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# Synthesis of disiloxanes containing hydroxyalkyl groups

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## Abstract

Four 1,3-bis($\omega$-hydroxyalkyl)tetramethyldisiloxanes $[HO(CH_2)_nSiMe_2]_2O$ (I; ($n = 3$–$6$) were synthesized by methanolysis of the corresponding trimethylsilyl-terminated disiloxanes (III). The latter were obtained from 1,1,3,3-tetramethyldisiloxane (II) and the appropriate ($\omega$-alkenyloxy)trimethylsilanes (IV). Under acidic conditions III formed in addition to I, the corresponding ($\omega$-hydroxyalkyl)pentamethyldisiloxanes $HO(CH_2)_nSiMe_2OSiMe_3$ (V; $n = 3$–$6$).

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## Introduction

In the series of 1,3-bis($\omega$-hydroxyalkyl)tetramethyldisiloxanes of the formula $[HO(CH_2)_nSiMe_2]_2O$ (I), the lower members ($n = 1$–$4$) have been described by several authors [1–6]. However, the physical properties published (e.g. boiling points, refractive indices) are contradictory. Moreover, spectroscopic data (IR, NMR) have not yet been reported. We have now devised a simple synthesis of higher members ($n = 3$–$6$) of the homologous series of compounds I.

## Results and discussion

The synthesis started from the readily available 1,1,3,3-tetramethyldisiloxane (II) as a compound which already contained the Si–O–Si link [7]. The well-known addition of silicon hydrides to olefinic compounds [8,9] was used to introduce the alkyl groups. Thus, we obtained the trimethylsilyl-terminated disiloxanes (III) by reaction of protected alkenols (IV) with II in presence of $H_2PtCl_6$. The protection [10] is essential because OH groups react with Si–H bonds under the conditions used [11,12].

Up to this point, we followed the route used by Greber and Jäger [4], who prepared 1,3-bis(3-trimethylsiloxypropyl)tetramethyldisiloxane (III; $n = 3$).

Two different methods for the removal of the trimethylsilyl group of compounds III were examined. First, we studied the acidic hydrolysis of the propyl substituted

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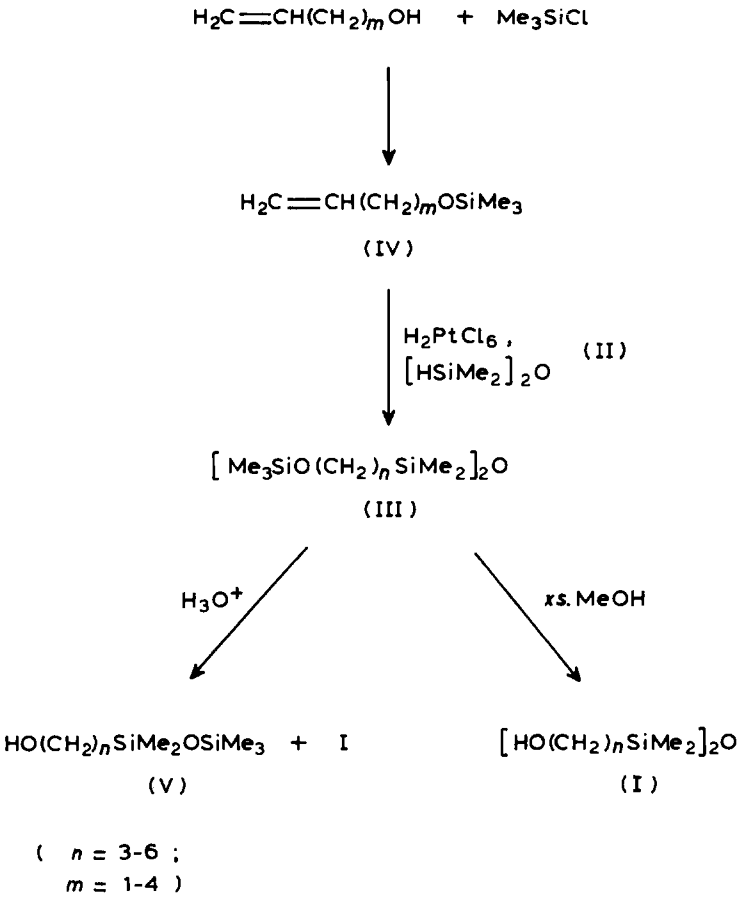

Scheme 1

disiloxane (III; $n = 3$) as described by Greber and Jäger [4]. In contrast to their results, we obtained (3-hydroxypropyl)pentamethyldisiloxane (V; $n = 3$) as the main product (69% yield) and the desired 1,3-bis(3-hydroxypropyl)tetramethyldisiloxane (I; $n = 3$) in only poor yield (30%). Further studies showed that the higher members ($n = 4$–6) of the series of compounds III also formed both the corresponding disiloxanes I and V when submitted to acidic hydrolysis. We suggest that the terminating Si–O–C group as well as the central Si–O–Si link in III is cleaved under these conditions. Thus, the formation of I and V can be accounted for by a restribution. As can be seen from Table 1, the yields of V decrease with increasing chain length, and the corresponding disiloxanes I become the main products. Since the acidic hydrolysis of compounds III appeared to be unsuitable for the syntheses of I, we studied the deblocking of III under neutral conditions.

We obtained the desired diols I as main products by reaction of the corresponding disiloxanes III with a hundredfold excess of methanol at room temperature for 3 h. Evaporation of the MeOH followed by distillation of the residue under reduced pressure gave pure products. High yields, short reaction times, and the ease of

Table 1

Physical properties and yields of $[HO(CH_2)_nSiMe_2]_2O$ (I) and $HO(CH_2)_nSiMe_2OSiMe_3$ (V)

| $n$ | I | | | V | | |
|---|---|---|---|---|---|---|
| | B.p. (°C/hPa) | $n_D^{20}$ | Yield (%) [a,b] | B.p. (°C/hPa) | $n_D^{20}$ | Yield (%) [b] |
| 3 | 112–113/0.15 | 1.4460 [c] | 69/30 | 52–53/0.2 | 1.4200 [c] | 69 [d] |
| 4 | 125–126/0.15 | 1.4498 | 84/47 | 62–63/0.25 | 1.4238 | 29 [d] |
| 5 | 146–147/0.1 | 1.4527 | 78/51 | 65–66/0.1 | 1.4270 | 15 [d] |
| 6 | 152–154/0.05 | 1.4542 | 92/74 | 69–71/0.1 | 1.4300 | 6 [d] |

[a] Methanolysis of $[Me_3SiO(CH_2)_nSiMe_2]_2O$ (III). [b] Acidic hydrolysis of $[Me_3SiO(CH_2)_nSiMe_2]_2O$ (III). [c] $[Me_3SiO(CH_2)_nSiMe_2]_2O \text{ (III)} + H_2O \rightarrow 2\ HO(CH_2)_nSiMe_2OSiMe_3$ (V). [d] 25°C.

isolation of the products are the advantages of methanolysis over acidic hydrolysis.

With one exception the diols I are stable at room temperature and during vacuum distillation. 1,3-Bis(4-hydroxybutyl)tetramethyldisiloxane (I; $n = 4$) distilled without visible decomposition but contained about 20 mol-% of 2,2-dimethyl-1-oxa-2-sila-cyclohexane (VI; $n = 4$) after several days storage at room temperature.

$$\underset{\text{(I)}}{[HO(CH_2)_nSiMe_2]_2O} \rightleftharpoons 2\,\underset{\text{(VI)}}{\overline{O(CH_2)_nSi}Me_2} + H_2O$$

However, we did not observe the formation of 2,2-dimethyl-1-oxa-2-sila-cyclopentane (VI; $n = 3$) on distillation of 1,3-bis(3-hydroxypropyl)tetramethyldisiloxane (I; $n = 3$) that was reported by Speier et al. [1].

The structures of I and V were confirmed by NMR ($^{13}C$, $^{29}Si$) spectroscopy (Table 2 and 3). In both series the chemical shifts $\delta(^{13}C)$ of the carbons of the hydroxyalkyl chains are similar to those for the corresponding alkanols [13, p. 156]. Compared with I, the $^{13}C$ and $^{29}Si$ NMR spectra of V exhibit an additional resonance due to the $SiMe_3$ group. This resonance can be distinguished easily from $SiMe_2$ by its splitting pattern in proton coupled $^{29}Si$ NMR spectra. The chemical shifts $\delta(^{29}Si)$ of I and V occur in the range expected for $OSi(alkyl)_3$ [14].

The disiloxanes I and V were further characterized by IR spectroscopy. Within each homologous series, the frequencies are found to be independent of the hydroxyalkyl substituent. However, the C–H stretching bands of the $CH_2$ group at 2940 and 2860 cm$^{-1}$ become stronger with increasing chain length. It must be

Table 2

Chemical shifts [a] $\delta(^{29}Si)$ (ppm) and $\delta(^{13}C)$ (ppm) for $[HO(CH_2)_nSiMe_2]_2O$ (I) (the C attached to Si is C(1))

| $n$ | Si | C(Me$_2$) | C(1) | C(2) | C(3) | C(4) | C(5) | C(6) |
|---|---|---|---|---|---|---|---|---|
| 3 | 8.26 | 0.50 | 14.50 | 27.00 | 65.29 | | | |
| 4 | 7.74 | 0.60 | 18.53 | 20.07 | 36.69 | 62.23 | | |
| 5 | 7.61 | 0.60 | 18.79 | 23.63 | 29.97 | 32.92 | 62.53 | |
| 6 | 7.60 | 0.61 | 18.74 | 23.75 | 33.10 | 26.07 [b] | 33.70 | 62.52 |

[a] In $C_6D_6$ at 300 K, TMS ($\delta = 0$ ppm) as internal standard. [b] Assignment based on γ-effect of OH group [13, p. 95].

Table 3

Chemical shifts [a] $\delta(^{29}Si)$ (ppm) and $\delta(^{13}C$, ppm) for $HO(CH_2)_nSi^{\star}Me_2OSiMe_3$ (V) (the C attached to $Si^{\star}$ is C(1))

| $n$ | $Si^{\star}$ | Si | C(Me$_2$) | C(Me$_3$) | C(1) | C(2) | C(3) | C(4) | C(5) | C(6) |
|---|---|---|---|---|---|---|---|---|---|---|
| 3 | 8.22 | 7.63 | 0.42 | 2.06 | 14.50 | 27.05 | 65.37 | | | |
| 4 | 7.85 | 7.40 | 0.49 | 2.09 | 18.50 | 19.97 | 36.77 | 62.27 | | |
| 5 | 7.76 | 7.22 | 0.48 | 2.08 | 18.71 | 23.58 | 29.96 | 32.88 | 62.48 | |
| 6 | 7.87 | 7.29 | 0.51 | 2.08 | 18.57 | 23.57 | 32.92 | 25.81 [b] | 33.45 | 62.19 |

[a] In $C_6D_6$ at 300 K, TMS ($\delta = 0$ ppm) as internal standard. [b] Assignment based on γ-effect of OH group [13, p. 95].

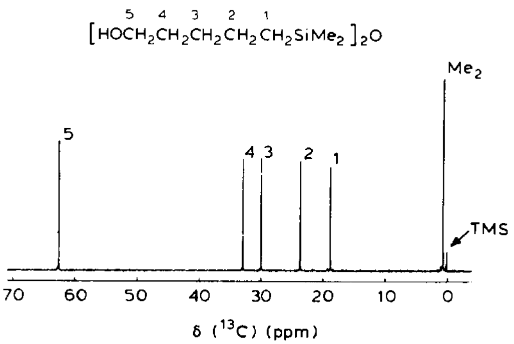

Fig. 1. Proton-decoupled $^{13}C$ NMR spectrum of 1,3-bis(5-hydroxypentyl)tetramethyldisiloxane in $C_6D_6$ at 300 K using TMS ($\delta = 0$ ppm) as internal standard.

noticed that the IR spectra of V are similar to those of the corresponding diols I in respect of frequencies and intensities.

## Experimental

Infrared spectra were recorded as liquid capillary films with a Perkin–Elmer 281 spectrometer. FT-NMR spectra ($^{13}C$, $^{29}Si$) were measured at 300 K with a Bruker WM 300 and Bruker CXP 300 using $C_6D_6$ as solvent and TMS ($\delta = 0$ ppm) as internal standard.

Allyl alcohol and 3-buten-1-ol were commercial products. 4-Penten-1-ol and 5-hexen-1-ol were prepared by ring cleavage of 2-chloromethyltetrahydrofuran [15] and 2-chloromethyltetrahydropyran [16], respectively. 1,1,3,3-Tetramethyldisiloxane (II), was made by hydrolysis of dimethylchlorosilane [7].

### *Preparation of (ω-alkenyloxy)trimethylsilanes (IV)*

2 mol (242.4 g) *N,N*-dimethylaniline and 2 mol (217.4 g) $Me_3SiCl$ were mixed in 600 ml of anhydrous diethyl ether, and 2 mol of ω-alkenol were added with vigorous stirring and cooling in an ice-bath. The mixture was then refluxed for 3 h. The hydrochloride formed was filtered off, and after addition of a small amount of sodium the filtrate was distilled to give compounds $H_2C{=}CH(CH_2)_mOSiMe_3$ (IV). *(2-Propenyloxy)trimethylsilane (IV; $m = 1$):* b.p. 98–99 °C, $n_D^{20}$ 1.3940, 65% yield [10].

*(3-Butenyloxy)trimethylsilane (IV; m = 2):* b.p. 118–120 °C, $n_D^{20}$ 1.4026, 66% yield [10].

*(4-Pentenyloxy)trimethylsilane (IV; m = 3):* b.p. 144–145 °C, $n_D^{20}$ 1.4110, 50% yield [10].

*(5-Hexenyloxy)trimethylsilane (IV; m = 4):* b.p. 55–58 °C/14 hPa, $n_D^{20}$ 1.4212, 44% yield [17].

### *Preparation of 1,3-bis(ω-trimethylsiloxyalkyl)tetramethyldisiloxanes (III)*

1,1,3,3-Tetramethyldisiloxane (II) (0.1 mol; 13.4 g) was slowly added to 0.2 mol of the (ω-alkenyloxy)trimethylsilane (IV) containing a catalytic amount $H_2PtCl_6$ at 90 °C. The mixture was stirred for a further 2 h at 120 °C. Subsequent distillation under reduced pressure gave the compounds $[Me_3SiO(CH_2)_nSiMe_2]_2O$ (III).

*1,3-Bis(3-trimethylsiloxypropyl)tetramethyldisiloxane (III; n = 3):* b.p. 101–102 °C/0.2 hPa, $n_D^{20}$ 1.4240, 65% yield [4]. $^{13}C$ (δ, ppm): 65.46, 27.17, 14.59, 0.46 ($Me_2$), −0.28 ($Me_3$); $^{29}Si$ (δ, ppm): 7.67 ($SiMe_2$), 15.67 ($SiMe_3$).

*1,3-Bis(4-trimethylsiloxybutyl)tetramethyldisiloxane (III; n = 4):* b.p. 115–116 °C/0.2 hPa, $n_D^{20}$ 1.4270, 65% yield. $^{13}C$ (δ, ppm): 61.80, 36.49, 19.84, 18.28, 0.53 ($Me_2$), −0.35 ($Me_3$); $^{29}Si$ (δ, ppm): 8.13 ($SiMe_2$), 15.57 ($SiMe_3$).

*1,3-Bis(5-trimethylsiloxypentyl)tetramethyldisiloxane (III; n = 5):* b.p. 131–132 °C/0.08 hPa, $n_D^{20}$ 1.4318, 73% yield. $^{13}C$ (δ, ppm): 62.14, 32.72, 29.81, 23.39, 18.64, 0.55 ($Me_2$), −0.35 ($Me_3$); $^{29}Si$ (δ, ppm): 7.69 ($SiMe_2$), 15.65 ($SiMe_3$).

*1,3-Bis(6-trimethylsiloxyhexyl)tetramethyldisiloxane (III; n = 6):* b.p. 153–155 °C/0.1 hPa, $n_D^{20}$ 1.4342, 52% yield. $^{13}C$ (δ, ppm): 62.27, 33.41, 25.87, 32.97, 23.60, 18.64, 0.58 ($Me_2$), −0.33 ($Me_3$); $^{29}Si$ (δ, ppm): 7.60 ($SiMe_2$), 15.59 ($SiMe_3$).

IR frequencies for III ($cm^{-1}$): 2960, 2935, 2900, 2860, 1410, 1385, 1250, 1100, 1060, 875, 840, 795, 755, 745, 700.

### *Methanolysis of 1,3-bis(ω-trimethylsiloxylalkyl)tetramethyldisiloxanes (III)*

A mixture of 0.05 mol of III and 200 ml anhydrous methanol was stirred for 3 h at room temperature. The methanol was evaporated and the residue was distilled under reduced pressure to yield $[HO(CH_2)_nSiMe_2]_2O$ (I).

Physical properties (Table 1) and NMR data (Table 2) for I are listed above. IR frequencies of I ($cm^{-1}$): 3340, 2960, 2935, 2860, 1415, 1255, 1180, 1060, 840, 795, 700. After storage at room temperature for several days, 1,3-bis(4-hydroxybutyl)tetramethyldisiloxane (I; $n = 4$) contained about 20 mol-% of 2,2-dimethyl-1-oxa-2-sila-cyclohexane (VI; $n = 4$). $^{29}Si$ (δ, ppm): 14.88; $^{13}C$ (δ, ppm): 65.22, 30.99, 22.54, 13.72, −1.48 [13, p. 318].

### *Acidic hydrolysis of 1,3-bis(ω-trimethylsiloxyalkyl)tetramethyldisiloxanes (III)*

A mixture of 10 ml hydrochloric acid (0.5 *n*), 5 ml diethyl ether and 0.05 mol of III was stirred vigorously for 15 h at room temperature. The ethereal layer was washed with dilute $NaHCO_3$ and then three times with water, and was subsequently dried over anhydrous $MgSO_4$. After removal of all volatile compounds at normal pressure, distillation of the residue in vacuo gave $[HO(CH_2)_nSiMe_2]_2O$ (I) and the corresponding $HO(CH_2)_nSiMe_2OSiMe_3$ (V).

Physical properties (Table 1) and NMR data (Table 3) for V are listed above.

IR frequencies of V ($cm^{-1}$): 3340, 2960, 2940, 2860, 1415, 1255, 1180, 1060, 840, 805, 780, 750, 700, 680, 620.

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