Journal of Organometallic Chemistry 696 (2011) 2754–2757

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

Note

Synthesis of 6-, 7- and 8-membered cyclosiloxanes having multifunctional groups

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ARTICLE INFO

Article history:
Received 16 March 2011
Received in revised form
19 April 2011
Accepted 26 April 2011

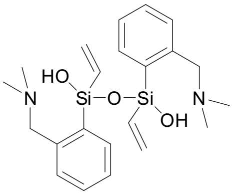
Keywords:
Organosilicon compound
Cyclic siloxane
Intramolecular donor atom
Vinylsiloxane
Si—Si bond

ABSTRACT

Cyclosiloxanes having intramolecular donor atoms, a Si—Si bond, and vinyl groups were synthesized as useful precursors for ring-opening polymerization. 1,1,3,3-Tetrakis(dimethylaminomethylphenyl)-5,5-dimethylcyclotrisiloxane was also synthesized and characterized by single crystal X-ray structural analysis, which shows strong coordination from N to Si in the solid state.

1. Introduction

The cyclic siloxanes $(R_2SiO)_n$, have great importance as ring-opening polymerization precursors to high molecular weight siloxane polymers [1], and are widely used in industry. Recently we synthesized diastereomeric 1,3-dihydroxy-1,3-divinyldisiloxanes [2] (**1**) having intramolecular donor atoms, which are useful precursor for cyclosiloxanes, linear siloxanes and metallosiloxanes [3].



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Our interest in this area focuses on the synthesis of cyclic siloxanes having intramolecular donor atoms, Si—Si bonds and vinyl moieties as functional groups. First, disiloxane-1,3-diols with intramolecular donor atoms can give polysiloxanes with variable physical properties depending on the temperature, because the degree of coordination of the intramolecular donor atom with silicon atom is temperature-dependent [4]. For example, polysiloxanes bearing intramolecular donor atoms may have a rigid structure as temperature decreases since the coordination of N to Si is intensified. Furthermore the incorporation of transition metals into polysiloxanes is possible through N-metal coordination bonds. Second, Si—Si bonds in cyclic polysilanes exhibit unusual chemical and physical properties [5], such as having electronic transitions in the UV—Vis region, forming radicals by their reductive bond cleavages, and electrochemical/thermal oxidation resulting in the formation of Si—O—Si bonds [6]. Third, the attachment of vinyl groups to cyclosiloxanes allows their vulcanization by photolysis and Si—C bond formations by hydrosilylation [7]. To incorporate these three functionalities into a cyclosiloxane, a cyclosiloxane having donor atoms, a Si—Si bond, and vinyl groups was designed. We report here syntheses and characterizations of 6-, 7- and 8-membered ring 2-(*N*,*N*-dimethylaminomethyl)phenylsiloxane derivatives as well as crystal structure of 1,1,3,3-tetrakis(dimethylaminomethylphenyl)-5,5-dimethylcyclotrisiloxane.

2. Experimental

2.1. Materials and instruments

In all reactions in which air-sensitive chemicals were used, the reagents and solvents were dried prior to use. Diethyl ether was distilled from Na/Ph_2CO. Other starting materials were purchased as reagent grade and used without further purification. Glassware was flame-dried under nitrogen or argon flushing prior to use. All manipulations were performed using standard Schlenk techniques under a nitrogen or argon atmosphere. ^1H, ^{13}C and ^{29}Si NMR spectra

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doi:10.1016/j.jorganchem.2011.04.025

were recorded on a Bruker Avance II$^+$ BBO 400 MHz S1 spectrometer. The chemical shift were referenced to internal $CDCl_3$ (^{1}H and ^{13}C NMR) or external tetramethylsilane (^{29}Si NMR). Analyses of product mixtures were accomplished using an HP 5890 II Plus instrument with FID (HP-5, 30m column) with dried *n*-decane as an internal standard and with TCD (OV-1, 1/8 in. 6 ft column). Mass spectra were recorded on a low-resolution (Agilent Technologies GC/MS: 6890N, 5973N mass selective detector) EI mass spectrometer and a high-resolution (JEOL JMS-600W-Agilent 6890 Series) instrument. The preparations of disiloxane-1,3-diols **1** and **5** were reported in a previous paper [2,8].

2.2. Synthesis of **2**

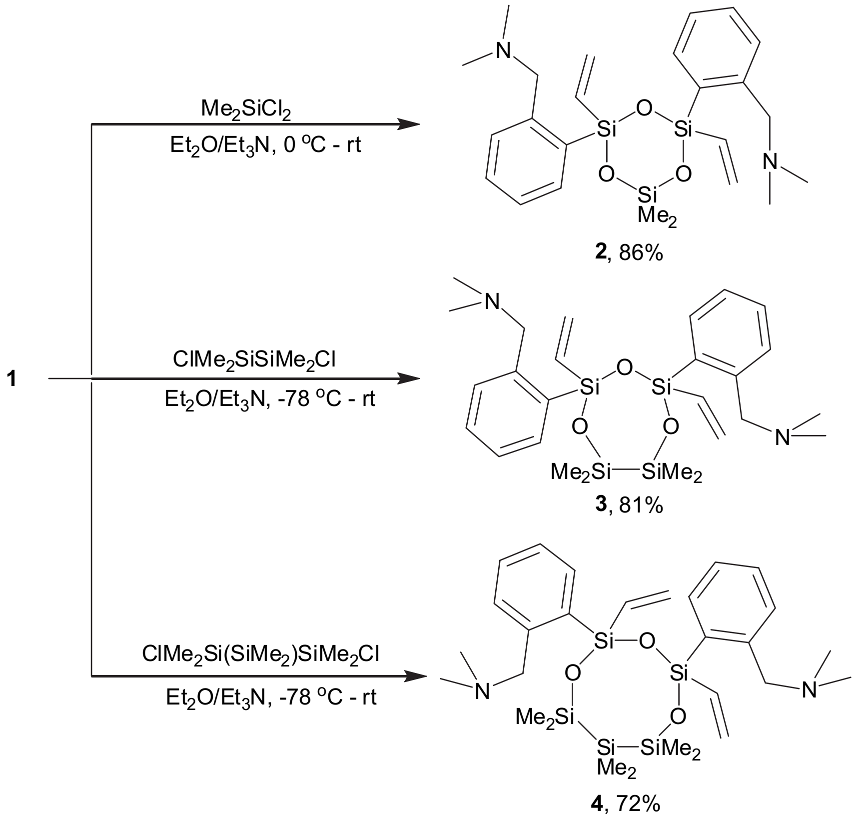
To a solution of 1.0 g (2.3 mmol) of **1** and 0.80 mL (5.7 mmol) of triethylamine in 25 mL of diethyl ether was slowly added 0.30 g (2.3 mmol) of dichlorodimethylsilane at 0 °C. The reaction mixture was allowed to warm slowly to room temperature and stirred for 12 h. After filtration of the precipitated Et_3NHCl, volatiles were distilled under vacuum. The crude reaction product was purified by preparative GC to afford **2** as oil. The NMRs were tentatively assigned to *cis/trans* isomers (86%, 0.96 g). HRMS: $C_{24}H_{36}N_2O_3Si_3$ 484.2034 (M$^+$, calcd), 484.2031 (M$^+$, found). ***Trans*-2**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.15 (s, 6H), 2.15 (s, 12H), 3.45–3.60 (m, 4H), 5.63–6.28 (m, 6H), 7.08–7.84 (m, 8H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 1.1 ($Si(CH_3)_2$), 45.0 ($N(CH_3)_2$), 64.0 (NCH_2), 126.3, 127.4, 129.5, 131.5, 134.7, 136.5, 137.6, 146.4 ($CH_2{=}CH$, C_6H_4). ^{29}Si NMR (80 MHz, $CDCl_3$): δ −45.6 (SiAr), −8.8 ($SiMe_2$). ***Cis*-2**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.10 (s, 3H), 0.27 (s, 3H), 2.10 (s, 12H), 3.45–3.60 (m, 4H), 5.63–6.28 (m, 6H), 7.08–7.84 (m, 8H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 1.0, 1.3 ($Si(CH_3)_2$), 44.9 ($N(CH_3)_2$), 63.9 (NCH_2), 126.3, 127.4, 129.8, 132.2, 134.7, 136.2, 137.8, 146.2 ($CH_2{=}CH$, C_6H_4). ^{29}Si NMR (80 MHz, $CDCl_3$): δ −44.3 (SiAr), −8.5 ($SiMe_2$).

2.3. Synthesis of **3**

To a solution of 1.0 g (2.3 mmol) of **1** and 0.80 mL (5.7 mmol) of triethylamine in 25 mL of diethyl ether was slowly added 0.43 g (2.3 mmol) of 1,2-dichloro-1,1,2,2-tetramethyldisilane at −78 °C. The reaction mixture was allowed to warm to room temperature and stirred for 10 h. After filtration of the precipitated Et_3NHCl, volatiles were distilled under vacuum. The crude reaction product was purified by preparative GC to afford **3** as oil. The NMRs were tentatively assigned to *cis/trans* isomers (81%, 1.0 g). HRMS: $C_{26}H_{42}N_2O_3Si_4$ 542.2272 (M$^+$, calcd) 542.2265 (M$^+$, found). ***Trans*-3**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.33 (s, 12H), 2.16 (s, 12H), 3.48 (AB system, *J* = 13.2 Hz, 2H), 3.73 (AB system, *J* = 13.2 Hz, 2H), 5.72–6.32 (m, 6H), 7.11–7.93 (m, 8H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 1.9, 2.0 ($Si(CH_3)_2$), 45.2 ($N(CH_3)_2$), 64.2 (NCH_2), 126.2, 128.1, 129.9, 132.7, 134.8, 136.2, 137.5, 146.0 ($CH_2{=}CH$, C_6H_4). ^{29}Si NMR (80 MHz, $CDCl_3$): δ −45.46 (SiAr), 3.16 ($SiMe_2$). ***Cis*-3**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.25 (s, 6H), 0.27 (s, 6H), 2.09 (s, 12H), 3.40 (AB system, *J* = 13.2 Hz, 2H), 3.58 (AB system, *J* = 13.2 Hz, 2H), 5.72–6.32 (m, 6H), 7.11–7.93 (m, 8H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 1.9, 2.2 ($Si(CH_3)_2$), 45.2 ($N(CH_3)_2$), 64.0 (NCH_2), 126.1, 127.9, 129.9, 132.7, 134.6, 136.1, 137.7, 146.0 ($CH_2{=}CH$, C_6H_4). ^{29}Si NMR (80 MHz, $CDCl_3$): δ −45.38 (SiAr), 3.23 ($SiMe_2$).

2.4. Synthesis of **4**

To a solution of **1** and triethylamine in diethyl ether was added 1,3-dichloro-1,1,2,2,3,3-hexamethyltrisilane at −78 °C in a manner



Scheme 1. Synthesis of 6-, 7- and 8-membered cyclosiloxanes.

similar to that described above. The purification procedure was analogous to that for **3**. The *cis/trans* mixture **4** was obtained as oil in 72% yield (0.98 g). HRMS: $C_{28}H_{48}N_2O_3Si_5$ 600.2511 (M^+, calcd) 600.2507 (found). ^1H NMR (400 MHz, $CDCl_3$): δ (−)0.35–0.37 (m, 18H), 2.07 (s, 6H), 2.14 (s, 6H), 3.36–3.52 (m, 4H), 5.65–6.25 (m, 6H), 7.11–7.82 (m, 8H). ^{13}C NMR (100 MHz, $CDCl_3$): δ −6.94, −6.88, −6.6 ($Si(CH_3)_2$), 45.4, 45.5 ($N(CH_3)_2$), 63.6, 63.8 (NCH_2), 126.0–137.4 ($CH_2{=}CH$, C_6H_4).

2.5. Synthesis of **6**

0.10 g (0.78 mmol) of dichlorodimethyldisilane at 0 °C was slowly added to a solution of 0.50 g (0.78 mmol) of **5** and 0.35 mL (2.5 mmol) of triethylamine in 15 mL of diethyl ether in a manner similar to that described above. Product **6** was obtained as colorless crystals in 83% yield (0.45 g) by recrystallization from cosolvent (*n*-hexane:diethyl ether = 1:1). ^1H NMR (400 MHz, $CDCl_3$): δ 0.14 (s, 6H), 1.86 (s, 24H), 3.26 (AB system, $J = 13.8$ Hz, 4H), 3.46 (AB system, $J = 13.8$ Hz, 4H), 7.04–7.67 (m, 16H, C_6H_4). ^{13}C NMR (100 MHz, $CDCl_3$): δ 1.3 ($Si(CH_3)_2$), 45.3 ($N(CH_3)_2$), 63.9 (NCH_2), 126.0, 127.4, 129.5, 135.9, 136.6, 145.0 (C_6H_4). ^{29}Si NMR (80 MHz, $CDCl_3$): δ −15.8 ($SiMe_2$), −43.3 (SiAr). Anal. Calcd for $C_{38}H_{54}N_4O_3Si_3$: C, 65.28; H, 7.79; N, 8.01. Found: C, 65.24; H, 7.82; N, 7.98.

2.6. X-ray structure determination

A specimen of suitable size and quality was coated with Paratone oil and mounted onto a glass capillary. Reflection data for **6** were collected on a Bruker APEX II CCD-based diffractometer with graphite-monochromated MoKα radiation ($\lambda = 0.71073$Å). The hemisphere of reflection data were collected as ω scan frames with 0.3O/frame and an exposure time of 10s/frame. Cell parameters were determined and refined by SMART program [9]. Data reduction was performed using SAINT software [10]. The data were corrected for Lorentz and polarization effects. An empirical absorption correction was applied using the SADABS program [11]. The structures of the compounds were solved by direct methods and refined by full matrix least-squares methods using the SHELXTL program package with anisotropic thermal parameters for all non-hydrogen atoms [12]. X-ray crystal structures of **6** were drawn by Mercury program ver. 2.3.

3. Results and discussion

First, dimethyldichlorosilane was used as a ring closer in order to synthesize cyclosiloxane using diastereomeric disiloxane-1,3-diols **1**. The reaction of **1** with Me_2SiCl_2 in the presence of triethylamine as HCl acceptor, gave the corresponding 6-membered ring isomeric siloxanes **2**, which were monitored by GC/MS (Scheme 1). The product **2** was obtained as oil in 86% yield which was separated by preparative GC. In ^1H NMR data, three resonances from $SiCH_3$ group in **2** indicate the formation of a *cis/trans* mixture.

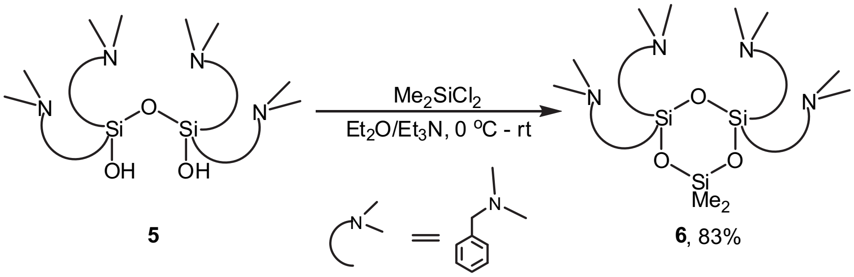
Table 1
Crystallographic data and structure refinement for **6**

Empirical formula	$C_{38}H_{54}N_4O_3Si_3$
Formula weight	699.12
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	C2/c
a (Å)	15.2425(17)
b (Å)	12.0426(12)
c (Å)	22.051(2)
α (°)	90
β (°)	95.785(6)
γ (°)	90
V ($Å^3$)	4027.0(7)
Z	4
ρ_{calc}($g\ cm^{-3}$)	1.153
μ (mm^{-1})	0.157
F(000)	1504
T (K)	296(2) K
Crystal size	*0.20*0.20*0.15*
hkl range	$-20 \le h \le 18, -15 \le k \le 15, -28 \le l \le 29$
Measd reflns	43647
Unique reflns (R_{int})	4848 (0.0396)
Final R indices ($I > 2\sigma(I)$)[a,b]	$R_1 = 0.0421$, $wR_2 = 0.1179$
R indices (all data)	$R_1 = 0.0603$, $wR_2 = 0.1322$
GOF on F^2	1.001
ρ_{fin} (max/min) (e $Å^{-3}$)	0.440 and −0.219

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$.
[b] $wR_2 = \{[\sum w(F_o^2 - F_c^2)^2]/[\sum w(F_o^2)^2]\}^{1/2}$.

The reactions of **1** with $ClMe_2SiSiMe_2Cl$ and $ClMe_2Si(SiMe_2)SiMe_2Cl$ were carried out in a manner similar to that described above. The corresponding 7- and 8-membered ring siloxanes, **3** and **4** were obtained as oils in less than 60% yield. To increase yields of **3** and **4**, lower initial reaction temperatures (−78 °C) were applied than that (0 °C) in the preparation of 6-membered cyclosilane. Under this condition, compounds **3** and **4** were formed in rather high yields considering the ring strain of 7- and 8-membered cyclic compounds. It is noteworthy that compound **4** having three Si–O–Si bonds and three consecutive Si atoms is a promising precursor for block copolymer consisting of siloxanes and trisilanes. Polysilane-siloxanes hybrid materials could not only improve the desired properties of polysilanes such as their solubility and thermoformability, but could also lead to new features of these polymers. For example, the spectral properties of hybrid polysilane-siloxanes were discovered, which were applied as radiation sensitive materials (photoresists) in a lithographic process [13].

Compounds **3** and **4** were purified by preparative GC. Unfortunately the *cis/trans* isomers could not be fully separated, and several trials to recrystallize them failed. Thus we were not able to identify whether the N atom was coordinated to Si atom or not. This prompted us to design a model cyclic siloxane containing two dimethylaminomethylphenyl groups bonded to the same silicon atom, which naturally allows only one cyclic product to be formed



Scheme 2. Synthesis of **6**.

without *cis/trans* isomers. 1,1,3,3-Tetrakis(dimethylaminomethylphenyl)cyclosiloxane **6** as a model compound was synthesized from the reaction of disiloxane-1,3-diol **5** with dimethyldichlorosilane. Compound **6** was isolated as colorless crystals in 83% yield by recrystallization from cosolvent (*n*-hexane:diethyl ether = 1:1) (Scheme 2).

The structure of **6** bearing pentacoordinate silicon atoms was characterized by X-ray crystallography (Table 1). The nitrogen (N2) atoms are situated 2.892 Å from the silicon atom which is similar to the normal coordination distance of 2.8 Å [4], while the nitrogens (N1) do not coordinate to Si in the condensed phase (Fig. 1). Interestingly, our result for the coordination mode of amino groups to Si is somewhat different from other examples: silicon atoms in cyclo*tetra*siloxane [(Me)($C_6H_4CH_2NMe_2$-2)-SiO]$_4$ were tetra-coordinated [14] and silicon atoms in cyclo*di*siloxane [($C_6H_4CH_2NMe_2$-2)$_2$SiO]$_2$ were hexa-coordinated [15]. The Si1-O1 bonds (1.6502(7) Å) which are located opposite to the amino groups (N2), are slightly elongated in comparison with the Si1-O2 (1.6373(11) Å) and Si2-O2 (1.6346(11) Å) bonds, possibly due to the coordination of the N2 atom. The structure shows a distorted trigonal bipyramid geometry, of which three atoms, C1, C10 and O2, construct a deformed trigonal plane (angles: N2-Si1-C1, 76.75(6)°; N2-Si1-C10, 71.58(6)°; N2-Si1-O2, 74.41(5)°) and two atoms, N2 and O1, occupy axial positions. The distortion along the axial direction is demonstrated by the N2–Si1–O1 angle of 175.54(6)°. The sum of internal angles in the 6-membered ring is almost 720° (718.4°) showing only a small deviation from planarity.

Thermal and base-catalyzed ring-opening polymerizations are now being applied to the synthesized cyclosiloxanes.

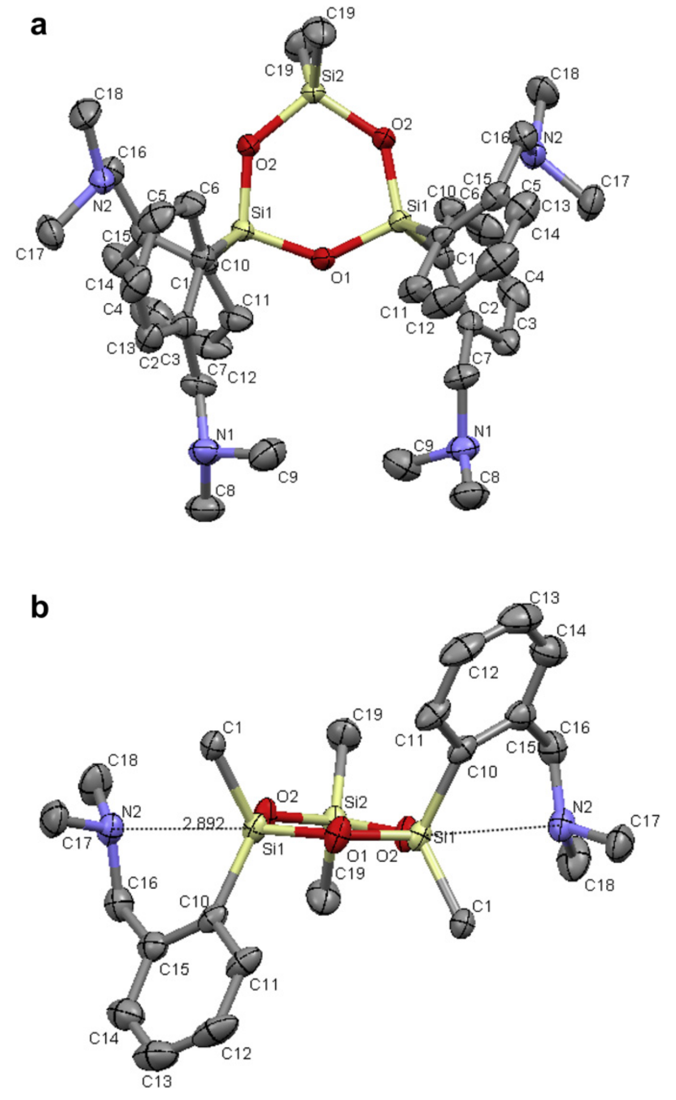


Fig. 1. ORTEP drawing of **6** shown with 30% thermal ellipsoid. Selected bond lengths (Å) and angles (°): Si1-C10, 1.8779(18); Si2-C19, 1.836(2); O(2)-Si(1)–O(1), 105.58(6); Si1#–O(1)-Si1, 134.24(10); O2#-Si2-O2, 107.57(8); Si2-O2-Si1, 132.95(7); C9-N1-C7, 111.21(18); C9-N1-C8, 110.48(19); C7-N1-C8, 110.55(18); C16-N2-C18, 110.90(18); C16-N2-C17, 112.39(16); C18-N2-C17, 110.80(17). (a) Top view. Hydrogen atoms are omitted for clarity. (b) Side view. Two dimethylaminomethylphenyl groups (except C1) and hydrogen atoms are omitted for clarity.

Acknowledgements

This research was supported by a grant from the Fundamental R&D Program for Core Technology of Materials funded by the Ministry of Knowledge Economy, Republic of Korea.

Appendix A. Supplementary Material

CCDC 816353 contains the supplementary crystallographic data for **6**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif.

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