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

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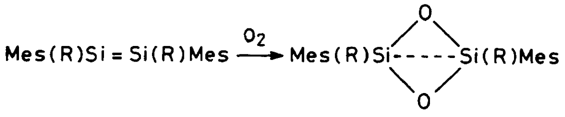
Reaction of *trans*-1,2-di-t-butyl-1,2-dimesityldisilaethylene in solution with dioxygen at −78 °C produces the disiloxirane (**7**) and a compound believed to be the 1,2-disiladioxetane (**8a**); the latter compound rearranges quantitatively to the known 1,3-cyclodisiloxane (**5**) above 0 °C.

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]

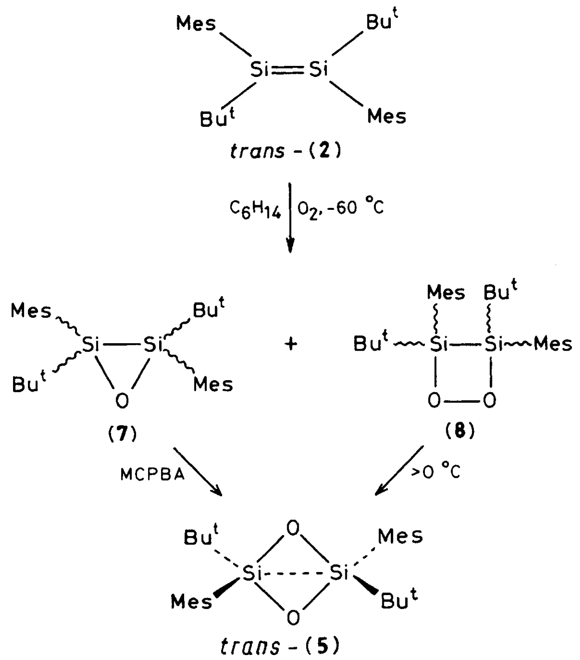
Oxygen reacted with the powdered solids (**1**)—(**3**) at 25 °C to give quantitative yields of (**4**)—(**6**) respectively. However, when *trans*-(**2**) in pentane solution at 25 °C was treated with oxygen, the products were 60% of *trans*-(**5**) and 40% of disiloxirane (**7**), the first example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



(**1**) R = Mes
(**2**) R = Bu^t
(**3**) R = N(SiMe$_3$)$_2$

(**4**) R = Mes
(**5**) R = Bu^t
(**6**) R = N(SiMe$_3$)$_2$

Mes = 2,4,6-trimethylphenyl

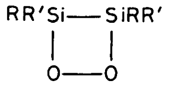


Scheme 1

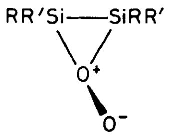
Compound (**7**) is inert to oxygen, even in benzene at 80 °C, but can be further oxidized to *trans*-(**5**) by treatment with *m*-chloroperbenzoic acid (MCPBA) at −78 °C (Scheme 1).

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 ^{29}Si 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**).

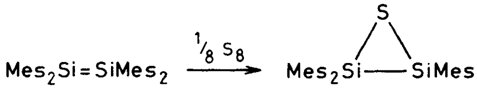
Likely structures for (**8**), by analogy with the structures of known and suspected olefin–oxygen adducts,[3,4] are the 1,2-disiladioxetane (**8a**) or the disilaethylene perepoxide (**8b**).§ Under the likely assumption of a *trans* structure for (**8b**), the inversion barrier at the trivalent oxygen should lead to inequivalence of the t-butyl groups. However, no splitting of the t-butyl resonance is seen in the ^{1}H 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



(**8a**)



(**8b**)



(**1**) (**9**)

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† Compound (**7**): ^{1}H n.m.r. (C$_6$D$_6$) δ 0.98 (s, 18H), 2.10 (s, 6H), 2.67 (s, 6H), 2.79 (s, 6H), 6.76 (s, 4H); ^{29}Si{^{1}H} n.m.r. (C$_6$D$_6$) δ − 7.8 p.p.m., (CDCl$_3$) 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) − C$_9$H$_{12}$, 40%]. Exact mass for C$_{26}$H$_{40}$Si$_2$O calcd. *m/z* 424.2607, found *m/z* 424.2616.

‡ Compound (**8**): ^{1}H n.m.r. (C$_6$D$_6$) δ 1.13 (s, 18H), 2.08 (s, 6H), 2.48 (s, 6H), 2.53 (s, 6H), 6.71 (s, 4H); ^{29}Si{^{1}H} n.m.r. (C$_6$D$_6$) 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) − C$_9$H$_{12}$, 12.3%]. Exact mass for C$_{26}$H$_{40}$Si$_2$O$_2$ calcd. *m/z* 440.2556, found *m/z* 440.2564.

§ In an attempt to differentiate between these two structures, the ^{17}O 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. ($\Delta\nu_{1/2}$ = 300 Hz) was observed due to *ca.* 10% of (**5**) present as an impurity. The ^{17}O 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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2 Deshielded ^{29}Si n.m.r. signals have been reported for $Me_3SiOOCF_3$ (δ +34.3 p.p.m.) and $Me_3SiOOMe$ (δ +22.0 p.p.m.): H. C. Marsmann and H. G. Horn, *Z. Naturforsch., Teil B*, 1972, **27**, 1448. Compound (**5**) shows a ^{29}Si n.m.r. signal at δ +13.3 p.p.m.

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5 An analogous compound, *O*-isopropylethyleneoxonium fluoroborate, has an inversion barrier of 10 kcal mol^{-1} (1 kcal = 4.18 kJ): J. B. Lambert and D. H. Johnson, *J. Am. Chem. Soc.*, 1968, **90**, 1349.

6 D. J. De Young and R. West, unpublished results.

¶ Compound (**9**): ^1H n.m.r. (C_6D_6) δ 2.02 (s, 12H), 2.55 (s, 24H); ^{29}Si n.m.r. (C_6D_6) 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 $C_{36}H_{44}Si_2S$ calcd. m/z 564.2691, found m/z 564.2704.