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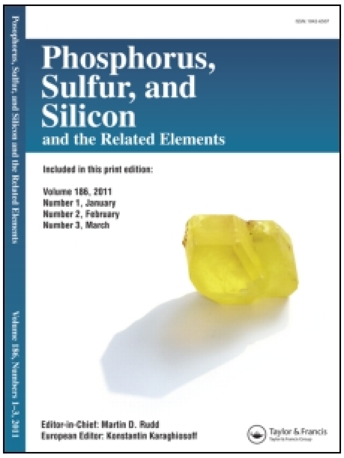

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Syntheses, Structures, and Properties of Ladder Oligosilanes

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Synthesis, structures, and oxidation of the ladder oligosilanes, such as bicyclo[2.2.0]hexasilane, tricyclo-[4.2.0.$0^{2,5}$]octasilane, tetracyclo[4.4.0.$0^{2,5}$.$0^{7,10}$]decasilane, and pentacyclo[6.4.0.$0^{2,7}$.$0^{3,6}$.$0^{9,12}$]dodecasilane, are reported.

Keywords: Ladder oligosilane; Structure; Domino oxidation

INTRODUCTION

The rapid growth of the chemistry of polycyclic compounds of group 14 elements Si, Ge, and Sn in the past 15 years has stimulated interest amongst both experimental and theoretical chemists.[1] During the course of our investigation on the chemistry of cyclopolysilanes,[2] we prepared the first bicyclo[2.2.0]hexasilane $[RSiSiR][R_2SiSiR_2]_2$ (R = *i*-Pr) (**1**)[3] and the first octasilacubane $[(t\text{-}BuMe_2Si)Si]_8$.[4] We have thus studied the chemical and physical properties of these oligosilanes.[5]

SYNTHESES

The ladder oligosilanes are prepared by lithium-promoted cross-

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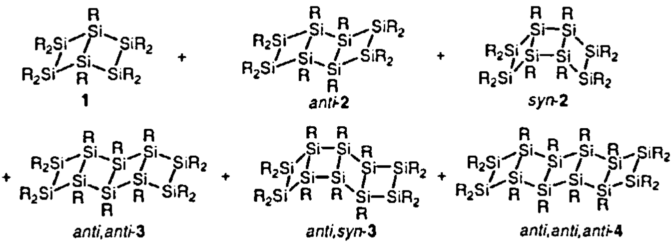
coupling of $Cl_2(i\text{-}Pr)SiSi(i\text{-}Pr)Cl_2$ and $Cl(i\text{-}Pr)_2SiSi(i\text{-}Pr)_2Cl$.[3,5] Each ladder oligosilane can be separated by use of chromatographic methods (a preparative reversed-phase HPLC) as colorless (**1** and *anti*-**2**) and yellow (*syn*-**2**, *anti,anti*-**3**, *anti,syn*-**3**, and *anti,anti,anti*-**4**) crystals.

$$Cl_2RSiSiRCl_2 \; + \; ClR_2SiSiR_2Cl \xrightarrow[THF]{Li}$$

R = i-Pr



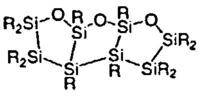
It is noted that *anti*-**2** and *syn*-**2** can also be synthesized by the homo-coupling of the 1,1,4,4-tetrachlorotetrasilane $Cl_2(i\text{-}Pr)Si[(i\text{-}Pr)_2Si]_2Si(i\text{-}Pr)Cl_2$ with lithium in 49 and 36% yields, respectively.[5b]

The structures of the ladder oligosilanes were confirmed by X-ray crystallography.[5] The *anti* ladder oligosilanes have a helical structure and can be seen as silicon double helices, in which two linear oligosilane chains screw in one way and are bridged by Si-Si bonds. The twist angles between the terminal Si–Si rungs are 44.0° (*anti*-**2**), 63.0° (*anti,anti*-**3**), and 80.3° (*anti,anti,anti*-**4**). It is obvious that the helical structures of ladder oligosilanes arise from the systematic catenation of folded cyclotetrasilane rings.

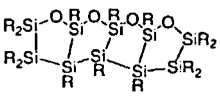
OXIDATION

Polyoxidation of the ladder oligosilanes with *m*-chloroperoxybenzoic acid (MCPBA) exhibits unique regioselectivity; the domino oxidation of the Si–Si bonds takes place to produce novel ladder polyoxa compounds.[6] When *anti*-**2** was oxidized with 3 equivalents of MCPBA, the trioxide **5** was obtained in 81% yield. Similarly, the oxidation of *anti,anti*-**3** and *anti,anti,anti*-**4** with 4 and 5 equivalents of MCPBA yielded tetraoxide **6** and pentaoxide **7**, respectively, in moderate yields. Therefore, the ladder oligosilanes were found to be oxidized in a quite unique manner; one of two Si-Si chains is oxidized selectively, and novel ladder compounds consisting of oligosiloxane and oligosilane chains were formed. As far as we know, the compounds such as **5**, **6**, and **7** have not been reported in carbon analogs.

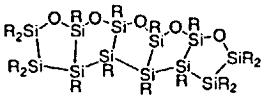
R = *i*-Pr



5 (81%)



6 (35%)



7 (41%)

The X-ray crystallography disclosed that these molecules have a curved shape containing a oligosiloxane chain as an outer arch and a oligosilane chain as an inner arch. They retain the *anti* structure of the starting ladder oligosilanes, and each five-membered ring is catenated in a corrugated manner.

The oxidation products **5**, **6**, and **7** are interesting from the viewpoint of their electronic properties.[6] They exhibit intense absorptions 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 (**5**:

273 nm (ε 7600), **6**: 292 nm (ε 25000), **7**: 297 nm (ε 51900)). The intense absorption on the order 10^4 is remarkable because these molecules contain no chromophores which give such an intense absorption.

Acknowledgment

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