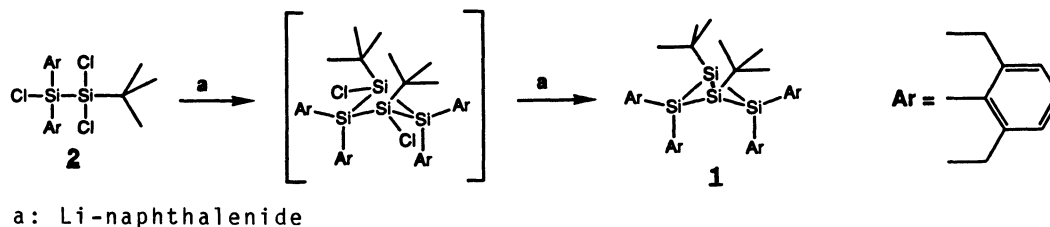


Generation of the Dianion from
Tetrasilabicyclo[1.1.0]butane Derivatives#

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Reductive cyclization of $R_2ClSi-SiCl_2R'$ with 5 equiv. of lithium naphthalenide followed by aqueous workup provides the corresponding cyclotetrasilane $[(R_2SiSiHR')_2]$. Similar treatment converts $RC_2SiSiClHR$ into a stereoisomeric mixture of cyclotetrasilanes $[(RHSi)_4]$. Evidence is presented to indicate that the tetrasilabicyclo[1.1.0]butane derivatives formed as intermediates in these reactions are transformed into the dianions corresponding to the products.

The strained ring systems consisting solely of silicon, germanium, or tin atoms have continued to arouse synthetic and theoretical interest,¹⁾ as exemplified by the recent synthesis of 1,3-di-*t*-butyl-2,2,4,4-tetrakis(2,6-diethylphenyl)tetrasilabicyclo[1.1.0]butane (**1**) from trichlorodisilane **2** (Scheme 1).²⁾ This bicyclo compound **1** exhibited many unusual properties. The high reactivity of the crucial central Si(1)-Si(3) bond was of particular interest, and we expected it would be further enhanced by replacing the *t*-butyl substituents attached to Si(1) and Si(3) with aryl groups. We have now found that reductive cyclization of trichlorodisilane **3** under similar conditions to those applied for **2** provides, upon aqueous workup, cyclotetrasilane **4** rather than tetrasilabicyclo[1.1.0]butane **5**. The bicyclo compound **5** apparently undergoes further reduction with the excess reductant present in the reaction medium (see Schemes 2 and 3 for the structures of **3-5**). This finding is summarized below together with the first recording of cyclotetrasilane derivatives of the $(RHSi)_4$ type.³⁾

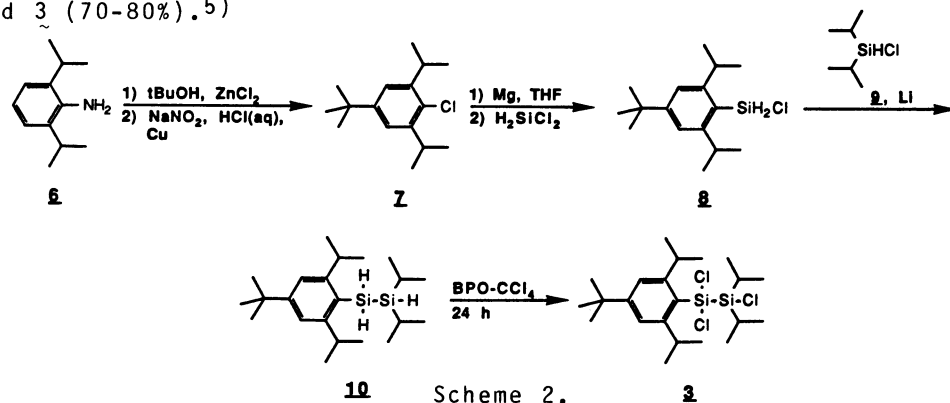


Scheme 1.

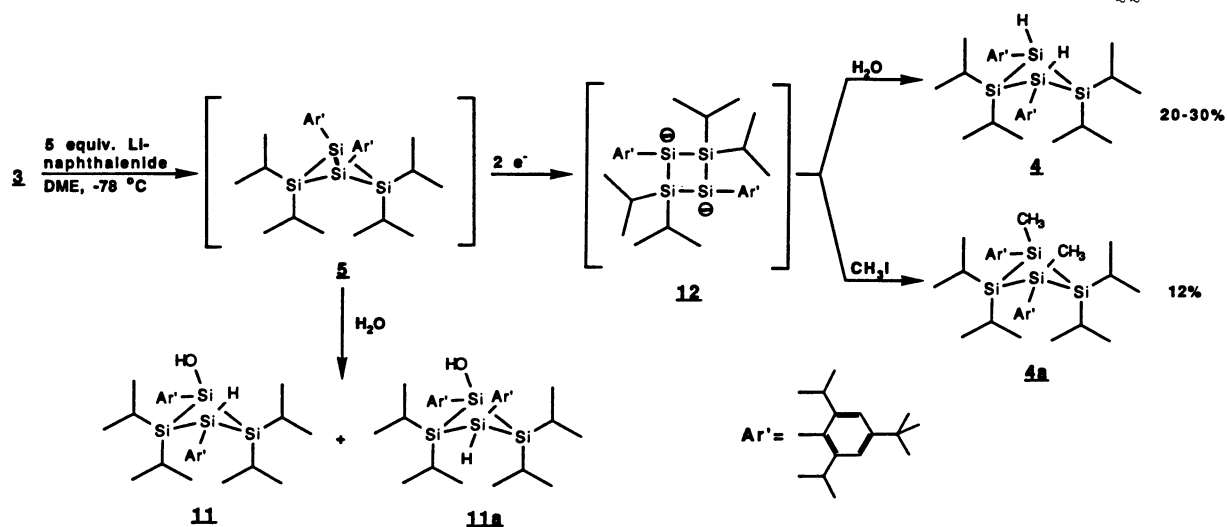
The synthesis of trichlorodisilane **3** was carried out in a standard fashion (Scheme 2). Thus a sequence of two reactions, a Friedel-Crafts alkylation and Sandmeyer chlorination, of 2,6-diisopropylaniline provided the chloride **7** (50%

Dedicated to Professor Teruaki Mukaiyama on the occasion of his 60th Birthday.

yield), which after conversion into the corresponding Grignard reagent was coupled with dichlorosilane to yield the chlorosilane **8** (40%). Treatment of a mixture of **8** and diisopropylchlorosilane **9** (2 equiv.)⁴ with lithium dispersion (3 equiv.) afforded the disilane **10** (75-85%) which was chlorinated with CCl₄-benzoyl peroxide to afford **3** (70-80%).⁵



A solution of **3** in dimethoxyethane (DME) was added to five equiv. of lithium naphthalenide in DME at $-78\text{ }^{\circ}\text{C}$ (Scheme 3). The resulting mixture became intensely red during 1 h stirring (-78 ° to $0\text{ }^{\circ}\text{C}$) and was quenched in the following two ways. With a pH 7 buffer solution, *cis*-1,3-bis(4-*t*-butyl-2,6-diisopropylphenyl)-2,2,4,4-tetraisopropylcyclo-tetrasilane (**4**) [¹H NMR (C₆D₆) δ 7.38(s, 4H), 4.82(s, 2H), 3.76(sept, 7 Hz, 4H), 1.7-1.6(m, 4H), 1.42(d, 7 Hz, 24H), 1.40(d, 7 Hz, 12H), 1.32(s, 18H), 1.18(d, 7 Hz, 12H)] was the sole isolable product (33%), while methyl iodide quenching provided the corresponding dimethyl derivative (**4a**) (12%).



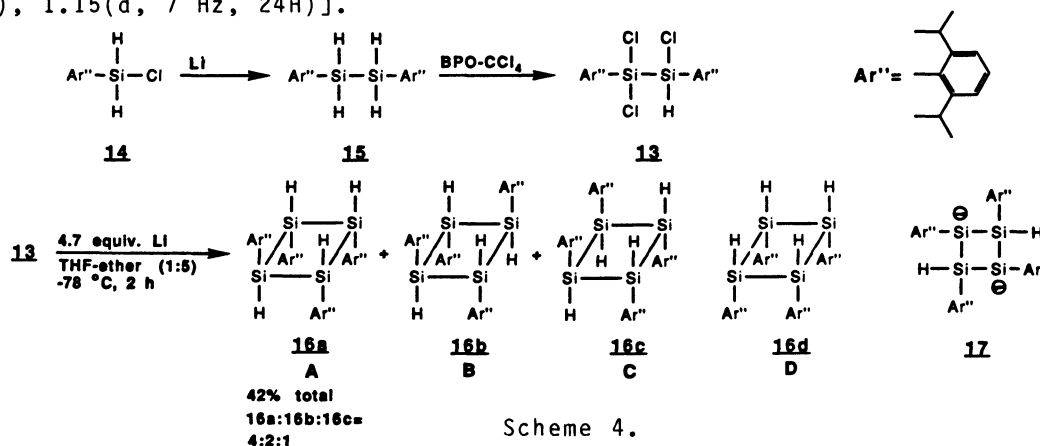
Scheme 3.

The use of three and a half equiv. of the reductant in the above reaction led, upon H₂O workup, to the formation of a 4:1 mixture (37%) of the 1-hydroxycyclo-tetrasilanes (**11** and **11a**) corresponding to **4** [**11**:¹H NMR (C₆D₆) δ 7.44(s, 2H), 7.42(s, 2H), 4.83(s, 1H), 3.84(m, 4H), 2.00(sept, 7 Hz, 2H), 1.70(sept, 7 Hz, 2H), 1.6-1.4(m, 36H), 1.38(s, 9H), 1.31(s, 9H), 1.23(d, 7 Hz, 6H), 1.16(d, 7 Hz, 6H)] [**11a**:¹H NMR (C₆D₆) δ 7.37(s, 2H), 7.33(s, 2H), 5.11(s, 1H), 3.94(sept, 7 Hz, 2H), 3.60(sept, 7 Hz, 2H), 1.75(m, 4H), 1.6-1.4(m, 36H), 1.31(s, 9H), 1.29(s, 9H), 1.24(d, 7 Hz, 6H), 1.18(d, 7 Hz, 6H)] in addition to **4** (22%). From our earlier

observation that the Si(1) and Si(3) bond of 1 is hydrolytically cleaved with great ease, the precursor of 11 and 11a is undoubtedly the bicyclo[1.1.0]butane derivative 5 with the aryl substituents attached to the bridgehead silicon atoms. A set of experiments clearly demonstrated that the combined yield of 11 and 11a was maximized with 3.5 equiv. of reductant (either lithium naphthalenide or lithium dispersion), and increasing the amount of the reductant to more than 3.5 equiv. invariably led to the formation of larger quantities of 4 at the expense of 11 and 11a. Therefore, these results indicate that the dianion 12 is derived from 5 rather than from dichlorocyclotetrasilane precursors of 5. It should be mentioned at this point that the Si(1)-Si(3) bond of 1 having the alkyl substituents resisted reductive cleavage with lithium naphthalenide even at room temperature.²⁾

The trichlorodisilane 13 was prepared from 14 via 15. Chlorination of 15 was interrupted after the introduction of three chlorine atoms to obtain 13 in 56% yield (Scheme 4).

Reductive coupling of 13 with an excess reductant appears to proceed via a bicyclo[1.1.0]butane derivative in a manner analogous to that described above. Thus, addition of 13 (0.5 M, 2 mL of THF) to lithium dispersion (4.7 equiv., 10 mL of ether) at -78 °C followed by 2 h stirring at the same temperature provided a deep green mixture, which upon quenching with an aqueous NH₄Cl solution gave rise to a 4:2:1 stereoisomeric mixture of three 1,2,3,4-tetrakis(2,6-diisopropylphenyl)-cyclotetrasilanes (16a-c), [16a:¹H NMR (C₆D₆) δ 7.25-6.9(m, 12H), 5.74(t, 10.8 Hz, 1H), 5.55(t, 3.0 Hz, 1H), 5.42(dd, 10.8 Hz, 3.0 Hz, 2H), 4.11(sept, 6.9 Hz, 2H), 3.87(sept, 6.9 Hz, 4H), 3.48(sept, 6.9 Hz, 2H), 1.30(d, 6.9 Hz, 12H), 1.11(d, 6.9 Hz, 12H), 1.07(d, 6.9 Hz, 12H), 1.00(d, 6.9 Hz, 12H)] [16b:¹H NMR (C₆D₆) δ 7.20(t, 7.2 Hz, 4H), 7.06(d, 7.2 Hz, 8H), 5.31(s, 4H), 3.91(sept, 6.9 Hz, 8 H), 1.18(d, 6.9 Hz, 48H)] [16c:¹H NMR (C₆D₆) δ 5.49(s, 4H), 3.89(sept, 7 Hz, 8H), 1.17(d, 7 Hz, 24H), 1.15(d, 7 Hz, 24H)].



There are four possible stereoisomers (A, B, C, D). Providing all the aryl groups undergo free rotation along the axis connecting an aryl group to the silicon atom, 16b, c, and d have four-fold symmetry, whereas 16a has two-fold symmetry. Therefore, A is assigned to the cyclotetrasilane 16a (3 Si-H signals) which was obtained in the largest quantity. If one ignores the possibility that either 16b or 16c is D,⁷⁾ these compounds may be assigned the stereostructures B and C,

respectively, for the following reason. While both compounds show only one Si-H signal (singlet), the methyl signals (of the isopropyl groups) of 16b and 16c appear as one doublet and two doublets, respectively, indicating that the substituents of the latter are more congested. Models suggest the aryl rotation referred to above is in all likelihood frozen more readily with 16c than with 16b.

All of 16a-c undoubtedly have formed from the corresponding dianion 17. This dianion as well as 12 are potential precursors for the construction of polycyclic systems.

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