

Formation of a Disiloxirane in the Oxidation of 1,2-Dimesityl-1,2-di-*t*-butyldisilathylene

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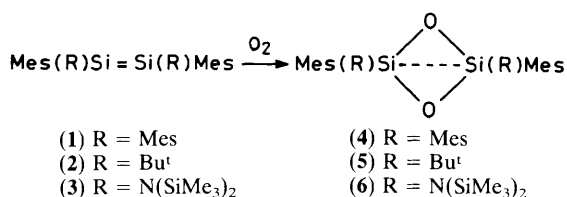
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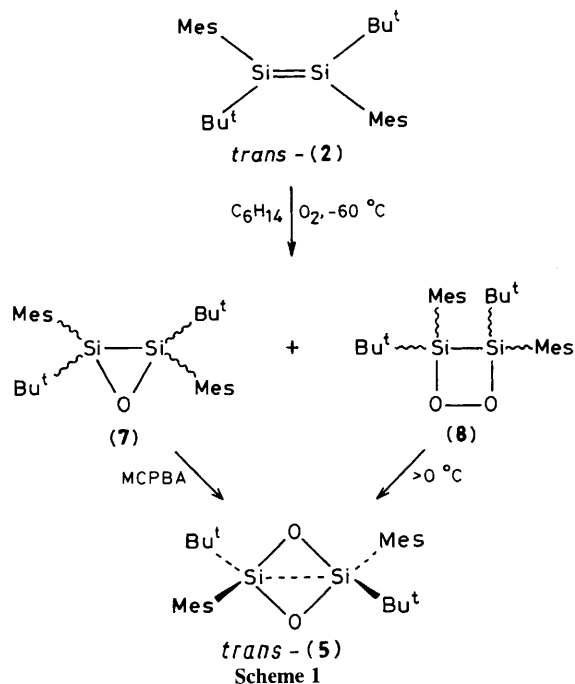
Reaction of *trans*-1,2-di-*t*-butyl-1,2-dimesityldisilaethylene in solution with dioxygen at -78°C produces the disiloxirane (7) and a compound believed to be the 1,2-disiladioxetane (8a); the latter compound rearranges quantitatively to the known 1,3-cyclodisiloxane (5) above 0°C .

The synthesis of stable disila-olefins (disilenes), which contain a silicon-silicon double bond, has led to new routes to organosilicon compounds which cannot be made by conventional methods.¹ One of the more interesting reactions of this type is the oxidation of disila-olefins to produce 1,3-cyclodisiloxanes.^{1b,1d}

Oxygen reacted with the powdered solids (1)–(3) at 25°C to give quantitative yields of (4)–(6) respectively. However, when *trans*-(2) in pentane solution at 25°C was treated with oxygen, the products were 60% of *trans*-(5) and 40% of disiloxirane (7), the first example of a disila-olefin epoxide.[†]



Mes = 2,4,6-trimethylphenyl

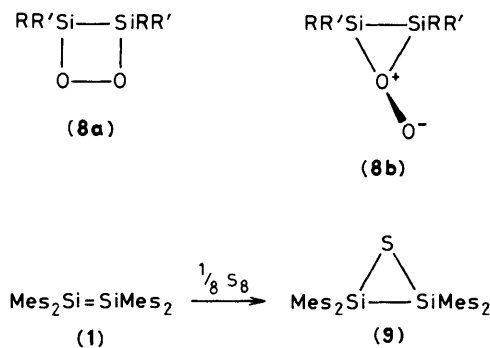


[†] Compound (7): ¹H n.m.r. (C₆D₆) δ 0.98 (s, 18H), 2.10 (s, 6H), 2.67 (s, 6H), 2.79 (s, 6H), 6.76 (s, 4H); ²⁹Si{¹H} n.m.r. (C₆D₆) δ - 7.8 p.p.m., (CDCl₃) δ - 8.2 p.p.m.; u.v.-visible (3-methylpentane) 203 (ε = 63 000), 247 nm (20 000); mass spectrum (30 eV) *m/z* 424 (*M*⁺, 0.3%), 367 (*M*⁺ - Bu^t, 99%), 247 [(*M*⁺ - Bu^t) - C₉H₁₂, 40%]. Exact mass for C₂₆H₄₀Si₂O calcd. *m/z* 424.2607, found *m/z* 424.2616.

Compound (7) is inert to oxygen, even in benzene at 80°C , but can be further oxidized to *trans*-(5) by treatment with *m*-chloroperbenzoic acid (MCPBA) at -78°C (Scheme 1).

When oxidation with oxygen of *trans*-(2) was carried out in pentane or tetrahydrofuran solution at -78°C the major product was compound (8),[‡] an isomer of (5). Some of (7) was also produced. Compound (8) is stable at -22°C but at 0°C and above, either in solution or in the solid state under Ar, it rearranges quantitatively to *trans*-(5); the half life at 25°C is *ca.* 1 day. The mass spectrum of (8) is very similar to that of (5) showing a parent ion at *m/z* 440 (4.3%) and a loss of *t*-butyl at *m/z* 383 (100%). Rearrangement of (8) to (5) in the mass spectrometer cannot be ruled out at this point. The ²⁹Si n.m.r. spectrum of (8) shows a very deshielded signal at δ +54.9 p.p.m.² The i.r. spectrum contains a strong, sharp band at 1060 cm⁻¹ characteristic of Si-O absorption, and two moderately strong bands at 805 and 726 cm⁻¹ which are not seen in that of (5).

Likely structures for (8), by analogy with the structures of known and suspected olefin-oxygen adducts,^{3,4} are the 1,2-disiladioxetane (8a) or the disilaethylene perepoxide (8b).[§] Under the likely assumption of a *trans* structure for (8b), the inversion barrier at the trivalent oxygen should lead to inequivalence of the *t*-butyl groups. However, no splitting of the *t*-butyl resonance is seen in the ¹H n.m.r. spectrum of (8) at temperatures down to -82°C . Although a very low inversion barrier for structure (8b) cannot be ruled out,⁵ this



[‡] Compound (8): ¹H n.m.r. (C₆D₆) δ 1.13 (s, 18H), 2.08 (s, 6H), 2.48 (s, 6H), 2.53 (s, 6H), 6.71 (s, 4H); ²⁹Si{¹H} n.m.r. (C₆D₆) δ + 54.9 p.p.m.; u.v.-visible (3-methylpentane) 198 (ε = 71 000), 247 nm (14 800); mass spectrum (30 eV) *m/z* 440 (*M*⁺, 4.3%), 383 (*M*⁺ - Bu^t, 100%), 263 [(*M*⁺ - Bu^t) - C₉H₁₂, 12.3%]. Exact mass for C₂₆H₄₀Si₂O₂ calcd. *m/z* 440.2556, found *m/z* 440.2564.

[§] In an attempt to differentiate between these two structures, the ¹⁷O n.m.r. spectrum of 20% labelled (8) was recorded at 25°C . No signal for (8) was seen at 0°C or 25°C , although a sharp singlet at δ +82.6 p.p.m. (Δ*v*_{1/2} = 300 Hz) was observed due to *ca.* 10% of (5) present as an impurity. The ¹⁷O resonance for (8) must be very broad and hence unobservable under our conditions.

n.m.r. evidence favours structure (8a). Also consistent with structure (8a) are the facts that (8) does not react with the powerful deoxygenating agents, *trans*-(2) and triphenylphosphine and that there is no very strong i.r. absorption for (8) attributable to the O–O stretching mode, which should be intense for (8b).

Assuming structure (8a) to be correct, the reaction of oxygen with *trans*-(2) at low temperatures in solution is summarized in Scheme 1. Addition of oxygen is stereoselective and probably stereospecific; the ¹H n.m.r. spectra for both (7) and (8) are consistent with their existence as single stereoisomers, and the rearrangement of (8), like the further oxidation of (7), produces exclusively *trans*-(5). Oxygenation of mixtures of *cis*- and *trans*-(2) gave (7) and (8) which appear from their ¹H n.m.r. spectra to be isomeric mixtures approximately in the same ratio as in the starting materials; rearrangement of (8) so formed gave a similar mixture of *cis*- and *trans*-(5).

In a reaction related to these, tetramesityldisilaethylene (1) has been found to react with elemental sulphur in benzene solution to yield mainly the episulphide (9),⁶ identified by ¹H n.m.r. and mass spectrometry.¶

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¶ Compound (9): ¹H n.m.r. (C₆D₆) δ 2.02 (s, 12H), 2.55 (s, 24H); ²⁹Si n.m.r. (C₆D₆) δ +59.0 p.p.m.; mass spectrum (30 eV) *m/z* 564 (*M*⁺, 3.8%), 445 (*M*⁺ – Mes, 85.4%), 376 (*M*⁺ – 2Mes, 20.1%). Exact mass for C₃₆H₄₄Si₂S calcd. *m/z* 564.2691, found *m/z* 564.2704.