Reactions of cage metal siloxanes with functionalized organochlorosilanes

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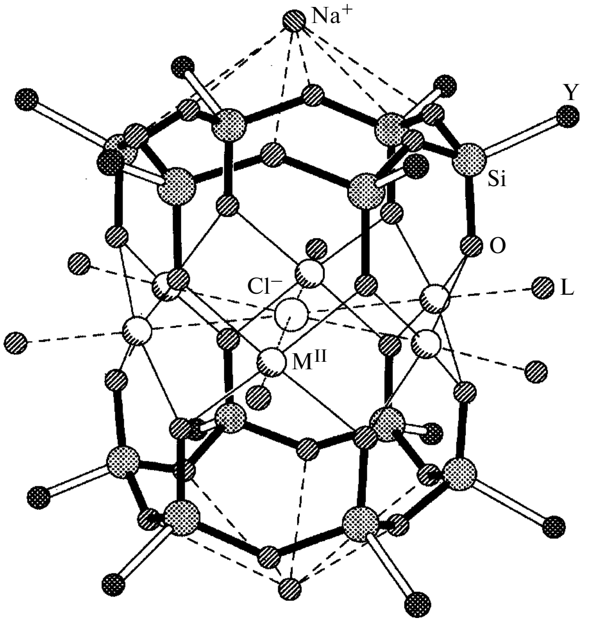
The reactions of [(2-acetoxyetoxy)methyl]dimethylchlorosilane and 1-acetoxy-2-(dimethylchlorosilylmethoxy)benzene with the cage phenylcopper and phenylmanganese siloxanes leads to the cleavage of the M—O—Si bond to give metal chlorides and six-unit cyclosiloxanes with an acetoxy group in the organic substituent at the silicon atom. Methanolysis of these acetoxy derivatives does not affect the ring structure and affords the corresponding polyhydric alcohols.

Key words: cage metal siloxanes, organochlorosilanes, organocyclosiloxanes with functional groups in the organic substituents at silicon.

Destructive trimethylsilylation of cage phenylmetal siloxanes on treatment with trimethylchlorosilane results in the destruction of the cage structure shown in Fig. 1 to give metal chloride and (trimethylsilyloxy)organocyclosiloxanes in which all the phenyl groups at the silicon atoms are arranged on one side of the ring plane and the introduced trimethylsilyl groups are on the other side.[1]



M^{II} = Mn^{II}, Cu^{II}
Y = Me, Ph, vinyl
L = EtOH, BuOH

Fig. 1. Cage structure of organometallic siloxanes.

It was of interest to carry out destructive trimethylsilylation using functionalized triorganochlorosilanes instead of trimethylchlorosilane. The reaction with these chlorosilanes can be promising for the preparation of functionalized stereoregular cyclosiloxanes for extending the scope of application of these compounds in the synthesis of siloxane polymers and copolymers.

The purpose of this work is to study the reaction of the cage phenylmanganese and phenylcopper siloxanes (**1**, **2**) with triorganochlorosilanes $AcO(CH_2)_2OCH_2SiMe_2Cl$ (**3**) and with *o*-$AcOC_6H_4OCH_2SiMe_2Cl$ (**4**), described in our previous study.[2]

Results and Discussion

We found that the reactions of chlorosilanes **3** and **4** with the cage phenylmanganese and phenylcopper siloxanes **1** and **2** result in high yields of cyclosiloxanes **5** and **6**, containing acetoxy groups in the Si-substituents (Scheme 1).

Scheme 1

$$\underset{\mathbf{1,\ 2}}{(PhSiO_{1.5})_6(MO)_6(PhSiO_{1.5})_6} + 12\ \underset{\mathbf{3,\ 4}}{AcO—A—OCH_2SiMe_2Cl}$$

$$\downarrow$$

$$2\ \underset{\mathbf{5,\ 6}}{[(PhSiO)OSiMe_2CH_2O—A—OAc]_6} + 6\ MCl_2$$

M = Mn (**1**), Cu (**2**); A = CH_2CH_2 (**3**, **5**), *o*-C_6H_4 (**4**, **6**)

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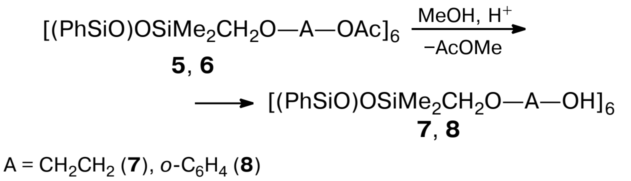
Unlike crystalline products of trimethylsilylation of cage phenylmetal siloxanes, the prepared compounds are thick noncrystallizing liquids.

As shown in our previous study[2] for the corresponding disiloxanes, acetoxy groups are converted into hydroxy groups on acid methanolysis. Methanolysis of cyclosiloxanes **5** and **6** gives compounds **7** and **8**, containing OH groups, in high yields (Scheme 2).

Scheme 2



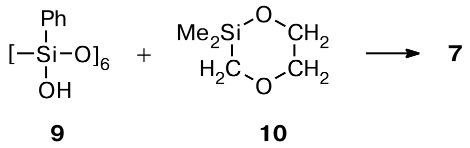
$$[(PhSiO)OSiMe_2CH_2O{-}A{-}OAc]_6 \xrightarrow[-AcOMe]{MeOH,\ H^+} [(PhSiO)OSiMe_2CH_2O{-}A{-}OH]_6$$

5, **6** → **7**, **8**

A = CH_2CH_2 (**7**), *o*-C_6H_4 (**8**)

The structure of cyclosiloxanes **5**—**8** was confirmed by elemental analysis, ^1H NMR spectra, and gel permeation chromatography. Compound **7** was also synthesized *via* an alternative route by condensation of crystalline *cis*-(hexaphenyl)[hexa(hydroxy)]cyclohexasiloxane (**9**)[3] with 2,2-dimethyl-1,4-dioxa-2-silacyclohexane (**10**) (Scheme 3).

Scheme 3



This reaction is based on the ability of heterocycle **10** that we studied previously[4] to condense with silanols with ring opening to give the Si—O—Si fragment (Scheme 4).

Scheme 4

$$Me_3SiOH + \mathbf{10} \longrightarrow Me_3SiOSiMe_2CH_2O(CH_2)_2OH$$

Recently, it was shown[5] that sodium phenylsilanolate, which is the initial product in the synthesis of metal siloxanes, is the cyclotrisiloxane $[PhSi(ONa)O]_3$. We found that the reaction of this compound with chlorosilane **3** gives rise to cyclosiloxane **5**, containing six Si atoms in the ring. Methanolysis of this product yields hexahydric cyclic alcohol **7**, as confirmed by gel permeation chromatography.

Figure 2 shows the gel chromatograms for cyclosiloxanes containing acetoxy groups and the corresponding alcohols. To confirm the six-unit ring structure for the resulting derivatives, we also recorded the gel chromatogram of the crystalline product formed from cage phenylcopper siloxane and trimethylchlorosilane.[1] The pattern of the chromatograms and the volume of the eluent spent indicate that all the compounds we prepared are similar to the trimethylsilyl derivative of cyclosiloxane containing six siloxane units.

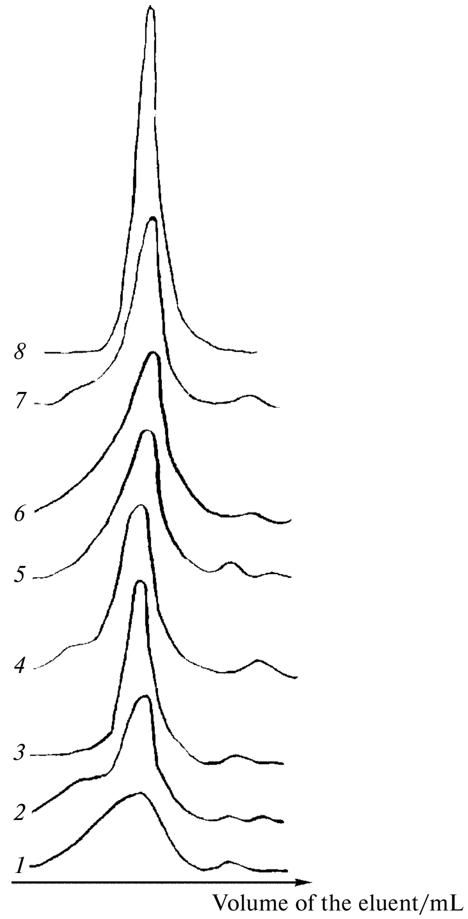


Fig. 2. Gel chromatograms of cyclosiloxane **5** prepared by the reaction of chlorosilane **3** with phenyl manganese siloxane **1** (*1*), the product of its methanolysis (*2*), chlorosilane **3** with phenylcopper siloxane **2** (*3*) and the product of its methanolysis (*4*), chlorosilane **3** with sodium phenylsilanolate (*5*) and the product of its methanolysis (*6*), product **7** prepared by condensation of siloxane **9** with dioxasilacyclohexane **10** (*7*), and the product of trimethylsilylation of phenylcopper siloxane (*8*).

Thus, the reaction of cage metal siloxanes with organochlorosilanes is general; the use of organochlorosilanes with functional groups in organic substituents opens up prospects for the synthesis of polyfunctional cyclosiloxanes, which can serve as the starting compounds in the synthesis of polymers.

Experimental

^1H NMR spectra were recorded on a Bruker WP-200SY spectrometer (200 MHz) in CCl_4 using Me_4Si as the internal standard. Gel chromatograms were measured on a Waters-510 instrument equipped with a UV detector and Ultrastyragel columns (10^2, 10^3 and 10^4 Å, THF as the eluent, flow rate

1 mL min^{-1}, 35 °C). The products of the reaction between Me_3SiCl and cage phenyl copper siloxane and sodium phenylsilanolate were prepared by previously described procedures.^{1,5}

2,4,6,8,10,12-Hexaphenyl-2,4,6,8,10,12-hexa[(2-acetoxyethoxy)methyl(dimethyl)silyloxy]cyclohexasiloxane (5). ***A.*** A solution of chlorosilane **3** (4.8 g, 22 mmol) in 10 mL of toluene was added with stirring to a suspension of cage siloxane **1** (3.0 g, 1.5 mmol) in 40 mL of toluene. As the chloride was added, the color of the reaction mixture changed from dark-brown to gray. After heating for 3 h at 100 °C, the precipitated $MnCl_2$ was filtered off and toluene and excess chlorosilane **3** were removed using a rotary evaporator to give 5.05 g (89%) of compound **5** as a transparent colorless thick liquid. The Beilstein test showed the absence of chloride. Found (%): C, 49.06; H, 6.76; Si, 17.71. $C_{78}H_{120}Si_{12}O_{30}$. Calculated (%): C, 50.06; H, 6.45; Si, 17.97. ^{1}H NMR, δ: 0.40 (s, 6 H, Me_2Si); 2.10 (s, 3 H, Ac); 3.25 (s, 2 H, CH_2Si); 3.80 (t, 2 H, CH_2O); 4.25 (t, 2 H, CH_2O); 7.50 (m, 5 H, Ph).

B. Chlorosilane **3** (2.5 g, 12 mmol) was added with vigorous stirring to a suspension of cage siloxane **2** (2 g, 0.98 mmol) in 40 mL of benzene. As chlorosilane was added, the suspension color changed from blue to brown. After heating for 3 h at 80 °C, the precipitate was filtered off and benzene was removed *in vacuo* to give 2.7 g (79%) of compound **5** as a light-yellow transparent thick liquid. Found (%): C, 49.30; H, 6.66; Si, 17.29. $C_{78}H_{120}Si_{12}O_{30}$. Calculated (%): C, 50.06; H, 6.45; Si, 17.97. ^{1}H NMR, δ: 0.35 (s, 6 H, Me_2Si); 2.00 (s, 3 H, Ac); 3.20 (s, 2 H, CH_2Si); 3.60 (t, 2 H, CH_2O); 4.15 (t, 2 H, CH_2O); 7.35 (m, 5 H, Ph).

C. A solution of chlorosilane **3** (4.2 g, 20 mmol) in 10 mL of toluene was added to sodium phenylsilanolate (3.2 g, 20 mmol) suspended in 40 mL of toluene. After heating for 4 h at 100 °C, the reaction mixture was filtered to remove NaCl and the filtrate was concentrated *in vacuo* to give 5.95 g (95%) of compound **5**. Found (%): C, 50.02; H, 6.52; Si, 17.17. $C_{78}H_{120}Si_{12}O_{30}$. Calculated (%): C, 50.06; H, 6.45; Si, 17.97. ^{1}H NMR, δ: 0.34 (s, 6 H, Me_2Si); 2.20 (s, 3 H, Ac); 3.28 (s, 2 H, CH_2Si); 3.75 (t, 2 H, CH_2O); 4.30 (t, 2 H, CH_2O); 7.50 (m, 5 H, Ph).

2,4,6,8,10,12-Hexaphenyl-2,4,6,8,10,12-hexa[(2-hydroxyethoxy)methyl(dimethyl)silyloxy]cyclohexasiloxane (7). ***A.*** A solution of cyclosiloxane **5** (1 g, 0.5 mmol) in MeOH (1.0 g, 3 mmol) acidified with 0.01 mL of HCl was kept for 24 h at ~20 °C. After that, AcOMe was evaporated first under normal pressure and then *in vacuo* to give 0.9 g (99%) of compound **7** as a colorless thick liquid. Found (%): C, 48.28; H, 6.96; Si, 21.14. $C_{66}H_{108}Si_{12}O_{24}$. Calculated (%): C, 48.85; H, 6.71; Si, 20.77. ^{1}H NMR, δ: 0.30 (s, 6 H, MeSi); 3.20 (s, 2 H, CH_2Si); 3.70 (t, 2 H, CH_2O); 4.20 (t, 2 H, CH_2O); 7.30 (m, 5 H, Ph).

B. Compound **5** (1.05 g, 0.56 mmol) was dissolved in 1.15 g of MeOH acidified with 0.01 mL of HCl. After 24 h, the product was evacuated to a constant weight to give 0.9 g (98%) of compound **7** as a colorless thick liquid. Found (%): C, 48.59; H, 6.76; Si, 21.21. $C_{66}H_{108}Si_{12}O_{24}$. Calculated (%): C, 48.85; H, 6.71; Si, 20.77. ^{1}H NMR, δ: 0.30 (s, 6 H, Me_2Si); 3.17 (s, 2 H, CH_2Si); 3.70 (t, 2 H, CH_2O); 4.18 (t, 2 H, CH_2O); 7.26 (m, 5 H, Ph).

C. A solution of compound **5** (1.45 g, 0.77 mmol) in MeOH (1.5 g, 47 mmol) acidified with HCl was kept for 24 h, AcOMe was evaporated, and the residue was evacuated to a constant weight to give 1.3 g (99%) of compound **7**. Found (%): C, 47.65; H, 6.80; Si, 20.45. $C_{66}H_{108}Si_{12}O_{24}$. Calculated (%): C, 48.65; H, 6.71; Si, 20.77. ^{1}H NMR, δ: 0.15 (s, 6 H, Me_2Si); 3.30 (s, 2 H, CH_2Si); 3.70 (t, 2 H, CH_2O); 4.15 (t, 2 H, CH_2O); 7.50 (m, 5 H, Ph).

2,4,6,8,10,12-Hexaphenyl-2,4,6,8,10,12-hexa[(2-acetoxyphenoxy)methyl(dimethyl)silyloxy]cyclohexasiloxane (6). A solution of chlorosilane **4** (1.55 g, 5.9 mmol) in 10 mL of toluene was added to a suspension of cage siloxane **2** (1 g, 0.49 mmol) in 30 mL of toluene. As chlorosilane was added (5 min), the color of the reaction mixture gradually changed from blue to brown. After a 3.5-h heating at ~100 °C, the mixture was filtered to remove the precipitate and the filtrate was concentrated to give 1.8 g (85%) of compound **6** as a red-brown transparent thick liquid. Found (%): C, 57.19; H, 5.87; Si, 14.38. $C_{102}H_{120}Si_{12}O_{30}$. Calculated (%): C, 56.63; H, 5.59; Si, 15.58. ^{1}H NMR, δ: 0.22 (s, 6 H, Me_2Si); 2.13 (s, 3 H, Ac); 3.49 (s, 2 H, CH_2Si); 6.95 (m, 9 H, Ph, H arom.).

2,4,6,8,10,12-Hexaphenyl-2,4,6,8,10,12-hexa[(2-hydroxyphenoxy)methyl(dimethyl)silyloxy]cyclohexasiloxane (8). A solution of cyclosiloxane **6** (1.5 g, 0.78 mmol) in MeOH (1.5 g, 47 mmol) acidified with HCl was kept for 24 h at ~20 °C and evacuated to give 1.25 g (94%) of compound **8** as a reddish transparent thick liquid. Found (%): C, 56.08; H, 5.51; Si, 17.20. $C_{90}H_{108}Si_{12}O_{24}$. Calculated (%): C, 56.56; H, 5.69; Si, 17.63. ^{1}H NMR, δ: 0.25 (s, 6 H, Me_2Si); 3.55 (s, 2 H, CH_2Si); 7.05 (m, 9 H, Ph, H arom.).

Condensation of *cis*-(hexaphenyl)[hexa(hydroxy)]cyclohexasiloxane (9) with 2,2-dimethyl-1,4-dioxa-2-silacyclohexane (10). A solution of siloxane **9** (1 g, 1.2 mmol) and silacyclohexane **10** (1.05 g, 7.9 mmol) in 10 mL of AcOBu containing Et_3N and DMSO (each 0.05 mL) was heated with stirring for 1.5 h at ~60 °C. Evaporation of AcOBu and excess **10** *in vacuo* gave 1.93 g (99%) of compound **7** as a colorless transparent thick liquid. Found (%): C, 49.13; H, 6.51; Si, 20.16. $C_{66}H_{108}Si_{12}O_{24}$. Calculated (%): C, 48.85; H, 6.71; Si, 20.77. ^{1}H NMR, δ: 0.25 (s, 6 H, Me_2Si); 3.20 (s, 2 H, CH_2Si); 3.57 (t, 2 H, CH_2O); 4.25 (t, 2 H, CH_2O); 7.45 (m, 5 H, Ph).

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