

# The Reaction of Tetramesityldisilene with Cyclohexene Oxide and Cyclohexene Sulfide

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Reaction of tetramesityldisilene, **1**, with cyclohexene oxide in benzene at 80 °C gives silyl enol ether, **2**, as the major product along with the products of epoxide deoxygenation, cyclohexene and the known tetramesityldisilaoxirane, **3**; reaction of **1** with cyclohexene sulfide occurs rapidly at room temp. to give the known tetramesityldisilathirane, **6**, and cyclohexene.

Since the synthesis of the first stable disilene over ten years ago, a great deal of chemistry of the silicon-silicon double bond has been investigated. Reactions with inorganic reagents have produced intriguing ring systems containing oxygen, sulfur, selenium, tellurium, phosphorus<sup>1</sup> and arsenic,<sup>2</sup> as well as disilene transition metal complexes and simple 1,2-addition products.<sup>3</sup> With organic reagents, disilenes have yielded mainly cycloadducts: [2 + 2] cycloadditions are found with alkynes,<sup>3</sup> ketones, aldehydes,<sup>4</sup> thiocarbonyl,<sup>5</sup> organic nitrosyl<sup>6</sup> and azo compounds,<sup>7</sup> [2 + 1] with carbenes<sup>8</sup> and isocyanides,<sup>9</sup> and [2 + 3] cycloadditions with aryl azides.<sup>1</sup>

One area of disilene chemistry that has not been studied is reactivity with small-ring organic heterocycles. The combination of the strain energy of three- and four-membered oxygen, sulfur and nitrogen ring compounds and the affinity of disilene for heteroatoms suggests the potential for interesting reactivity. Here, we report on the reactions of tetramesityldisilene, **1**, with cyclohexene oxide and cyclohexene sulfide.

When combined with a slight excess of cyclohexene oxide in [<sup>2</sup>H<sub>6</sub>]benzene, **1** did not react at room temp. Upon heating to 80 °C, however, the disilene was completely consumed within 24 h to give only two silicon-containing products, the silyl enol ether, **2**,† and the known tetramesityldisilaoxirane, **3**‡ (Scheme 1). Compound **3** is the product of epoxide deoxygenation, along with cyclohexene, which was also observed in the reaction mixture: the ratio of **2** to cyclohexene was 12:1.§ When conducted on a preparative scale (0.3 mmol of disilene), reaction was nearly complete after 7 days at 80 °C. Compound **2** was isolated in 45% yield after chromatography, and crystals suitable for X-ray analysis were obtained (see Fig. 1).¶

Perhaps the most closely related transformation to form a silyl enol ether is that reported independently by Brook *et al.*<sup>11</sup> and Hudrlík and coworkers,<sup>11</sup> in which silyl epoxides were

converted to silyl enol ethers either by pyrolysis or with magnesium bromide. Epoxide deoxygenation, however, has a great deal of precedent.<sup>12</sup> With disilene, the reaction is probably best considered an electrophilic deoxygenation and in that sense is most analogous to epoxide deoxygenations by transition metals.

A mechanistic pathway to **2** would likely involve a zwitterionic intermediate from a Lewis acid-base interaction of the epoxide oxygen with the disilene double bond (Scheme 2). Sekiguchi has found evidence for an initial adduct similar to intermediate **4** for the reaction of alcohols with *cis*- and *trans*-1,2-dimethyl-1,2-diphenyldisilene.<sup>13</sup> Intermediate **4** could then give **2** *via* proton abstraction by silicon. Alternatively, ring opening of **4** to zwitterion **5** could be followed by proton abstraction to give **2** (path a, Scheme 2) or three-membered ring closure to give **3** and cyclohexene (path b).

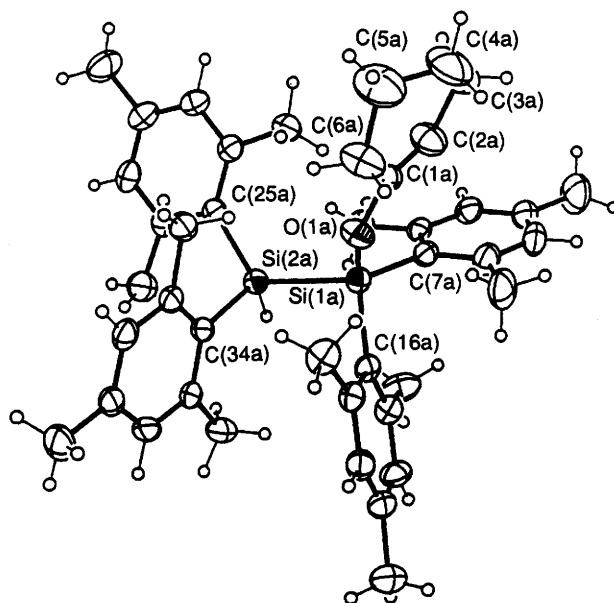


Fig. 1 Thermal ellipsoid diagram for **2**. Selected bond distances (Å): C(1a)–C(2a), 1.320(6); C(2a)–C(3a), 1.475(6); C(3a)–C(4a), 1.523(7); C(4a)–C(5a), 1.450(7); C(5a)–C(6a), 1.502(6); C(6a)–C(1a), 1.473(6); C(1a)–O(1a), 1.373(4); O(1a)–Si(1a), 1.654(3); Si(1a)–Si(2a), 2.371(2).

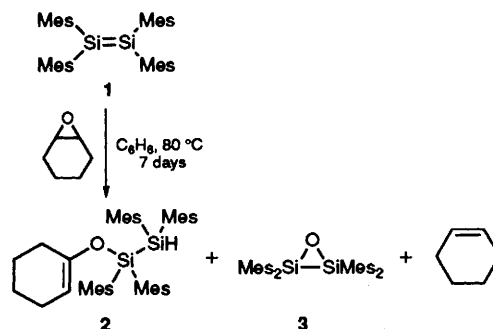
† Data for compound **2**: m.p. 213–219 °C. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>) δ 6.74 and 6.67 (s, 4H each, ArH), 5.64 (s, 1H, Si–H), 4.64 (m, 1H, vinyl H), 2.43 (s, 12H, *o*-Me), 2.32 (s, 12H, *o*-Me), 2.11 and 2.08 (s, *p*-Me), 2.30–1.30 (aliphatic multiplets). <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>, assignments based on DEPT 135 experiment) δ 150.0 (C=C–O), 145.4, 144.5, 139.0, 138.6, 134.1, 131.5 (substituted Ar C), 129.6, 128.9 (Ar C–H), 103.5 (C=C–O), 30.2 (–CH<sub>2</sub>–), 24.7 (–CH<sub>3</sub>), 24.4 (–CH<sub>2</sub>–), 24.1 (–CH<sub>3</sub>), 23.8 (–CH<sub>2</sub>–), 22.7 (–CH<sub>2</sub>–), 21.2 (–CH<sub>3</sub>), 21.1 (–CH<sub>3</sub>). INEPT <sup>29</sup>Si (C<sub>6</sub>D<sub>6</sub>) δ –8.36, –56.67 (Si–H, *J* –178 Hz). IR (neat)  $\nu$ /cm<sup>–1</sup> 2133 (Si–H), 1664, 1604. MS, 629 (M<sup>+</sup>–H), calc. for *m/z* 629.3635, found *m/z* 629.3621.

‡ Data for compound **3**: <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>) δ 6.61, 2.57, 2.02. INEPT <sup>29</sup>Si (C<sub>6</sub>D<sub>6</sub>) δ –26.88. For comparison of NMR data see ref. 10.

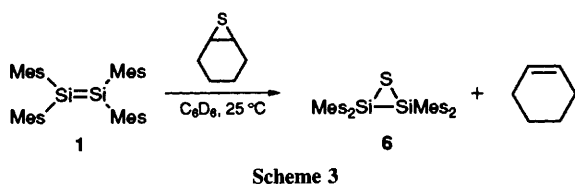
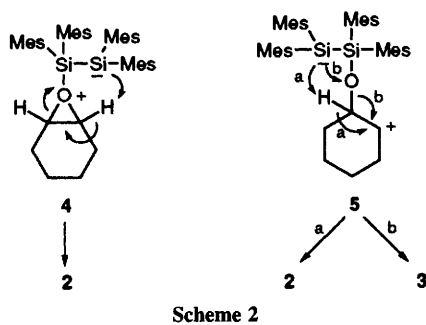
§ The ratio of **2**:**3** was 3:1. Presumably, disilene was also oxidized by adventitious oxygen.

¶ Crystal data: C<sub>42</sub>H<sub>54</sub>OSi<sub>2</sub>, *M* = 631.03, monoclinic, space group *P*2<sub>1</sub>/*c*, *a* = 25.288(5), *b* = 12.213(2), *c* = 23.959(5) Å, β = 91.02(3)°, *V* = 7398(2) Å<sup>3</sup>, *Z* = 8, *D*<sub>c</sub> = 1.133 Mg m<sup>–3</sup>, *F*(000) = 2736, *T* = 293(2) K, λ(Mo–Kα) = 0.71073 Å, μ = 0.126 mm<sup>–1</sup>, final *R* = 0.0490 for 9572 reflections with *I* > 2σ(*I*). Diffraction measurements were made on a Siemens PF4 diffractometer. The structure was solved by direct methods, and the non-hydrogen atoms were refined anisotropically by full-matrix least-squares analysis on *F*<sup>2</sup>.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.



Scheme 1 (Mes = mesityl)



The absence of a hydride migration to form a Lewis acid adduct of cyclohexanone from **4** or **5** may be somewhat surprising. Cyclohexanone reacts with **1** by [2 + 2] cycloaddition to give a known product, which was not detected in the reaction mixture by  $^{29}\text{Si}$  NMR spectroscopy.<sup>4</sup> Although this type of epoxide rearrangement is known to be rapid in benzene with boron trifluoride as a catalyst,<sup>14</sup> it apparently cannot compete in this situation with the other two reactions.

The reactivity of **1** with cyclohexene sulfide is more predictable, considering the relative strengths of carbon–oxygen (85.5 kcal mol<sup>-1</sup>; 1 cal = 4.184 J) and carbon–sulfur (65 kcal mol<sup>-1</sup>) bonds. When the episulfide was added to a solution of **1** in [ $^2\text{H}_6$ ]benzene, loss of the characteristic yellow–orange disilene colour occurred immediately.  $^1\text{H}$  NMR showed quantitative conversion to cyclohexene along with formation of the known disilathiane, **6** (Scheme 3).||

Although in part, these findings resemble reactions of disilenes with simple inorganic reagents, silyl enol ether formation is novel. It not only shows a divergence from typical epoxide reactivity with Lewis acid, but it also shows the

potential for additional unexpected disilene reactivity and should allow for thorough mechanistic study.

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|| Data for compound **6** were:  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ )  $\delta$  6.61, 2.53, 2.02. INEPT  $^{29}\text{Si}$  ( $\text{C}_6\text{D}_6$ )  $\delta$  -59.00. For comparison of NMR data see ref. 15.