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Organosiloxanes with functional groups

X *. Reactions of H-cyclosiloxanes with 1,4-bis(trimethylsiloxy)but-2-yne to multifunctional surface active compounds

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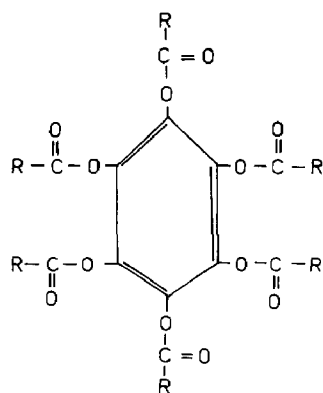
Abstract

The reaction of H-cyclosiloxanes $[\text{Me}(\text{H})\text{SiO}]_n$ (1, $n = 4$; 2, $n = 5$) with 1,4-bis(trimethylsiloxy)but-2-yne (3) in the presence of a Pt-catalyst has been studied. Depending on the molar ratio, mono-substituted and fully substituted products were obtained in nearly quantitative yield, of which the compound 1,4-bis(trimethylsiloxy)but-2-enecyclosiloxane exists in configurational isomers.

Introduction

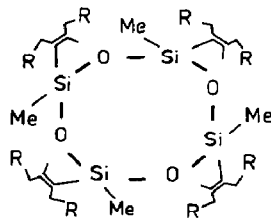
Amphiphilic molecules, generally consisting of a long hydrophobic hydrocarbon chain and a hydrophilic head group, are of great interest in science and industry. Their field of application ranges from biological membranes to microemulsions, and from soap manufacturing to transport processes in living organisms [1–3]. Multi-polar amphiphiles have previously been synthesized by Ringsdorf et al. [4]. In these compounds the hydrophobic groups were planar ring systems (benzene or triphenyl-

* For part IX see ref. 6.



R = alkyl

type A

R = OSiMe₃

type B

ene). Our interest, however, has been focussed on the synthesis of multipolar surface active compounds involving cyclosiloxanes (type **B**) rather than planar rings (type **A**). This paper reports a detailed study of the reaction of 1,4-bis(trimethylsiloxy)but-2-yne (**3**) with H-cyclosiloxanes (**1**) in terms of the effect of the molar ratio on yields. The products were characterized by NMR spectroscopy and glass capillary gas chromatography.

Results and discussion

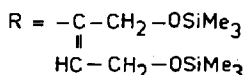
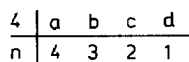
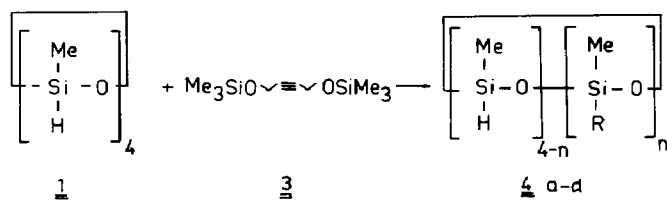
In the earlier papers of this series we described the preparation and characterization of some linear 2-siloxanyl-but-2-ene-1,4-diols [5,6]. This extended earlier work by Rejchsfeld et al. who reported the reaction of H-cyclosiloxanes with alkenes [7]. The reaction of H-tetramethylcyclotetrasiloxane (**1**) with 1,4-bis(trimethylsiloxy)but-2-yne (**3**) was investigated under analogous conditions.

Equimolar ratio of reactants 1 / 4

Using conventional synthetic procedures, a temperature range of 40 to 160 °C in the presence of H₂PtCl₆ as a catalyst, and a 1/4 ratio of the reactants (**1** and **3**), we were able to obtain the fully butene-substituted cyclosiloxane, 1,3,5,7-tetra[1,4-bis(trimethylsiloxy)but-2-ene]-1,3,5,7-tetramethylcyclotetrasiloxane (**4a**) and the three-fold substituted cyclosiloxane, 1,3,5-tris[1,4-bis(trimethylsiloxy)but-2-ene]-1,3,5,7-tetramethylcyclotetrasiloxane (**4b**) in an 80/20 ratio:

By increasing the molar ratio between the H-cyclotetrasiloxane (**1**) and the alkyne **3** to 1/5 the proportion of the product **4a** reached 98%. This is remarkable since there must be three of four stepwise additions to achieve the final products.

The structures of the two hydrosilylation products **4a** and **4b** were established from their proton, carbon and silicon NMR spectra. The ¹H NMR spectra of **4a** and **4b** in the methyl region represent, as expected, methyl resonances for the CH₃Si and (CH₃)₃SiO groups. Analysis of the vinyl regions of the spectra produced detailed information on the structure. In the ¹H-NMR spectra of **4a** the H=C=C proton signals (6.52 ppm) and the CH₂ signals (4.50 ppm) were clearly resolved and in the



^{13}C NMR spectra we found: C=C 138.68 to 142.57 ppm, CH_2 61.01 ppm, CH_3Si 1.29 ppm, $(\text{CH}_3)_3\text{SiO}$ -0.19, -0.41 ppm. In addition, the ^{29}Si NMR spectra showed the characteristic signals for mono- and bi-functional Si atoms at -33.21 to -33.47 ppm (CH_3Si) and 17.02 to 17.31 ppm ($(\text{CH}_3)_3\text{SiO}$).

As expected, in the IR spectrum of **4b** a weak band corresponding to the remaining Si-H band was found at 2150 cm^{-1} . Previous investigations on two compounds of comparable structure, tetramethyltetrachlorocyclotetrasiloxane [8] and tetramethyltetraphenylcyclotetrasiloxane [9], showed that compounds of such type occur in four configurational isomers. With the use of a well calibrated glass capillary column the gas chromatogram displays four peaks, obviously the four configurational isomers (Fig. 1). This result coherently explains the greater number of signals in the NMR spectra.

Molar ratio of reactants 1/1 to 2.5/1

The reaction of **1a** with **3** at a molar ratio of 1/1 is nonselective, and a mixture of all the four addition compounds **4a-4d** and even small amounts of the decomposition products are formed in addition to the theoretically favoured product **4d** (Fig.

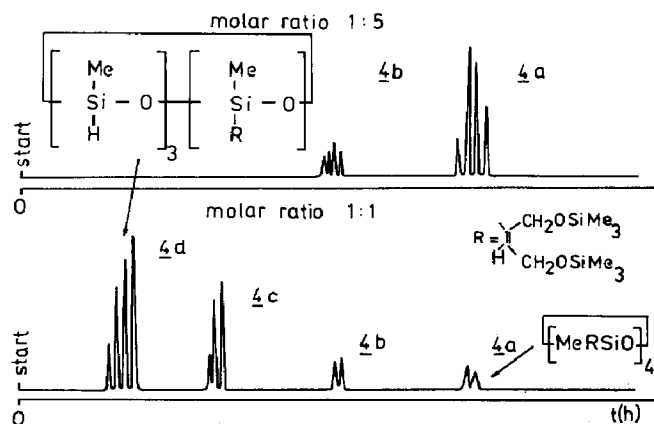


Fig. 1. Gas chromatograms of post-reaction mixtures of **1** and **3**; molar ratio 1/5 and molar ratio 1/1; conditioned at 250°C ; 20 m, 0.25 mm i.d.; temperature programmed from 180 to 300°C at 8 K/min

1), whose concentration in the post-reaction mixture was only 54.1%. The structures of these compounds were determined by the ^1H NMR spectrum of the post-reaction mixture.

The character of the ^{29}Si NMR spectrum also indicates the structures. In this spectrum besides the signals assigned to $\text{OSi}(\text{CH}_3)_3$ (20.19, 17.05 ppm) and SiCH_3 (-32.34 , -33.73 ppm) the following unidentified signals are present: 21.00, 20.89, 20.52, -27.18 , -28.89 , and -30.06 ppm.

Reducing the reaction temperature and providing an excess of **1** increase the selectivity of the reaction. **1** reacts with **3** at a molar ratio of 2.5/1 within the temperature range of 50 – 87°C yielding the following mixture: 82.1% **4d**, 1.9% **4c**, 1.4% **4b** and 1.1% **4a**. The mono- as well as the tetra-addition product can be prepared in high yields.

The reaction of pentamethylcyclopentasiloxane (**2**) with **3** was similar to that of **1**. By reaction of **2** and **3** at a molar ratio of 1/5 two products were formed: 1,3,5,7,9-penta[1,4-bis(trimethylsiloxy)but-2-ene]-1,3,5,7,9-pentamethylcyclopentasiloxane (**5a**) and 1,3,5,7-tetra[1,4-bis(trimethylsiloxy)but-2-ene]-1,3,5,7,9-pentamethylcyclopentasiloxane (**5b**).

In the ^1H NMR spectrum of this post-reaction mixture the following signals of protons were found: HSi 6.53 ppm, CH_2 4.55 ppm, CH_3Si 0.6 ppm and $(\text{CH}_3)_3\text{SiO}$ 0.23 ppm. The results show that the reactivity of the cyclosiloxanes **1** and **2** is comparable to that of branched and chain siloxanes. In analogy to chain siloxanes and as a direct result of the stereospecific *syn*-addition *E*-1,4-bis(trimethylsiloxy)-but-2-ene-cyclosiloxane molecules **4** and **5** are produced. The cyclic structure of the investigated siloxanes causes various configurational isomers to occur in addition. The main conclusion to be drawn from these results is that the synthesis of multifunctional surface-active compounds on the basis of cyclosiloxanes of type **B** is possible in principle.

Experimental

All reactions were carried out under prepurified nitrogen and the solvents were dried and freshly distilled under nitrogen before use. The cyclooligosiloxanes **1** and **2** $[\text{Me}(\text{H})\text{SiO}]_n$ ($n = 4, 5$) were prepared according to the procedure described in [10] and purified by distillation.

1,4-bis(trimethylsiloxy)but-2-yne (**3**) was obtained from the reaction of but-2-yne-1,4-diol with hexamethyldisilazane [6]. IR spectra were recorded on a UR-20 spectrometer (VEB Carl-Zeiss Jena). NMR spectra were measured on a Tesla BS 587 A (^1H NMR), a Varian CFT 20 (^{13}C NMR) and an MSL 400 Bruker (^{29}Si NMR). The GC analyses were performed on a GCHF 18.3 chromatograph (VEB Chromatron Berlin), with a specially made capillary system using a 19 m glass column, silylated by dimethylbenzyltetramethyldisilazane, 0.3% (w/v) SE-54 in pentane/ CH_2Cl_2 , cross-linked with DCUP.

(1) Reaction of **1** with **3** at a molar ratio of 1 / 4

3 (11.52 g, 0.05 mol) was placed in a 100 cm^3 three-necked flask equipped with a reflux condenser, thermometer, dropping funnel and magnetic stirrer and heated to 125°C . **1** (3.15 g, 0.0131 mol) and 0.01 cm^3 of the catalyst solution (0.1 *M* solution of $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ in isopropyl alcohol) were placed in the dropping funnel and

then into the reaction vessel over a period of 20 min. The temperature of this strongly exothermic reaction was kept below 140 °C, controlled by the rate of dropping and the temperature of the oil bath. After cooling the reaction mixture to room temperature, the product was obtained as a clear viscous yellow liquid. Compounds **4a** and **4b**: ¹H NMR: (HC=) 6.52, (CH₂) 4.50, (SiCH₃) 0.56, [OSi(CH₃)₃] 0.24 ppm, **4b**: (SiH) 5.40 ppm; ¹³C NMR: C=C 142.57, 142.46, 139.09, 138.94, 138.68, (CH₂) 61.07, (SiCH₃) 1.29, [OSi(CH₃)₃] -0.19, -0.41 ppm; ²⁹Si NMR: [OSi(CH₃)₃] 17.31, 17.02, (SiCH₃) -33.21, -33.36, -33.47 ppm.

(2) Reaction of 1 with 3 at a molar ratio of 1 / 1

The apparatus was assembled as described above, **3** (5.76 g, 0.025 mol) was placed in the reaction vessel, and at 40 °C **1** (6.30 g, 0.0262 mol) and 0.016 cm³ of the catalyst (0.1 M solution of H₂PtCl₆ · 6H₂O in isopropyl alcohol) were added. Within 3 min the temperature had risen rapidly to 160 °C, decreasing to 75 °C. For a further 90 min the temperature was maintained by heating at about 125 °C. After cooling a clear light-yellow liquid was obtained.

Spectroscopic investigation of the reaction mixture: ¹H NMR: (H-C) 6.86, 6.49, 6.37, (Si-H) 5.11, (CH₂) 4.49, 3.91, (Si-CH₃) 0.56, [OSi(CH₃)₃] 0.25 ppm, unidentified signals: 2.81, 2.53 and 1.27 ppm; ²⁹Si NMR: [OSi(CH₃)₃] 20.19, 17.05, (SiCH₃) -32.34, -33.73, unidentified signals: 21.00, 20.89, 20.52, -27.18, -29.89, -30.06 ppm.

(3) Reaction of 1 with 3 at a molar ratio of 2 / 1

1 (6.0 g, 0.025 mol) and one drop of the catalyst solution (0.01 M solution of H₂PtCl₆ · 6H₂O in isopropanol) were placed in the reaction vessel and heated to 50 °C. **3** (2.30 g, 0.01 mol) and one drop of the catalyst solution were placed in the dropping funnel. The reactants were dropped into the reaction vessel in three stages, an equal amount at each stage, at intervals of 30 min. A rapid temperature rise could not be observed. Then, the mixture was heated at 87 °C for 3 h. After cooling a clear light-yellow liquid was obtained as product. Characterization was carried out by gas chromatography.

(4) Reaction of 2 with 3 at a molar ratio of 1 / 5

3 (11.52 g, 0.05 mol) was placed in the reaction vessel and heated to 124 °C, **2** (3.00 g, 0.1 mol) and 0.032 cm³ of the catalyst solution (0.1 M solution of H₂PtCl₆ · 6H₂O in isopropanol) were then dropped in. The rate of addition and the temperature of the oil bath were maintained so that the reaction temperature did not exceed 140 °C. The temperature in the reaction vessel was maintained at 110–120 °C for a further 30 min and then the reaction mixture was cooled. A viscous clear yellow liquid was obtained.

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