## Reactions of 1,4-dioxa-2-silacyclohexanes with acetyl chloride

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The reactions of 1,4-dioxa-2-silacyclohexanes with acetyl chloride lead to the cleavage of the Si-O bond to form chlorotriorganosilanes containing the acetoxy group in the organic radical at the silicon atom. Hydrolysis of these chlorosilanes affords bis(acetoxy-alkoxy(aryloxy)methyl)disiloxanes, while the reactions with cage copper sodium phenylsiloxane give dodecaphenyl[dodeca(acetoxyorganodimethylsilyloxy)]cyclododecasiloxanes.

Key words: dioxasilacyclohexanes, metallosiloxanes, opening of siloxane rings, functionalized organocyclosiloxanes.

Previously,<sup>1,2</sup> the cleavage of the Si--O bond in heterocycles containing siloxane fragments has been studied using 2,2-dimethyl-1-oxa-2-silacyclohexane as an example. It was established that the reactions of this compound with organic acids in the presence of catalytic amounts of  $H_2SO_4$  were accompanied by the ring opening to form bis(4-acyloxybutyl)tetramethyldisiloxanes,<sup>1</sup> while the reactions with carboxylic acid chlorides afforded 4-acyloxybutylchlorodimethylsilanes.<sup>2</sup>

Reactions of AcCl with 1,4-dioxa-2-silacyclohexanes containing two reaction centers have not been studied previously.

The aim of this work is to develop a practical procedure for the synthesis of chlorotriorganosilanes containing functional groups in organic radicals. The reactions of these functionalized chlorotriorganosilanes with cage metallosiloxanes should afford stereoregular functionalized organocyclosiloxanes, which substantially extends the scope of destructive triorganosilylation of metallosiloxanes.

## **Results and Discussion**

We found that 2,2-dimethyl-1,4-dioxa-2-silacyclohexane reacts with AcCl only at the Si—O bond to form chlorotriorganosilane (Scheme 1). The reaction of a pyrocatechol cyclosiloxane derivative proceeds analogously. However, in this case the Si—O bond of the heterocycle is cleaved only in the presence of  $ZnCl_2$ . Apparently, this is attributable to partial stabilization of the Si—O bond due to the participation of the electron pair of the oxygen atom in the conjugated system with the aromatic ring.

Hydrolysis of compounds 1 and 2, which we have prepared for the first time, afforded bis(acetyl) derivatives, viz., disiloxanes 3 and 4, respectively (Scheme 2). Acid methanolysis of acetates 3 and 4 gave the corre-



sponding hydroxy derivatives  $[HO(CH_2)_2OCH_2SiMe_2]_2O$ (5) and  $[HOC_6H_4OCH_2SiMe_2]_2O$  (6).

Note that, to our knowledge, the procedure shown in Scheme 1 is virtually the only suitable procedure for the synthesis of chlorotriorganosilanes containing the acetoxy group in the organic radical, which can be readily converted to the hydroxy group.

Chlorotriorganosilanes 1 and 2 synthesized by us were used for decomposing cage copper sodium phenyl-siloxane.<sup>3</sup>

The destructive trimethylsilylation reaction is known in the chemistry of cage metallosiloxanes. Thus the reactions of Me<sub>3</sub>SiCl with cage metallosiloxanes are accompanied by destruction of the cage structure to

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form metal chloride and cyclosiloxane in which all organic radicals initially bonded with the silicon atoms are arranged on the same side of the plane of the ring, while all the trimethylsilyl groups that are introduced are on the opposite side of this plane.

In this work, we report the preliminary results of examination of the possibilities of extension of this method with the use of the above-described functionalized chlorotriorganosilanes.

It is known that cage copper sodium phenylsiloxane of the general formula  $(PhSiO_{1,5})_{12}(CuO)_4(NaO_{0,5})_4$  contains the 24-membered siloxane cyclic cage, which consists of 12 Si atoms and 12 O atoms.<sup>3</sup> This ring adopts a saddle-like conformation. Each three phenyl radicals at the three successive silicon atoms are in *trans* positions with respect to the next three phenyl radicals. Correspondingly, this spatial arrangement of the groups in the resulting cyclosiloxane remains unchanged after trimethylsilylation.

Analogously, the reactions of chlorotriorganosilanes 1 and 2 with copper sodium phenylsiloxane afforded dodecaphenyl[dodeca(2-acetoxyethoxymethyldimethylsilyloxy)] cyclododecasiloxane (PhSiO)<sub>12</sub>[OSiMe<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>OOCMe]<sub>12</sub> (7) and dodecaphenyl[dodeca(2-acetoxyphenoxymethyldimethylsilyloxy)] cyclododecasiloxane (PhSiO)<sub>12</sub>[OSiMe<sub>2</sub>CH<sub>2</sub>OC<sub>6</sub>H<sub>4</sub>OOCMe]<sub>12</sub> (8), respectively.

The resulting cyclosiloxanes were purified by reprecipitation with heptane from a toluene solution. Analysis of the isolated fractions by gel permeation chromatography demonstrated that cyclosiloxane 8, which was isolated after reprecipitation, contained disiloxane 4 as an admixture. The latter was formed upon decomposition of an excess of chlorosilane 2 with water. Additional reprecipitation afforded the pure product as a viscous oil that could not be crystallized.

Therefore, chlorotriorganosilanes containing a functional group in the organic radical at the silicon atom, which are prepared by the reactions of 1,4-dioxa-2-silacyclohexanes with AcCl, can be used for decomposing cage metallosiloxanes with the aim of synthesizing cyclosiloxanes containing functional groups in organic radicals.

## Experimental

The <sup>1</sup>H NMR spectra were recorded on a Bruker WP-200SY spectrometer (200 MHz) in CCl<sub>4</sub> with Me<sub>4</sub>Si as the internal standard. Gel permeation chromatography was carried out in THF on a Waters liquid chromatograph equipped with an M 484 UV--VIS detector (wavelength 260 nm) and two V-Styragel Linear columns (flow rate 1 mL min<sup>-1</sup>, 30 °C, polystyrene as the standard). The initial 1,4-dioxa-2-silacyclohexanes were synthesized according to procedures reported previously.<sup>4,5</sup> All products were distilled immediately before use.

[(2-Acetoxyetboxy)metbyl]dimethylchlorosilane (1). 2,2-Dimethyl-1,4-dioxa-2-silacyclohexane (6.7 g, 0.05 mol) was mixed with AcCl (7.9 g, 0.1 mol), which was accompanied by heat evolution (the mixture warmed up to 50 °C). The reaction mixture was kept at 20 °C for 20 h and AcCl was distilled off. The residue was distilled *in vacuo*. Compound 1 was isolated in a yield of 6.4 g (88%), b.p. 92 °C (10 Torr),  $d_4^{20}$  1.0604,  $n_D^{20}$  1.4352. Found (%): C, 39.65; H, 7.12; Si, 12.76; Cl, 16.91. C<sub>7</sub>H<sub>15</sub>ClO<sub>3</sub>Si. Calculated (%): C, 39.89; H, 7.17; Si, 13.33; Cl, 16.82. <sup>1</sup>H NMR,  $\delta$ : 0.40 (s, 6 H, MeSi); 1.95 (s, 3 H, MeCO); 3.24 (s, 2 H, CH<sub>2</sub>Si); 3.52 (t, 2 H, CH<sub>2</sub>O); 4.05 (t, 2 H, CH<sub>2</sub>O).

1-Acetoxy-2-(dimethylchlorosilylmethoxy)benzene (2). ZnCl<sub>2</sub> (0.05 g) was added to a mixture of 2,2-dimethyl-1,4-dioxa-2-sila-5,6-benzocyclohexane (18.01 g, 0.1 moi) and AcCl (15.6 g, 0.2 mol). The mixture warmed up to 35 °C. After 24 h, AcCl was distilled off and the residue was distilled *in vacuo*. Compound 2 was isolated in a yield of 20.1 g (78%), b.p. 118-120 °C (1 Torr),  $d_4^{20}$  1.1393,  $n_D^{20}$  1.5050. Found (%): C, 51.85; H, 6.28; Si, 10.68; Cl, 12.82. C<sub>11</sub>H<sub>15</sub>ClO<sub>3</sub>Si. Calculated (%): C, 51.05; H, 5.84; Si, 10.85; Cl, 13.69. <sup>1</sup>H NMR,  $\delta$ : 0.31 (s, 6 H, MeSi); 2.01 (s, 3 H, MeCO); 3.5 (t, 2 H, CH<sub>2</sub>O); 6.5-7.0 (m, 4 H, Ph).

Bis(2-acetoxyethoxymethyl)tetramethyldisiloxane (3). Chlorosilane 1 (6.32 g, 0.03 mol) was mixed with water (6 mL). The reaction mixture warmed up to 40 °C. After 2 h, ethyl acetate (10 mL) was added. The mixture was washed with water until the test for the presence of Cl<sup>-</sup> became negative and dried with Na<sub>2</sub>SO<sub>4</sub>. Ethyl acetate was distilled off and the residue was distilled *in vacuo*. Disiloxane 3 was isolated in a yield of 4.1 g (74%), b.p. 125–127 °C (1 Torr),  $d_4^{20}$  1.0320,  $n_D^{20}$  1.4333. Found (%): C, 46.40; H, 8.58; Si, 14.76. C<sub>14</sub>H<sub>30</sub>O<sub>7</sub>Si<sub>2</sub>. Calculated (%): C, 45.87; H, 8.25; Si, 15.32. <sup>1</sup>H NMR,  $\delta$ : 0.07 (s, 6 H, MeSi); 1.95 (s, 3 H, MeCO); 3.06 (s, 2 H, CH<sub>2</sub>Si); 3.51 (t, 2 H, CH<sub>2</sub>O); 4.07 (t, 2 H, CH<sub>2</sub>O).

1,2-Bis(2-acetoxyphenoxymethyl)tetramethyldisiloxane (4). Water (8 mL) was added with intense stirring to chlorosilane 2 (7.74 g, 0.03 mol). After 24 h, the product was extracted with benzene, washed with water until the test for the presence of Cl<sup>-</sup> became negative, and dried with Na<sub>2</sub>SO<sub>4</sub>. Benzene was distilled off and the residue was distilled *in vacuo*. Disiloxane 4 was isolated in a yield of 4.15 g (60%), b.p. 214-215 °C (2 Torr),  $d_4^{20}$  1.1235,  $n_D^{20}$  1.5105. Found (%): C, 56.94; H, 6.79; Si, 12.20. C<sub>22</sub>H<sub>30</sub>O<sub>7</sub>Si<sub>2</sub>. Calculated (%): C, 57.11; H, 6.53; Si, 12.14. <sup>1</sup>H NMR,  $\delta$ : 0.26 (s, 6 H, MeSi); 2.21 (s, 3 H, MeCO); 3.56 (s, 2 H, CH<sub>2</sub>O); 6.7-7.4 (m, 4 H, Ph).

Methanolysis of disiloxane 3. Disiloxane 3 (4.1 g, 0.011 mol) was dissolved in MeOH (55 mL), which was acidified with concentrated HCl (0.1 mL). After 24 h, the mixture was concentrated and the residue was distilled *in vacuo*. Compound 5 was isolated in a yield of 2.3 g (73%), b.p. 120 °C (2 Torr),  $n_D^{20}$  1.4450. Found (%): C, 42.00; H, 9.22; Si, 18.98. C<sub>10</sub>H<sub>26</sub>O<sub>5</sub>Si<sub>2</sub>. Calculated (%): C, 42.51; H, 9.27; Si, 19.88. Literature data:<sup>4</sup> b.p. 133 °C (3 Torr);  $n_D^{20}$  1.4445.

Methanolysis of disiloxane 4. The corresponding disiloxanediol 6 was synthesized from disiloxane 4 (3.1 g, 0.0067 mol) using an analogous procedure in a yield of 2.2 g (86%), m.p. 47 °C. Found (%): C, 56.45; H, 6.51; Si, 14.09.  $C_{18}H_{26}O_5Si_2$ . Calculated (%): C, 57.10; H, 6.92; Si, 14.84. Literature data:<sup>5</sup> m.p. 48 °C.

Reactions of chlorosilanes 1 and 2 with cage copper sodium phenylsiloxane. A solution of chlorosilane 1 (6 g, 0.03 mol) in toluene (10 mL) was added with intense stirring to a solution of cage copper sodium phenylsiloxane (3.18 g, 1.6 mmol) in toluene (10 mL). The mixture was stirred at ~20 °C for 2 h and then pyridine (1 mL) was added. The reaction mixture was heated at 60 °C for 1 h and water (50 mL) was added. The toluene layer was separated, the aqueous phase was extracted with toluene, and the combined toluene extracts were washed with water and dried with Na<sub>2</sub>SO<sub>4</sub>. The mixture was concentrated and the product was precipitated with heptane and dried. Compound 7 was obtained in a yield of 3.1 g (50%). Found (%): C, 51.14; H, 6.21; Si, 17.48. C<sub>156</sub>H<sub>240</sub>O<sub>60</sub>Si<sub>24</sub>. Calculated (%): C, 49.97; H, 6.45; Si, 17.97. <sup>1</sup>H NMR,  $\delta$ : 0.40 (s, 6 H, MeSi); 1.95 (s, 3 H, MeCO); 3.24 (t, 2 H, CH<sub>2</sub>Si); 3.90 (t, 2 H, CH<sub>2</sub>O); 4.0 (t, 2 H, CH<sub>2</sub>O); 7.4 (s, 5 H, Ph).

Compound 8 was obtained analogously from chlorosilane 2 (6 g, 0.023 mol) and copper sodium phenylsiloxane (2.66 g, 1.3 mmol) as a viscous oily liquid in a yield of 3.3 g (56%). Found (%): C, 56.57; H, 5.63; Si, 15.63.  $C_{204}H_{240}O_{60}Si_{24}$ . Calculated (%): C, 56.63; H, 5.59; Si, 15.58. <sup>1</sup>H NMR,  $\delta$ : 0.31 (s, 6 H, MeSi); 2.01 (s, 3 H, MeCO); 3.35 (s, 2 H, CH<sub>2</sub>O); 6.5–7.0 (m, 4 H, Ph).

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