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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 tetramesityldisilathiirane, 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, phosphorus¹ and arsenic,² as well as disilene transition metal complexes and simple 1,2-addition products.³ With organic reagents, disilenes have yielded mainly cycloadducts: [2 + 2] cycloadditions are found with alkynes,³ ketones, aldehydes,⁴ thiocarbonyl,⁵ organic nitrosyl⁶ and azo compounds,⁷ [2 + 1] with carbenes⁸ and isocyanides,⁹ and [2 + 3] cycloadditions with aryl azides.¹

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 $[{}^{2}H_{s}]$ 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.*¹¹ and Hudrlik and coworkers,¹¹ in which silyl epoxides were

[‡] Data for compound 3: ¹H NMR (C_6D_6) δ 6.61, 2.57, 2.02. INEPT ²⁹Si (C_6D_6) 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: $C_{42}H_{54}OSi_2$, M = 631.03, monoclinic, space group $P2_1/c$, a = 25.288(5), b = 12.213(2), c = 23.959(5) Å, $\beta = 91.02(3)^\circ$, V = 7398(2) Å³, Z = 8, $D_c = 1.133$ Mg m⁻³, F(000) = 2736, T = 293(2) K, $\lambda(Mo-K\alpha) = 0.71073$ Å, $\mu = 0.126$ mm⁻¹, final R = 0.0490 for 9572 reflections with $I > 2\sigma(I)$. 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^2 .

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. converted to silyl enol ethers either by pyrolysis or with magnesium bromide. Epoxide deoxygenation, however, has a great deal of precedent.¹² 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.¹³ 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 threemembered 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).



Scheme 1 (Mes = mesityl)

[†] Data for compound 2: m.p. 213–219 °C. ¹H NMR (C₆D₆) 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). ¹³C NMR (C₆D₆, 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 (–CH₂–), 24.7 (–CH₃), 24.4 (–CH₂–), 24.1 (–CH₃), 23.8 (–CH₂–), 22.7 (–CH₂–), 21.2 (–CH₃), 21.1 (–CH₃). INEPT ²⁹Si (C₆D₆) δ = 8.36, -56.67 (Si–H, J –178 Hz). IR (neat) v/cm⁻¹ 2133 (Si–H), 1664, 1604. MS, 629 (M⁺–H), calc. for *m/z* 629.3635, found *m/z* 629.3621.



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 ²⁹Si NMR spectroscopy.⁴ Although this type of epoxide rearrangement is known to be rapid in benzene with boron trifluoride as a catalyst,¹⁴ 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⁻¹; 1 cal = 4.184 J) and carbon-sulfur (65 kcal mol⁻¹) bonds. When the episulfide was added to a solution of 1 in [${}^{2}H_{6}$]benzene, loss of the characteristic yellow-orange disilene colour occurred immediately. ${}^{1}H$ NMR showed quantitative conversion to cyclohexene along with formation of the known disilathiirane, 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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 $[\]parallel$ Data for compound 6 were: ¹H NMR (C₆D₆) δ 6.61, 2.53, 2.02. INEPT ²⁹Si (C₆D₆) δ -59.00. For comparison of NMR data see ref. 15.