

Addition Reactions of Maleic Anhydride to a Disilene and a Tetrasilabuta-1,3-diene: Formation of Bi- and Tetracyclic Compounds^{1,2}

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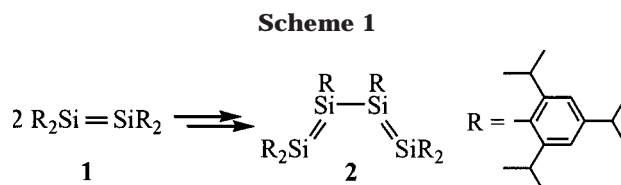
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Received March 7, 2001

Summary: The reaction of hexakis(2,4,6-triisopropylphenyl)tetrasilabutadiene with maleic anhydride (**3**) furnishes the 2,9-dioxa-5,6,7,8-tetrasilatetracyclodecan-3-one derivative **4**, presumably by a sequence of two consecutive [2 + 2] cycloadditions. Tetrakis(2,4,6-triisopropylphenyl)disilene reacts with **3** to afford the bicyclic 1,2-dihydrofuro[3,2-d][1,2,3]oxadisilol-5(6H)-one derivative **5** via a formal [2 + 3] cycloaddition and a 1,2-hydrogen shift. The structures of **4** and **5** were determined by X-ray crystallography.

Compounds with acyclic Si–Si double bonds have been known for 20 years, and their chemistry has probably been more or less completely explored.³ This is, however, not the case with the cyclic disilenes that were isolated for the first time in the past few years or for the first, and as yet only, tetrasilabutadiene **2**,³ prepared from the disilene **1**^{4,5} by a sequence of metalation, halogenation, and coupling reactions (Scheme 1).⁶

Compound **2** reacts readily with small molecules such as, for example, water,⁷ ammonia,⁸ or hydrazine¹ to furnish the corresponding tetrasilanes by 2-fold 1,2-addition reactions. Although the molecule **2** exists in the solid state and in solution as the *s-cis* (*s-gauche*) form that should favor [4 + 2] cycloadditions of the Diels–Alder type, to date all reactions of **2** with olefins, acetylenes, and the C=O bonds of ketones have remained unsuccessful. These findings are assumed to be a consequence of the large 1,4-separation of 5.4 Å between the terminal silicon atoms as well as the steric shielding of these double bonds. We now report on the



reaction of **2** with maleic anhydride (**3**) that proceeds through a formal [4 + 4] cycloaddition and on the addition of **3** to the disilene **1**, that leads to the formation of an unexpected product.

When the reddish brown solution of **2** in toluene is heated with an excess of maleic anhydride, pale yellow crystals can be isolated from the reaction mixture in 75% yield.⁹ Analytical data demonstrate that the compound is composed of the starting materials **2** and **3** in a 1:1 ratio (Scheme 2). As a consequence of the many, in part overlapping, signals, the ¹H and ¹³C NMR spectra do not provide much conclusive information about the structure of the formed compound. Also, the four signals in the ²⁹Si NMR spectrum merely demonstrate the nonequivalence of the silicon atoms.

(1) Silicon Compounds with Strong Intramolecular Steric Interactions. 77. Part 76: Boomgaarden, S.; Saak, W.; Marsmann, H.; Weidenbruch, M. *Z. Anorg. Allg. Chem.*, in press.

(2) Dedicated to Professor Michael G. Voronkov on the occasion of his 80th birthday.

(3) For recent reviews see: (a) Okazaki, R.; West, R. *Adv. Organomet. Chem.* **1996**, *39*, 231. (b) Weidenbruch, M. *Eur. J. Inorg. Chem.* **1999**, 373. (c) Power, P. P. *Chem. Rev.* **1999**, *99*, 3463. (d) Weidenbruch, M. In *The Chemistry of the Functional Groups, Supplement Si*; Rappoport, Z., Apeloig, Y., Eds.; Wiley: Chichester, U.K., in press. (e) See also: Iwamoto, T.; Tamura, M.; Kabuto, C.; Kira, M. *Science* **2000**, *290*, 504.

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(9) **5,5,6,7,8,8-Hexakis(2,4,6-triisopropylphenyl)-2,9-dioxa-5,6,7,8-tetrasilatetracyclo[4.3.1.0^{1,7}.0^{4,10}]decan-3-one (4)**. To a solution of **2** (0.36 g, 0.27 mmol) in toluene (50 mL) was added an excess of maleic anhydride (0.1 g, 1.0 mmol). The mixture was allowed to react for 6 h in boiling toluene and stirred for additional 8 h at room temperature. The solvent was removed in vacuo and the residue dissolved in *n*-pentane. Excess maleic anhydride was filtered off. The solvent was removed in vacuo and the residue redissolved in methylcyclopentane (20 mL). Cooling at 4 °C furnished 0.29 g (0.2 mmol; 75% yield) of pale yellow crystals of **4**: mp 225 °C; ¹H NMR δ 0.31 (d, 6 H, ³J = 6.6 Hz), 0.59 (d, 6 H, ³J = 6.6 Hz), 0.67 (d, 6 H, ³J = 6.5 Hz), 0.76 (d, 6 H, ³J = 6.6 Hz), 0.81 (d, 6 H, ³J = 6.6 Hz), 0.93 (d, 6 H, ³J = 6.6 Hz), 0.96 (d, 6 H, ³J = 6.6 Hz), 1.01 (d, 12 H, ³J = 7.1 Hz), 1.07 (d, 6 H, ³J = 7.1 Hz), 1.39 (d, 6 H, ³J = 6.6 Hz), 1.49 (d, 6 H, ³J = 6.5 Hz), 1.52 (d, 6 H, ³J = 6.1 Hz), 1.56 (d, 6 H, ³J = 6.6 Hz), 1.59 (d, 6 H, ³J = 6.6 Hz), 1.61 (d, 6 H, ³J = 6.5 Hz), 1.88 (d, 6 H, ³J = 6.6 Hz), 2.54 (sept, 1 H), 2.61 (sept, 4 H), 2.68 (sept, 4 H), 2.81 (sept, 1 H), 2.99 (sept, 1 H), 3.20 (sept, 1 H), 3.33 (sept, 2 H), 3.44 (sept, 1 H), 3.53 (sept, 1 H), 3.66 (sept, 1 H), 3.71 (sept, 1 H), 3.80 (d, 1 H, ³J = 12.1 Hz), 4.54 (d, 1 H, ³J = 12.1 Hz), 6.74 (d, 1 H, ⁴J = 1.1 Hz), 6.80 (d, 1 H, ⁴J = 1.6 Hz), 6.88 (d, 1 H, ⁴J = 1.1 Hz), 6.96 (d, 1 H, ⁴J = 1.6 Hz), 6.98 (d, 1 H, ⁴J = 1.6 Hz), 7.02 (d, 1 H, ⁴J = 1.6 Hz), 7.08 (d, 4 H, ⁴J = 1.6 Hz), 7.13 (d, 1 H, ⁴J = 1.1 Hz), 7.28 (d, 1 H, ⁴J = 1.6 Hz); ¹³C NMR δ 23.39, 23.52, 23.60, 23.63, 23.82, 23.91, 23.95, 24.10, 24.47, 24.68, 24.99, 25.07, 25.27, 25.38, 25.49, 25.63, 25.73, 26.43, 26.49, 26.63, 27.07, 27.20, 27.45, 27.53, 27.66, 28.42, 31.09, 33.99, 34.16, 34.33, 34.50, 34.60, 35.06, 35.41, 35.81, 36.27, 36.95, 37.60, 38.28, 45.63, 50.00, 58.66, 72.20, 85.76, 119.06, 121.29, 121.78, 122.94, 123.23, 123.36, 123.58, 123.76, 123.89, 124.03, 125.15, 127.81, 128.00, 128.19, 128.29, 128.50, 129.28, 131.85, 132.53, 134.32, 150.13, 150.40, 150.52, 150.62, 150.81, 150.94, 153.35, 153.53, 154.30, 154.78, 155.50, 156.22, 156.78, 156.83, 157.48, 158.26, 173.74; ²⁹Si NMR δ 10.51, 11.22, 19.19, 42.90. Anal. Calcd for C₉₄H₁₄₀O₃Si₄: C, 78.93; H, 9.86. Found: C, 78.67; H, 9.92.

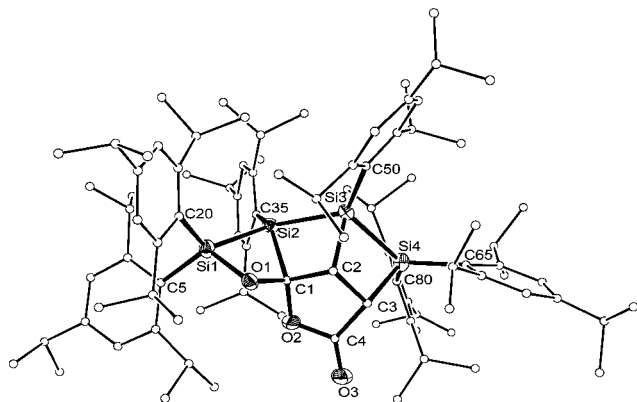
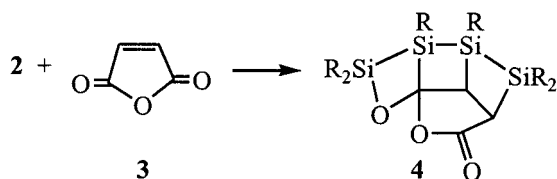


Figure 1. Molecule of **4** in the crystal form (hydrogen atoms omitted). Ellipsoids are drawn at 50% probability. Selected bond lengths (Å) and bond angles (deg): Si(1)–Si(2) = 2.4004(12), Si(2)–Si(3) = 2.4609(12), Si(3)–Si(4) = 2.5210(12), Si(1)–O(1) = 1.681(3), Si(2)–C(1) = 2.011(5), Si(3)–C(2) = 1.947(7), Si(4)–C(3) = 2.000(7); Si(1)–Si(2)–Si(3) = 118.49(4), Si(2)–Si(3)–Si(4) = 107.99(4).

Scheme 2



The constitution of the isolated product was elucidated by X-ray crystallography (Figure 1) as the tetracyclic system **4**.¹⁰ An interesting feature of the structure of **4** is that the Si–Si bonds are stretched to different extents and show values between 2.40 and 2.52 Å.

The mechanism of formation of the tetracyclic compound **4** is not yet known. A feasible sequence involves a [2 + 2] cycloaddition of one of the Si=Si double bonds of **2** to the highly reactive C=O group, followed by a second cycloaddition of the remaining Si=Si bond across the C=C double bond to complete the formation of the final product **4**. To obtain a better insight into the course of this reaction, we have also treated the structurally similar compounds cyclopenten-3-one, 1*H*-pyrrole-2,5-dione, methyl vinyl ketone, and 4-methyl-1,2,4-triazolidine-3,5-dione with **2** under otherwise identical conditions. However, in no case did we find any sign of a reaction.

Since compound **3** apparently exhibits a high reactivity toward Si–Si multiple bonds, we also examined its reaction with the disilene **1** (Scheme 3). The pale orange crystals obtained in 83% yield gave analytical data indicative of a 1:1 adduct of **1** and **3**.¹¹ Again, the spectroscopic data did not provide useful information about the constitution of the isolated product and X-ray crystallography was once more necessary for the final elucidation of the structure (Figure 2).¹² The compound

(10) Crystal data for **4**: C₉₁H₁₄₀O₃Si₄, fw = 1430.42, triclinic, space group *P1*, *a* = 13.7864(5) Å, *b* = 13.9557(5) Å, *c* = 23.3036(6) Å, α = 90.803(4)°, β = 100.516(4)°, γ = 100.446(4)°, *V* = 4330.1(2) Å³, *Z* = 2, *D*_{calcd} = 1.97 g cm⁻³, μ = 0.116 mm⁻¹, *T* = 193(2) K, crystal size 1.00 × 0.48 × 0.24 mm³, Stoe-IPDS area detector, structure solution by direct methods, refinement on *F*² (2θ_{max} = 52°), 15 660 unique reflections, *R*₁ = 0.0759, *wR*₂(all data) = 0.1893, *GOF*(*F*²) = 1.059. The atoms O(1)–O(3) and C(1)–C(4) are disordered and were refined on two positions with occupancy factors of 0.75 and 0.25.¹²

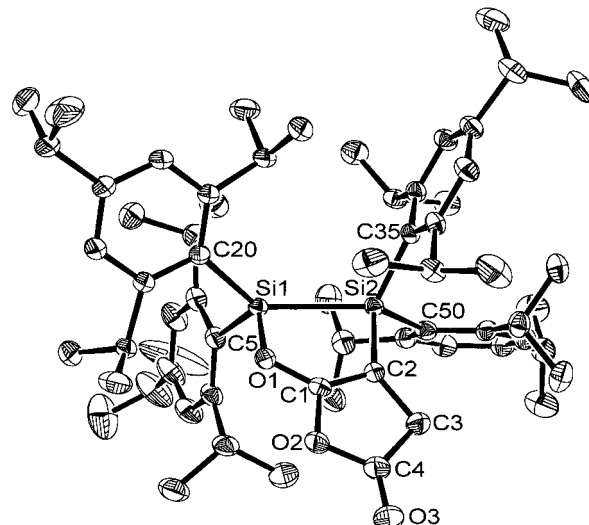
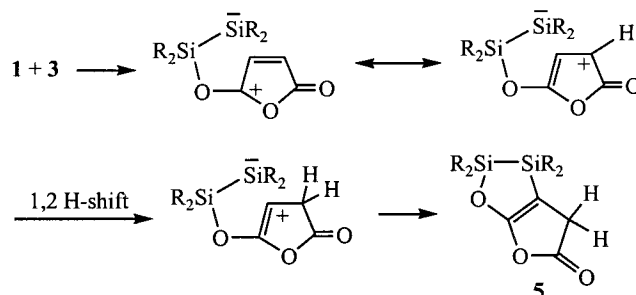


Figure 2. Molecule of **5** in the crystal form (hydrogen atoms omitted). Ellipsoids are drawn at 50% probability. Selected bond lengths (Å) and bond angles (deg): Si(1)–Si(2) = 2.5578(10), Si(1)–O(1) = 1.725(2), Si(2)–C(2) = 1.9473(16), C(1)–C(2) = 1.327(4), C(1)–O(1) = 1.323(3), C(1)–O(2) = 1.385(3), O(2)–C(4) = 1.390(4), C(3)–C(4) = 1.513(4), C(2)–C(3) = 1.512(4); O(1)–Si(1)–Si(2) = 89.39(7), Si(1)–Si(2)–C(2) = 84.80(9), Si(2)–C(2)–C(1) = 116.3(2), C(2)–C(1)–O(1) = 116.6(2), C(1)–O(1)–Si(1) = 116.62(16).

Scheme 3



crystallizes as two independent molecules, pairs of which occupy the unit cell. The most conspicuous feature in the structure of **5** is the Si–Si bond length of 2.56 Å, thus exceeding the normal value by 0.22 Å.

The bicyclic system **5** can formally be considered as a [2 + 3] cycloadduct of **1** and **3** after a spontaneous 1,2-hydrogen shift. The driving force for the formation of this compound is assumed to be the oxophilicity of

(11) **1,2-Dihydro-1,1,2,2-tetrakis(2,4,6-triisopropylphenyl)furo[3,2-*d*][1,2,3]oxadisilol-5(6*H*)-one (5)**. To a solution of **1** (1.3 g, 1.5 mmol) in toluene (50 mL) was added an excess of maleic anhydride (0.5 g, 5 mmol). The mixture was allowed to react in boiling toluene for 8 h and then stirred at room temperature for an additional 12 h. The solvent was removed in vacuo and the residue dissolved in *n*-pentane (30 mL). Excess maleic anhydride was filtered off. Cooling at 4 °C furnished 1.2 g (1.24 mmol; 83% yield) of pale orange crystals of **5**: mp 165 °C; ¹H NMR δ 0.55 (d, 6 H, ³*J* = 6.6 Hz), 0.63 (d, 6 H, ³*J* = 6.6 Hz), 0.83 (d, 6 H, ³*J* = 6.5 Hz), 0.87 (d, 6 H, ³*J* = 6.6 Hz), 1.15 (d, 12 H, ³*J* = 6.6 Hz), 1.17 (d, 6 H, ³*J* = 6.6 Hz), 1.18 (d, 6 H, ³*J* = 6.6 Hz), 1.34 (d, 6 H, ³*J* = 6.6 Hz), 1.37 (d, 6 H, ³*J* = 6.6 Hz), 1.48 (d, 6 H, ³*J* = 6.5 Hz), 1.51 (d, 6 H, ³*J* = 6.6 Hz), 2.7 (sept, 2 H), 6.9 (overlapping signals, 12 H), 6.98 (s, 2 H), 7.08 (s, 2 H), 7.11 (s, 2 H), 7.12 (s, 2 H); ¹³C NMR δ 2.89, 14.22, 22.67, 23.88, 23.91, 23.99, 24.28, 24.40, 24.60, 24.74, 24.99, 25.40, 26.32, 30.43, 34.38, 34.44, 34.64, 35.18, 40.03, 80.82, 121.17, 122.37, 123.20, 125.65, 128.51, 129.28, 134.33, 134.46, 134.51, 150.31, 150.60, 151.58, 154.54, 154.86, 155.73, 166.11, 174.23; ²⁹Si NMR δ -22.3, 20.87. Anal. Calcd for C₆₄H₉₄O₃Si₂: C, 79.44; H, 9.79. Found (for unsolvated **5**): C, 79.22; H, 9.90.

silicon. This leads to a dipolar addition product that, in turn, affords a new intermediate through carbenium ion rearrangement in combination with a 1,2-hydrogen shift. The last step of the sequence would then be a ring closure reaction to furnish **5**.

Such a reaction mode has not previously been observed in disilene chemistry. The closest precedent is the reaction of Si–Si double bonds with epoxides that proceeds through a comparable mechanism, leading,

(12) Crystal data for **5**: $C_{64}H_{94}O_3Si_2 \cdot \frac{1}{2}C_5H_{12}$, fw = 1003.65, triclinic, space group $P\bar{1}$, $a = 13.6481(4)$ Å, $b = 21.8535(8)$ Å, $c = 23.5864(9)$ Å, $\alpha = 110.880(4)^\circ$, $\beta = 96.190(4)^\circ$, $\gamma = 104.359(4)^\circ$, $V = 6216.1(4)$ Å³, $Z = 4$, $D_{\text{calcd}} = 1.072$ g cm⁻³, $\mu = 0.099$ mm⁻¹, $T = 193(2)$ K, crystal size $0.50 \times 0.40 \times 0.27$ mm³, Stoe-IPDS area detector, structure solution by direct methods, refinement on F^2 ($2\theta_{\text{max}} = 52^\circ$), 22 514 unique reflections, $R1 = 0.0630$, $wR2(\text{all data}) = 0.1793$, $GOF(F^2) = 0.966$. The data have been deposited with the Cambridge Crystallographic Data Centre: CCDC-158 101 (**4**) and CCDC-158 100 (**5**).

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among others, to the formation of similar products, albeit with saturated five-membered rings.¹³ Similar to the unsuccessful attempts with **2**, reactions of compound **1** with cyclopenten-3-one, 1*H*-pyrrole-2,5-dione, methyl vinyl ketone, and 4-methyl-1,2,4-triazolidine-3,5-dione did not occur, again demonstrating the unusual reactivity of the anhydride **3** toward Si–Si multiple bonds.

Acknowledgment. Financial support of our work by the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie, and the EU (INTAS) is gratefully acknowledged.

Supporting Information Available: Lists of atomic coordinates, anisotropic displacement parameters, and bond lengths and angles for **4** and **5**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

OM010182L