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Cyclization of 1,2-bis(bromomethyl)-1,1,2,2-tetramethyldisilane, 2, with the dianion of methylphenylsulphone in tetrahydrofuran at -78°C produces the 4-phenylsulphone substituted 1,2-disilacyclopentane derivative, 4, in 59% yield. Ring opening of 2 with potassium t-butoxide occurs quantitatively to provide 1-(t-butoxy)-2-(2-propenyl)-1,1,2,2-tetramethyldisilane, 5. Addition of the monoanion of methylphenylsulphoxide to 2 in THF at -78°C provides the intermediate adduct, 7, which is cyclized at -78°C with addition of one equivalent of lithium diisopropylamide to provide the 4-phenylsulphoxide substituted 1,2-disilacyclopentane derivative, 6, in 30% yield from 2. Flash vacuum thermolysis of 6 at 100°C (10<sup>-3</sup> torr) provides 1,1,2,2-tetramethyl-1,2-disilacyclopent-3-ene, 1, in 40% yield.

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A New Strategy for the Construction of Carbocyclic Alkenyl Silanes:  
The Synthesis of 1,1,2,2-tetramethyl-1,2-disilacyclopent-3-ene



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Interim Report

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A NEW STRATEGY FOR THE CONSTRUCTION OF CARBOCYCLIC ALKENYL SILANES:  
THE SYNTHESIS OF 1,1,2,2-TETRAMETHYL-1,2-DISILACYCLOPENT-3-ENE

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*Summary:* Cyclization, followed by thermal *syn*-elimination of a sulphoxide group provides entry into a new class of strained carbocyclic alkenyl silanes, 1,2-disilacyclopent-3-enes (1).

The investigation of new routes to polycarbosilanes is a target of opportunity for the creation, and further development, of advanced materials for applications in a diverse range of areas such as high temperature ceramics, microlithography and nonlinear optics.<sup>1,2</sup> We have undertaken, therefore, the formulation of a new synthetic strategy for the construction of strained carbocyclic alkenyl silane monomers which can subsequently provide these desired materials through ring-opening polymerization (ROP) processes, and more specifically, through ROP via olefin metathesis.<sup>3</sup> Herein, we report the application of this strategy to the synthesis of the previously unknown 1,2-disilacyclopent-3-ene ring system, 1.<sup>4</sup>



The initial attempt at the synthesis of 1 centered on the cyclization of 5 g (17 mmol) of 1,2-bis(bromomethyl)-1,1,2,2-tetramethyldisilane (2)<sup>5</sup> in tetrahydrofuran (THF) (0.5 M) at -78°C through the dropwise addition of one equivalent of a solution (0.5 M in THF) of the dianion of methylphenylsulphone (3) [prepared from 3 and two equivalents of *n*-butyllithium at 0°C] to produce, after quenching with saturated aqueous ammonium chloride, extraction, and purification by flash chromatography on silica gel (4:1 diethyl ether/hexane as elutant), 2.9 g (59% yield) of the crystalline 1,2-disilacyclopentane derivative 4 (Scheme 1).<sup>6</sup> This reaction, which is being developed as a new route to 1,2-disilacyclopentanes, is notable in that one probably would not have predicted its success *a priori* due to the anticipated steric hinderance presented for S<sub>N</sub>2 attack at the neopentyl-like carbon atoms of 2.

For the production of 1 from 4, it has been documented that base-induced elimination of sulphones occurs readily with even hydroxide ion (OH<sup>-</sup>).<sup>7</sup>

However, with one equivalent of potassium t-butoxide in THF at  $-78^{\circ}\text{C}$ , 4 was quantitatively converted to the ring-opened product 5 (Scheme 1).<sup>8</sup> Other strong bases, such as n-butyllithium or lithium diisopropylamide (LDA) in THF at  $-78^{\circ}\text{C}$  effected only deprotonation to form the  $\alpha$ -carbanion of the sulphone derivative. This inertness of 4 towards base-induced elimination is rationalized on the basis that the sulphone group is rigidly fixed in an equatorial position of an envelope conformation, even at  $110^{\circ}\text{C}$ , as determined by variable temperature  $^1\text{H}$  NMR. In this arrangement, there are no  $\beta$ -hydrogens in a *trans* relationship to the leaving group for E2-like elimination to occur and it is clear from these observations that other synthetic routes to 1 which require base-induced elimination of a leaving group will also likely suffer from nucleophilic ring-opening reactions at silicon.

The thermal syn-elimination of a sulfoxide group under mild temperatures is well-documented.<sup>9</sup> Thus, we have explored the cyclization of 2 under similar conditions to produce the sulfoxide analogue 6 (Scheme 2). Accordingly, treatment of 10 g (36 mmol) of 2 in THF (1 M) at  $-78^{\circ}\text{C}$  with a solution (0.3 M) of one equivalent of the monoanion of methylphenylsulfoxide (7) (prepared from 7 and LDA in THF at  $0^{\circ}\text{C}$ ) first produces the intermediate 8<sup>10</sup> which is then cyclized upon the addition of one equivalent of LDA (1 M in THF) at  $-78^{\circ}\text{C}$  to provide 2.7 g (26% yield) of the desired product 6 after purification by flash chromatography on silica gel (150:1 chloroform/methanol).<sup>11</sup>

In keeping with the prior report that a silicon atom at the  $\beta$ -position will facilitate sulfoxide elimination<sup>12</sup>, we observe that elimination of 6 to produce 1 occurs in solution between  $60^{\circ}$  -  $70^{\circ}\text{C}$ , as monitored by  $^1\text{H}$  NMR (300 MHz, benzene- $d_6$ ). However, for the large scale production of 1 (~1 g), the best method is through flash vacuum thermolysis<sup>13</sup> with a pot temperature of  $100^{\circ}\text{C}$  and a vacuum of  $10^{-7}$  torr. After thermolysis, the crude material is purified by chromatography on silica gel (pentane as elutant) to remove the small amount of disiloxane product that is produced.<sup>14</sup> Compound 1 is air-stable, however, upon heating above  $100^{\circ}\text{C}$  (neat, 1 atm), it rapidly polymerizes.

In conclusion, cyclization, followed by the thermal syn-elimination of a sulfoxide group provides entry into a new class of cyclic silicon-containing monomers that may have important applications in the production of advanced materials. We are currently investigating the ring-opening polymerization of 1 via thermal and olefin metathesis processes, as well as, extending the synthetic

methodology for the production of new silane monomers such as 1,2-disilacyclobut-3-enes.

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**References and Notes:**

1. Zeldin, M.; Wynne, K. J.; Allcock, H. R., eds. *Inorganic and Organometallic Polymers*, ACS Symposium Series, Vol. 360; American Chemical Society: Washington, D.C., 1988.
2. Chemla, D. S.; Zyss, J., eds. *Nonlinear Optical Properties of Organic Molecules and Crystals*, Vol. 1 and 2; Academic Press: New York, 1987.
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4. For the synthesis of the 3,4-benzo derivative of 1 see: Tsui, F. P.; Zon, G. *J. Organomet. Chem.* 1974, 70, C3.
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6. For 4: m.p. (recrystallized from diethyl ether at  $-20^{\circ}\text{C}$ )  $113-115^{\circ}\text{C}$ ;  $^1\text{H}$  NMR (300 MHz, benzene- $d_6$ )  $\delta$  -0.17 (s, 6H), -0.09 (s, 6H), 0.90 (t, 2H,  $J = 14$  Hz), 1.40 (dd, 2H,  $J = 4$  Hz,  $J = 14$  Hz), 3.05 (tt, 1H,  $J = 4$  Hz,  $J = 14$  Hz), 6.96 (m, 3H), 7.93 (m, 2H);  $^{13}\text{C}$  NMR (75 MHz, benzene- $d_6$ )  $\delta$  (proton-coupled) 4.02 (q), 18.56 (t), 63.46 (d), 128.31 (d), 128.81 (d), 129.40 (d), 132.76 (s); Anal. Calcd. for  $\text{C}_{13}\text{H}_{22}\text{SSi}_2\text{O}_2$ : C, 52.30; H, 7.43; S 10.74. Found: C, 52.04; H, 7.44; S, 10.55.
7. Wallace, T. J.; Hofman, J. E.; Schriesheim, A. J. *Am. Chem. Soc.* 1963, 85, 2739.
8. For 5 (purification by chromatography on silica gel, hexane as elutant):  $^1\text{H}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  0.03 (s, 6H), 0.20 (s, 6H), 1.21 (s, 9H), 1.56 (m, 2H), 4.81 (m, 1H), 5.78 (m, 1H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  -4.69 (q), 2.81 (q), 22.66 (t), 32.20 (q), 72.45 (s), 112.41 (t), 135.54 (d) Anal. Calcd. for  $\text{C}_{11}\text{H}_{26}\text{OSi}_2$ : C, 57.32; H, 11.37. Found:
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10. Compound 8 can be isolated by quenching the reaction before the addition of LDA:  $^1\text{H}$  (300 MHz, benzene- $d_6$ )  $\delta$  -0.17 (s, 3H), -0.16 (s, 3H), -0.06 (s, 3H), 0.05 (s, 3H), 0.78 (td, 1H,  $J = 4$  Hz,  $J = 13$  Hz), 1.03 (td, 1H,  $J = 4$  Hz,  $J = 13$  Hz), 2.16 (s, 2H), 2.41 (td, 1H,  $J = 4$  Hz,  $J = 13$  Hz), 2.63 (td, 1H,  $J = 4$  Hz,  $J = 13$  Hz) 6.95 - 7.07 (m, 3H), 7.48 (m, 2H);  $^{13}\text{C}$  NMR (75 MHz, benzene- $d_6$ )  $\delta$  -4.19 (q), -4.12 (q), 5.72 (t), 17.39 (t), 52.81 (t), 124.35 (d), 129.03 (d), 130.40 (d), 145.41 (s); Anal. Calcd. for  $\text{C}_{13}\text{H}_{23}\text{BrSSi}_2\text{O}$ : C, 42.96; H, 6.38; S, 8.82. Found: C, 43.09; H, 6.58; S, 8.54.

11. For 6:  $^1\text{H}$  NMR (300 MHz,  $40^\circ\text{C}$ , benzene- $d_6$ )  $\delta$  -0.14 (s, 3H), -0.05 (s, 3H), -0.02 (s, 3H), -0.00 (s, 3H), 0.77 - 0.98 (m, 3H), 0.94 (dt, 1H,  $J = 2.2$  Hz,  $J = 11.6$ ), 2.62 (tt, 1H,  $J = 4.3$  Hz,  $J = 13.5$  Hz), 7.00 - 7.13 (m, 3H,);  $^{13}\text{C}$  NMR (75 MHz, benzene- $d_6$ )  $\delta$  -4.10 (q), -4.03 (q), 15.35 (t), 19.40 (t), 63.41 (d), 125.12 (d), 128.70 (d), 130.14 (d), 147.14 (s); Anal. Calcd. for  $\text{C}_{13}\text{H}_{22}\text{OSSi}_2$ : C, 55.26; H, 7.85; S, 11.35. Found:

12. Fleming, I.; Perry, D. A. *Tetrahedron Lett.* 1981, 22, 5095.

13. Wiersum, U.E. *Recl. Trav. Chim. Pays-Bas* 1982, 101, 317, 365.

14. For 1:  $^1\text{H}$  NMR (300 MHz, benzene- $d_6$ )  $\delta$  0.10 (s, 6H), 0.19 (s, 6H), 1.55 (dd, 2H,  $J = 2.0$  Hz,  $J = 3.8$  Hz), 6.159 (dt, 1H,  $J = 2.0$  Hz,  $J = 11.3$  Hz), 6.89 (dt, 1H,  $J = 3.8$  Hz,  $J = 11.3$  Hz);  $^{13}\text{C}$  NMR (75 MHz, benzene- $d_6$ )  $\delta$  -4.13 (q), -3.54 (q), 23.92 ( ), 134.86 ( ), 149.91 ( ); IR (neat) 3079, 2953, 2895, 1631, 1420, 1396, 1248, 1152, 1049, 1035, 893, 829, 812, 798, 776  $\text{cm}^{-1}$ ;

Scheme 1

