Domino Oxidation of Ladder Oligosilanes: Formation of Novel Ladder Frameworks Containing Oligosiloxane and Oligosilane Chains

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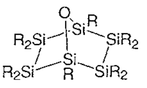
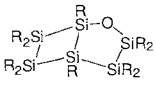
The domino oxidation predominates in the tri-, tetra-, and penta-oxidations of tricyclic, tetracyclic, and pentacyclic ladder oligosilanes **5**, **7**, and **9** with *m*-chloroperoxybenzoic acid. The structures of these products were determined by X-ray crystallography. The resulting domino oxidation products **6**, **8**, and **10** show intense absorption bands in the UV spectra.

The oxidation of Si–Si bonds with peracids has been known to be one of the fundamental reactions of oligo- and polysilanes.[1] Two examples of the polyoxidation of cyclo-oligosilanes have so far appeared in the literature. West and a co-worker reported that the successive oxidation of the stereoisomers of (*t*-BuMeSi)$_4$ is stereospecific and regioselective.[1g] Weber and a coworker reported that the successive insertion of oxygen atoms into the Si–Si bonds of (Me$_2$Si)$_6$ regularly occurs during the oxidation.[1h] Ladder oligosilanes, which have been studied by our group,[2] seem to be interesting targets of polyoxidation because these molecules have many kinds of Si–Si bonds. In a previous paper, we reported that the oxidation of decaisopropylbicyclo-[2.2.0]hexasilane (**1**) with a slightly deficient amount (0.7 equiv.) of *m*-chloroperoxybenzoic acid (MCPBA) gave the monooxide **2** (32%) and **3** (18%) and dioxide **4** (39%).[2e,6]


2: R = *i*-Pr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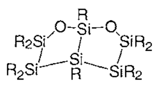
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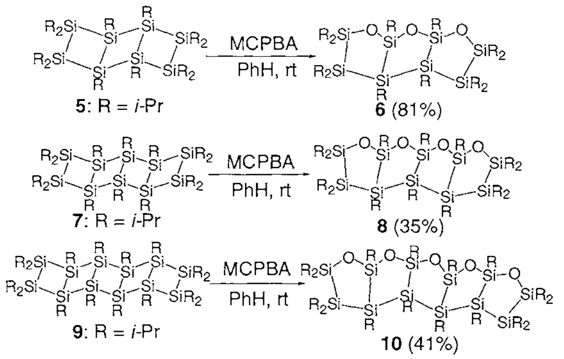
During the oxidation, we have also been interested in the formation of a significant amount of dioxa compound **4** because this result suggests that **3** is quite easily oxidized to **4** in spite of a deficient amount of MCPBA. We have thus found that when **1** was oxidized with 2 equivalents of MCPBA, **3** was completely transformed into **4**, and **4** and **2** were obtained as the final products. We have now extended the MCPBA polyoxidation to the other ladder oligosilanes. Here we report the domino oxidation of the ladder oligosilanes leading to other novel ladder compounds.[3,4]

When *anti*-dodecaisopropyltricyclo[4.2.0.0^{2,5}]octasilane (**5**) was oxidized with 3 equivalents of MCPBA, the trioxide **6** was obtained in 81% yield.[5] Similarly, the oxidation of *anti,anti*-tetradecaisopropyltetracyclo[4.4.0.0^{2,5}.0^{7,10}]decasilanes (**7**), and *anti,anti,anti*-hexadecaisopropylpentacyclo[6.4.0.0^{2,7}.0^{3,6}.0^{9,12}]-dodecasilane (**9**) with 4 and 5 equivalents of MCPBA yielded the tetraoxide **8**[7] and pentaoxide **10**,[8] respectively, in moderate yields. Therefore, the ladder oligosilanes were found to be oxidized in a quite unique manner; one of the two Si-Si chains is selectively oxidized, and novel ladder compounds consisting of oligosiloxane and oligosilane chains were formed.



The structures of the polyoxides **6**, **8**, and **10** were confirmed by X-ray crystallography.[9] Figures 1 and 2 show the ORTEP drawings of **6** and **10**. These molecules have a curved shape containing an oligosiloxane chain as the outer arch and an oligosilane chain as the inner arch. These molecules retain the *anti* structure of the starting ladder oligosilanes,[10] and each five-membered ring is catenated in a corrugated manner. Furthermore, the corrugated arch is twisted as shown in the Figures 1 and 2. The twisted structures arise from the systematic catenation of the five-membered rings which have an intermediate structure between the envelope and twist forms. The Si–Si bonds of the inner oligosilane chain are significantly long (**6**: 2.399(2)–2.409(2) Å. **8**: 2.404(3)–2.420(3) Å. **10**: 2.389(2)–2.434(3) Å), while the other Si–Si bond lengths are rather normal (**6**: 2.388(2)–2.390(2) Å. **8**: 2.375(3)–2.395(3) Å. **10**: 2.390(3)–2.410(2) Å). The enlarged steric repulsion among the isopropyl groups of the inner oligosilane chain, which is caused by the introduction of oxygen atoms to the opposite chain, seems to be the origin of the elongation of the Si–Si bonds.

There are several significant features of this polyoxidation. Only small or negligible amounts of intermediate oxidation products are detected during the reactions. For example, in the case of the tricyclooctasilane **5**, the intermediate mono- and dioxidation products were not detected even during the initial stage of the reaction, but **6** was formed instead. This means that the mono- and dioxidation products are highly activated toward oxidation, and are immediately oxidized to **6** after they are formed. The positional selectivity observed during the

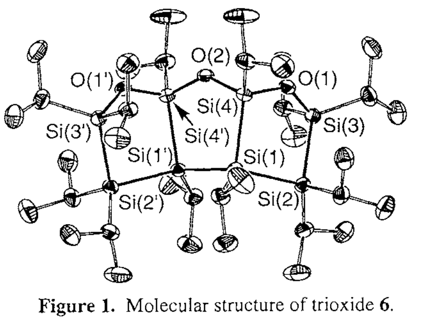


Figure 1. Molecular structure of trioxide **6**.

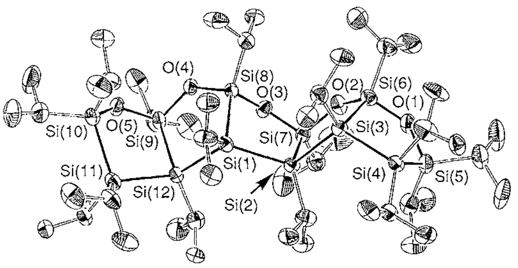


Figure 2. Molecular structure of pentaoxide **10**.

oxidation may be explained in terms of a significant enhancement of the reactivity of the Si–Si bonds adjacent to the oxygen due to an electronic effect[1g] as well as hydrogen bonding of MCPBA to the siloxane oxygen which brings the peracid into close proximity to the adjacent Si–Si bonds.[1h] When all the Si_4 rings were oxidized to the Si_4O rings, further oxidation did not proceed under the conditions employed and the polyoxidation products containing an oxygen atom in each ring were obtained. Apparently, release of the strain energy of the Si_4 rings seems to be another driving force of this particular polyoxidation.

The oxidation products **4**, **6**, **8**, and **10** are interesting from the viewpoint of their electronic properties. They exhibit intense absoptions in the UV region, and, as the number of the Si_4O rings increases, the absorption maxima of the longest wavelengths show a bathochromic shift, and the molecular extinction coefficient becomes far greater (**4**: 270 nm (ε 3200), **6**: 273 nm (ε 7600), **8**: 292 nm (ε 25000), **10**: 297 nm (ε 51900))(Figure 3). The intense absorption on the order 10^4 is remarkable because these molecules contain no chromophores which give such an intense absorption. Since the intense absorption is not observed in the ladder oligosilanes,[2] it is apparently due to the electronic effect of the oxygen atoms on the Si–Si σ–conjugation systems.

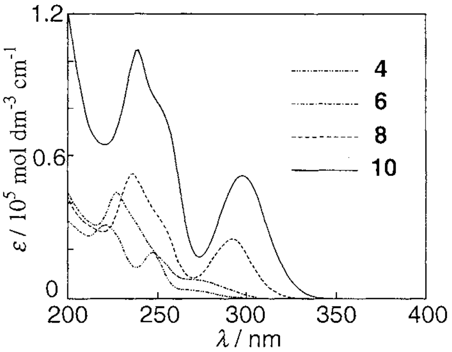


Figure 3. UV spectra of oxides **4–10** in hexane.

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References and Notes

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3 H. Matsumoto, 12th International Symposium on Organosilicon Chemistry, Sendai, May, 1999, Abstr., p. 74.

4 As far as we know, compounds such as **6**, **8**, and **10** have not been reported as carbon analogs with linear frameworks. We are grateful to the reviewer who indicated for us that there have so far been several reports on the syntheses and structures of carbon analogs with cyclic frameworks, such as 'oxa-bowls', [n]-oxa-[n]-peristylanes (G. Mehta and R. Vidya, *Tetrahedron Lett.*, **38**, 4173 (1997); G. Mehta and R. Vidya, *Tetrahedron Lett.*, **38**, 4177 (1997)) and the polyketal being composed of $(CR_2O)_6$ units incorporated with a $[1_6]$orthocyclophane. (W. Y. Lee, C. H. Park, and S. Kim, *J. Am. Chem. Soc.*, **115**, 1184 (1993)).

5 A solution of **5** (37.3 mg, 0.0503 mmol) and MCPBA (38.0 mg, assay 70%) in benzene (5 mL) was stirred at room temperature for 24 h. The solvent was removed by evaporation, and the residue was dissolved in hexane. The mixture was passed through a short column of silica gel, and the eluate was evaporated. Separation of the residue by recycle-type HPLC (ODS, methanol–THF (65 : 35)) gave **6** as colorless crystals (32.3 mg, 81%). M.p. 197–199 °C; ^1H NMR (C_6D_6) δ 1.05 (sept, J = 7.2 Hz, 2H), 1.14 (d, J = 7.3 Hz, 6H), 1.17 (sept, J = 7.3 Hz, 2H), 1.22 (d, J = 7.3 Hz, 6H), 1.28 (d, J = 7.3 Hz, 6H), 1.30 (d, J = 7.3 Hz, 6H;), 1.32 (d, J = 7.7 Hz, 6H), 1.33 (d, J = 7.6 Hz, 6H), 1.34 (d, J = 8.2 Hz, 6H), 1.35 (d, J = 7.0 Hz, 12H), 1.40 (d, J = 7.3 Hz, 6H), 1.42-1.55 (m, 16H), 1.68 (sept, J = 7.4 Hz, 2H), 1.78 (sept, J = 7.4 Hz, 2H); ^{13}C NMR (C_6D_6) δ 13.3, 14.2, 14.3, 16.5, 17.9, 18.0, 18.1, 18.4, 19.06, 19.09, 20.3, 22.7, 23.0, 23.2, 24.3, 25.6; ^{29}Si NMR (C_6D_6) δ –54.9, –2.7, –2.0, 14.9; IR (KBr, cm^{-1}) 2940, 2860, 1460, 1380, 1360, 1220, 1060, 940, 870, 690; UV (ε, hexane): λ_{max} 273 (7600, sh), 250 (17600, sh), 238 (31200, sh), 227 nm (44500); MS (70 eV): *m/z* (%): 788 (M^+, 43), 745 (100).

6 **4**: m.p. 262 °C; ^1H NMR (C_6D_6) δ 1.12–1.50 (m, 67H), 1.68 (sept, J = 7.4 Hz, 2H), 1.69 (sept, J = 7.5 Hz, 1H); ^{13}C NMR (C_6D_6) δ 12.1, 14.7, 14.9, 17.7, 17.75, 17.79, 17.9, 18.5, 18.8, 19.2, 19.9, 22.5, 22.8, 23.1, 23.2, 25.0; ^{29}Si NMR (C_6D_6) δ –74.3, –5.2, 3.1, 14.8; IR (KBr, cm^{-1}) 2940, 2860, 1460, 1380, 1360, 1220, 1060, 950, 870, 700; UV (ε, hexane): λ_{max} 270 (3200, sh), 247 (18900), 221 nm (30700); MS (70 eV): *m/z* (%) 630 (M^+, 72), 587 (100), 545 (47), 58 (42).

7 **8**: m.p. 172–173 °C; ^1H NMR (C_6D_6) δ 1.13–1.52 (m, 90H), 1.64 (sept, J = 7.4 Hz, 2H), 1.70 (sept, J = 7.3 Hz, 4H), 1.88 (sept, J = 7.3 Hz, 2H); ^{13}C NMR (C_6D_6) δ 12.9, 13.9, 14.7, 17.6, 17.66, 17.68, 17.8, 18.0, 18.4, 18.85, 18.90, 19.0, 19.2, 19.6, 22.6, 23.1, 23.2, 23.4, 24.6, 25.0, 25.8; ^{29}Si NMR (C_6D_6) δ –56.9, –34.7, –4.8, –3.0, –0.4, 14.9; IR (KBr, cm^{-1}) 2940, 2860, 1460, 1380, 1360, 1220, 1060, 990, 940, 870, 700; UV (ε, hexane) λ_{max} 292 (25000), 252 (32100, sh), 235 nm (52500); MS (70 eV) *m/z* (%): 946 (M^+, 20), 903 (100), 386 (33), 58 (34).

8 **10**: m.p. 236–237 °C; ^1H NMR (C_6D_6) δ 1.08–1.52 (m, 100H), 1.60 (sept, J = 7.5 Hz, 2H), 1.80 (sept, J = 7.3 Hz, 6H), 1.87 (sept, J = 7.4 Hz, 2H); ^{13}C NMR (C_6D_6) δ 13.5, 14.2, 14.36, 14.37, 16.9, 17.4, 17.7, 17.9, 18.0, 18.1, 18.2, 18.9, 19.07, 19.14, 19.4, 20.1, 22.6, 22.7, 22.8, 23.1, 24.4, 24.5, 25.7, 26.4; ^{29}Si NMR (C_6D_6) δ –52.7, –35.7, –5.1, –3.1, –1.5, 14.7; IR (KBr, cm^{-1}) 2940, 2870, 1460, 1380, 1360, 1260, 940, 880, 800; UV (ε, hexane) λ_{max} 297 (51900), 252 (79600, sh), 238 nm (104700); MS (70 eV): *m/z* (%): 1104 (M^+, 20), 525 (71), 490 (66), 386 (100).

9 Crystal data for **6**: $C_{36}H_{84}Si_8O_3$ (FW = 789.75), monoclinic, $C2/c$, a = 20.097(1), b = 10.791(1), c = 22.845(1) Å, β = 90.559(4)°, V = 4954.1(6) $Å^3$, Z = 4, D_{calcd} = 1.059 gcm^{-3}, R = 0.046 (R_w = 0.046) for 3039 independent reflections [$I > 3\sigma(I)$]. Crystal data for **10**: $C_{48}H_{112}Si_{12}O_5$ (FW = 1106.44), monoclinic, $P2_1/c$, a = 10.465(5) Å, b = 30.582(3) Å, c = 21.136(2) Å, β = 92.337(2)°, V = 6758(2) $Å^3$, Z = 4, D_{calcd} = 1.087 gcm^{-3}, 93 K, R = 0.082 (R_W = 0.093) for 7475 observed reflections [$I > 3\sigma(I)$].

10 The oxidation of polysilanes with peroxyacids has been reported to proceed with the retention of geometry,[1c,g] while in some cases, stereomutation has been reported.[1b,d]