condensation at higher concentrations to form polysilicic acids, and finally amorphous hydrated silica, $[SiO_{n/2}(OH)_{4-n}]_m$ [16]. Nevertheless, orthosilicic acid plays an important role in the living world [17,18]. Many marine organisms (e.g. diatoms, radiolaria etc.) take up $Si(OH)_4$ from their external environment to build up exoskeletons of silica (biosilification) [17,18]. While the specific binding sites for orthosilicic acids have not yet been identified, the high serine content in silicateins suggests the involvement of serine hydroxyl residues into the binding either by hydrogen bonding or formation of alkoxy silicate [18–21]. Although there is no direct evidence of the biosynthesis of Si–OC bonds, ^{29}Si-NMR spectroscopic studies reveal that alcohols may react with silicates in aqueous solution to form alkoxy silicate [22,23]. As there are no naturally occurring silicon compounds containing Si–C bonds, stable alkoxy silanols might be the only genuine model compounds for silicic acid in a biochemical perspective [24].

Structural information on chiral tri- and tetraalkoxysilanes has been published recently [25,26], however, no trialkoxysilanols containing chiral groups

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have been reported to date. In the present work we describe the syntheses and characterization of two stable trialkoxysilanols, $(RO)_3SiOH$, derived from the naturally occurring terpene alcohols (−)-menthol and [(1*S*)-*endo*]-(−)-borneol.

2. Results and discussion

2.1. Synthesis

The reaction of silicon tetrachloride with (−)-menthol or [(1*S*)-*endo*]-(−)-borneol in the presence of pyridine provided the trialkoxychlorosilanes $(MenO)_3SiCl$ (**1**) (Men = (−)-Menthyl) and $(BorO)_3SiCl$ (**2**) (Bor = [(1*S*)-*endo*]-(−)-Bornyl), respectively, in high yields (Eq. (1)).

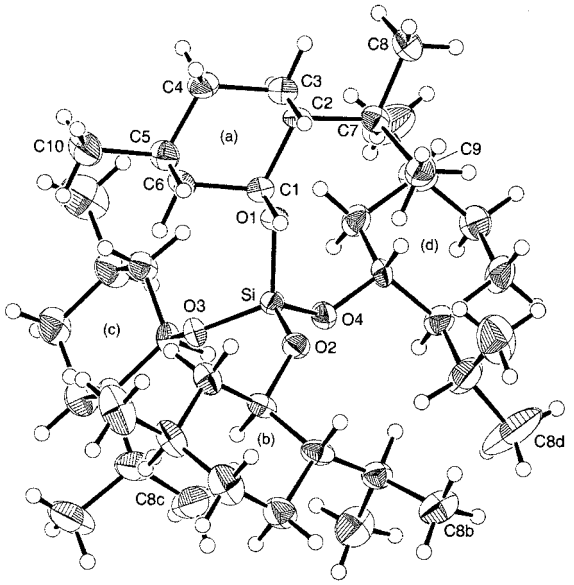

Fig. 1. Molecular structure and crystallographic numbering scheme employed for compound **3**. The numbering scheme for each of the menthyl rings follows that of ring (a).

Table 1
Geometric parameters (Å, °) for **3** and **5**

	3	**5a**	**5b**
Bond lengths			
Si–O1	1.615(5)	1.611(4)	1.608(4)
Si–O2	1.615(5)	1.647(4)	1.635(4)
Si–O3	1.624(4)	1.622(4)	1.610(4)
Si–O4	1.625(5)	1.610(4)	1.609(4)
Bond angles			
O1–Si–O2	108.0(2)	106.13(19)	106.3(2)
O1–Si–O3	114.7(3)	110.4(2)	109.6(2)
O1–Si–O4	107.3(2)	115.0(2)	115.2(2)
O2–Si–O3	106.7(3)	112.1(2)	112.2(2)
O2–Si–O4	113.7(3)	107.3(2)	107.3(2)
O3–Si–O4	106.7(2)	106.06(19)	106.5(2)
Si–O1–C1	123.7(4)		
Si–O2–C1	128.7(4)	120.3(3)	121.2(3)
Si–O3–C1	126.0(4)	124.8(3)	124.6(3)
Si–O4–C1	128.2(4)	126.7(3)	128.3(3)

$$SiCl_4 + 3ROH + 3C_5H_5N \xrightarrow[-3C_5H_5N\cdot HCl]{\text{toluene}} \underset{\substack{\mathbf{1}R = \text{Men}\\ \mathbf{2}R = \text{Bor}}}{(RO)_3SiCl} \quad (1)$$

The trialkoxychlorosilane **1** is a colorless oil whereas **2** is a high-melting solid. Both compounds may be handled under atmospheric conditions for a short time without noticeable hydrolysis.

Despite being stable towards hydrolysis for a short time, upon exposure to moist air for several weeks, $(MenO)_3SiCl$ (**1**) completely turns into a crystalline material and fumes of hydrogen chloride evolve from the opened vessel. The crystalline material was identified as a mixture of (−)-menthol and $(MenO)_4Si$ (**3**) from which the latter was isolated as colorless low-melting crystals in poor yields. The mechanism of the conversion from $(MenO)_3SiCl$ (**1**) to $(MenO)_4Si$ (**3**) is unknown, however, one possible reaction pathway might be the slow reversible redistribution of $(MenO)_3SiCl$ (**1**) into $(MenO)_4Si$ (**3**) and $(MenO)_2SiCl_2$, followed by the faster hydrolysis of the latter into (−)-menthol, hydrogen chloride and silica.

The mild hydrolysis of the tris(trialkoxy)chlorosilanes $(MenO)_3SiCl$ (**1**) and $(BorO)_3SiCl$ (**2**) with pyridine and an excess of water produced the expected trialkoxysilanols $(MenO)_3SiOH$ (**4**) and $(BorO)_3SiOH$ (**5**) in almost quantitative yields (Eq. (2)).

$$(RO)_3SiCl + H_2O + C_5H_5N \xrightarrow[-C_5H_5N\cdot HCl]{\text{ether/water}} \underset{\substack{\mathbf{4}R = \text{Men}\\ \mathbf{5}R = \text{Bor}}}{(RO)_3SiOH} \quad (2)$$

The trialkoxysilanol **4** is a colorless oil and **5** is a high-melting crystalline solid. Neither **4** nor **5** show any tendency towards hydrolysis or disproportionation. Compounds **1**–**5** were fully characterized by NMR spectroscopy and elemental analysis (Section 3). Suitable crystals for X-ray diffraction were obtained for **3** and **5** and thus their molecular structures were determined.

2.2. Molecular structures of $(MenO)_4Si$ (3) and $(BorO)_3SiOH$ (5)

The X-ray structure determinations of **3** and **5** confirm the composition of the compounds and reveal the expected features. The molecular structure of $(MenO)_4Si$ (**3**) is shown in Fig. 1 and selected geometric parameters are collected in Table 1. The silicon atom exists in a slightly distorted tetrahedral geometry with the range of Si–O bond distances being 1.615(5)–1.625(5) Å and O–Si–O angle range being 106.7(3)–114.7(3)°. Two independent molecules of $(BorO)_3SiOH$

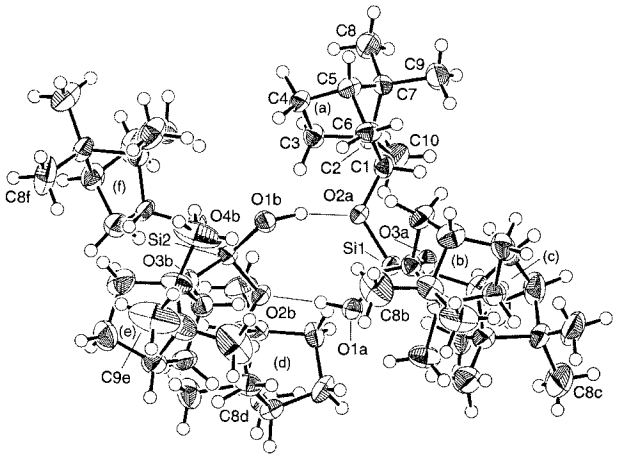

Fig. 2. Molecular structure and crystallographic numbering scheme employed for the two independent molecules of compound **5**. The numbering scheme for each of the bornyl rings follows that of ring (a). The O4a atom is obscured by the O3a atom.

Table 2
Crystallographic parameters for compounds **3** and **5**

	3	**5**
Empirical formula	$C_{40}H_{84}O_4Si$	$C_{30}H_{55}O_4Si$
Formula weight	657.19	507.85
Crystal system	Orthorhombic	Monoclinic
Space group	$P2_12_12_1$	$P2_1$
a (Å)	20.190(6)	14.318(7)
b (Å)	21.680(5)	12.120(4)
c (Å)	10.680(5)	18.657(2)
β (°)		110.41(2)
V (Å^3)	4675(2)	3034(2)
Z	4	4
D_{calc} (cm^{-3})	0.934	1.112
μ (cm^{-1})	0.81	1.08
$F(000)$	1480	1124
Crystal size (mm)	$0.13 \times 0.32 \times 0.45$	$0.11 \times 0.26 \times 0.40$
Unique data	5924	7577
Data with $[I \geq 2\sigma(I)]$	2252	3147
$R(F^2)$ for observed data	0.065	0.047
$wR(F^2)$ for all data	0.265	0.163
G	0.1513	0.0763
ρ (e Å^{-3})	0.50	0.25

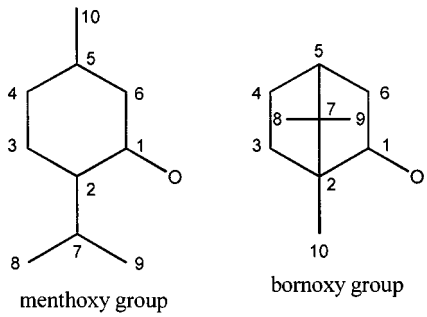

Chart 1.

comprise the crystallographic asymmetric unit of **5**. The molecules are illustrated in Fig. 2 and selected geometric parameters are collected in Table 1. Each silicon atom exists in a distorted tetrahedral geometry with the range of O–Si–O angles being 106.06(19)–115.0(2)° for Si(1) and 106.3(2)–115.2(2)° for Si(2), i.e. comparable to that seen in the structure of **3**. By contrast, the range of Si–O bond distances are broader in **5** owing to the presence of hydrogen bonding interactions between the molecules. As can be seen from Fig. 2, the two independent molecules associate by O–H···O hydrogen-bonding interactions where the acceptor oxygen atom is O2 in each case. This has the result that the Si–O2 distances are elongated compared to the remaining Si–O bond distances (Table 2). The details of the hydrogen bonding interactions are O1a–H···O2b 1.86 Å, O1a···O2b 2.784(5) Å and the angle at H 172°, and O1b–H···O2a 1.70 Å, O1b···O2a 2.748(6) Å and the angle at H 168°. The involvement of one alkoxy group in the hydrogen bonding gives rise to the formation of a hitherto unreported mode of association, e.g. an eight-membered [···OSiOH···OSiOH] ring.

The hydrogen bonding is also reflected in the IR spectrum (KBr) of **5** revealing a broad OH stretching vibration at 3380 cm^{-1}.

3. Experimental

3.1. General

All manipulations were performed under Ar using standard Schlenk and vacuum-line techniques unless otherwise stated. Solvents were distilled from the appropriate desiccants prior to use. (−)-Menthol, [(1*S*)-*endo*]-(−)-borneol, $SiCl_4$ and pyridine were obtained from Aldrich. NMR spectra in solution were recorded using a Varian 300 Unity Plus spectrometer (reference Me_4Si), whereas a JEOL Eclipse Plus 400 spectrometer was used for the ^{29}Si MAS-NMR spectra (secondary reference $(Me_3Si)_4Si$: $\delta = -9.9/-135.6$). The ^{1}H- and ^{13}C-NMR signals of the alkoxy groups were assigned using the numbering scheme in chart 1. The IR spectra were recorded on a BioRad FTIR spectrometer TTS 3000 MX. The elemental analyses were performed on an instrument from Carlo Erba Strumentazione (Model 1106).

3.2. Synthesis of the trialkoxychlorosilanes *(MenO)$_3$SiCl* (**1**) *and (BorO)$_3$SiCl* (**2**)

To a $C_6H_5CH_3$ solution of the appropriate terpene alcohol ((−)-menthol: 15.6 g or [(1*S*)-*endo*]-(−)-borneol: 15.4 g, 100 mmol) and pyridine (8.70 g, 110 mmol), $SiCl_4$ (5.66 g, 33.3 mmol) was added at 0 °C. The resulting mixture was heated at 80 °C for 3 h.

After cooling to room temperature (r.t.), the colorless precipitate of pyridinium chloride was filtered and the solvent removed under reduced pressure. The residue consists of pure product in 93 and 96% yield, respectively.

*3.2.1. $(MenO)_3SiCl$ (**1**), colorless oil*

^{1}H-NMR ($CDCl_3$): δ 3.76 (1H, td; H-1), 2.23 (1H, m; H-7), 2.11 (1H, m; H-6), 1.60 (1H, m; H-3), 1.58 (1H, m; H-4), 1.39 (1H, m; H-5), 1.22 (1H, m; H-2), 1.08 (1H, m; H-6′) 0.95 (1H, m; H-3), 0.90 (3H, d; H-8), 0.88 (3H, d; H-9), 0.84 (1H, m; H-4), 0.78 (3H, d; H-10). ^{13}C-NMR ($CDCl_3$): δ 74.4 (C-1), 49.5 (C-2), 44.3 (C-6), 34.4 (C-4), 31.6 (C-5), 25.3 (C-7), 22.7 (C-3), 22.2 (C-8), 21.1 (C-9), 15.7 (C-10). ^{29}Si-NMR ($CDCl_3$): δ −74.5.

Anal. Calc. for $C_{30}H_{57}ClO_3Si$ (529.32): C, 68.07; H, 10.85. Found: C, 68.15; H, 11.00%.

*3.2.2. $(BorO)_3SiCl$ (**2**): colorless solid, m.p. 207 °C*

^{1}H-NMR ($CDCl_3$): δ 4.26 (1H, m; H-1), 2.23 (1H, m; H-5), 2.00 (1H, m; H-6), 1.68 (1H, m; H-4), 1.62 (1H, m; H-3), 1.21 (1H, m; H-4′), 1.12 (1H, m; H-3′), 1.06 (1H, dd; H-6′), 0.86, 0.85, 0.84 (9H, s; H-8, H-9, H-10). ^{13}C-NMR ($CDCl_3$): δ 79.3 (C-1), 49.7 (C-2), 47.4 (C-7), 45.1 (C-5), 38.5 (C-6), 28.2 (C-3), 26.2 (C-4), 20.2 (C-8), 18.8 (C-9), 13.4 (C-10). ^{29}Si-NMR ($CDCl_3$): δ −73.0.

Anal. Calc. for $C_{30}H_{51}ClO_3Si$ (523.27): C, 68.86; H, 9.82. Found: C, 68.85; H, 9.80%.

*3.3. Slow hydrolysis of $(MenO)_3SiCl$ (**1**) in the presence of air moisture*

A few grams of $(MenO)_3SiCl$ (**1**) were kept in a loosely closed flask. After several weeks the original oil had almost completely solidified and upon opening the flask fumes of hydrogen chloride were noticed. According to ^{1}H- and ^{13}C-NMR spectra, the crude solidified material consisted of (−)-menthol and $(MenO)_4Si$ (**3**) from which the latter was isolated by recrystallization from C_6H_6 in ca. 30% yield.

*3.3.1. $(MenO)_4Si$ (**3**), colorless solid, m.p. 96 °C*

^{1}H-NMR ($CDCl_3$): δ 3.65 (1H, td; H-1), 2.32 (1H, m; H-7), 2.10 (1H, m; H-6), 1.61 (1H, m; H-3), 1.56 (1H, m; H-4), 1.33 (1H, m; H-5), 1.18 (1H, m; H-2), 1.05 (1H, m; H-6′) 0.95 (1H, m; H-3), 0.90 (3H, d; H-8), 0.89 (3H, d; H-9), 0.86 (1H, m; H-4), 0.74 (3H, d; H-10). ^{13}C-NMR ($CDCl_3$): δ 73.2 (C-1), 49.7 (C-2), 44.9 (C-6), 34.5 (C-4), 31.7 (C-5), 25.1 (C-7), 22.7 (C-3), 22.3 (C-8), 21.3 (C-9), 15.6 (C-10). ^{29}Si-NMR ($CDCl_3$): δ −86.0. ^{29}Si MAS-NMR: δ −83.2.

Anal. Calc. for $C_{40}H_{76}O_4Si$ (649.13): C, 70.01; H, 11.80. Found: C, 70.15; H, 11.85%.

*3.4. Synthesis of the trialkoxysilanols $(MenO)_3SiOH$ (**4**) and $(BorO)_3SiOH$ (**5**)*

At 0 °C a mixture of the trialkoxychlorosilane ($(MenO)_3SiCl$: 10.6 g or $(BorO)_3SiCl$: 10.5 g, 20.0 mmol) and pyridine (1.76 g, 22.0 mmol) in dry ether was slowly added to a mixture of ether (30 ml) and water (30 ml). After stirring at r.t. for 1 h, the layers were separated, the organic phase was washed twice with ice water (15 ml) and dried over Na_2SO_4. Ether and the excess pyridine were removed in vacuum at 0 °C and for a short time at r.t. leaving pure products in 94 and 95% yield, respectively.

*3.4.1. $(MenO)_3SiOH$ (**4**), colorless oil*

^{1}H-NMR ($CDCl_3$): δ 3.68 (1H, td; H-1), 2.24 (1H, m; H-7), 2.14 (1H, m; H-6), 1.63 (1H, m; H-3), 1.57 (1H, m; H-4), 1.37 (1H, m; H-5), 1.19 (1H, m; H-2), 1.08 (1H, m; H-6′) 1.05 (1H, m; H-3), 0.89 (3H, d; H-8), 0.87 (3H, d; H-9), 0.85 (1H, m; H-4), 0.76 (3H, d; H-10). ^{13}C-NMR ($CDCl_3$): δ 73.3 (C-1), 49.6 (C-2), 44.7 (C-6), 34.5 (C-4), 31.7 (C-5), 25.1 (C-7), 22.6 (C-3), 22.2 (C-8), 21.2 (C-9), 15.6 (C-10). ^{29}Si-NMR ($CDCl_3$): δ −82.2. IR (Nujol): ν(OH) 3410 cm^{-1}.

Anal. Calc. for $C_{30}H_{58}O_4Si$ (510.88): C, 70.53; H, 11.44. Found: C, 70.55; H, 11.50%.

*3.4.2. $(BorO)_3SiOH$ (**5**), colorless solid, m.p. 227 °C*

^{1}H-NMR ($CDCl_3$): δ 4.24 (1H, m; H-1), 2.23 (1H, m; H-5), 2.03 (1H, m; H-6), 1.68 (1H, m; H-4), 1.62 (1H, m; H-3), 1.21 (1H, m; H-4′), 1.11 (1H, m; H-3′), 1.05 (1H, dd; H-6′), 0.86, 0.85, 0.84 (9H, s; H-8, H-9, H-10). ^{13}C-NMR ($CDCl_3$): δ 78.2 (C-1), 49.6 (C-2), 47.4 (C-7), 45.1 (C-5), 38.8 (C-6), 28.3 (C-3), 26.2 (C-4), 20.2 (C-8), 18.8 (C-9), 13.5 (C-10). ^{29}Si-NMR ($CDCl_3$): δ −79.8. ^{29}Si MAS-NMR: δ −78.2. IR (KBr): ν(OH) 3380 cm^{-1}.

Anal. Calc. for $C_{30}H_{52}O_4Si$ (504.83): C, 71.38; H, 10.38. Found: C, 71.30; H, 10.45%.

3.5. Crystal structure determinations

Intensity data for colorless crystals of **3** and **5** were measured at 173 K on a Rigaku AFC7R diffractometer employing Mo–K_α radiation and the ω–2θ scan technique such that θ_{max} was 27.5°. Corrections were made for Lorentz and polarization effects [27]. Crystallographic data are summarized in Table 1. The structures were solved using heavy-atom methods for **3** [28] and direct methods for **5** [29] and refined by a full-matrix least-squares procedure based on F^2 [30] with a weighting scheme of the form $w = 1/[\sigma^2(F_o^2) + (gP)^2]$, where $P = (F_o^2 + 2F_c^2)/3$. All non-hydrogen atoms were refined with anisotropic displacement parameters and carbon-bound hydrogen atoms were included in the models in their idealized positions; the hydroxy protons in **5** were

located from a difference map but not refined. The absolute structures were determined from the chemistry and confirmed by the refinements. Final refinement details are given in Table 2 and the crystallographic numbering schemes employed are shown in Figs. 1 and 2, which were drawn at the 35% (**3**) and 50% (**5**) probability levels, respectively [31].

4. Supplementary material

Crystallographic data for **3** and **5** have been deposited at the Cambridge Crystallographic data Centre with deposition numbers 164376 and 164377, respectively. Copies of the information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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