

## Photolysis of 2,3:5,6-Dibenzo-7,7,8,8-tetraisopropyl-7,8-disilabicyclo[2.2.2]octa-2,5-diene: Evidence for [2 + 2] Cyclodimerization of a Disilene

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Evidence for disilene dimerization was obtained by generating tetraisopropylidisilene from the title compound *via* the photochemical retrodiene process which produced the expected dimerization product, octaisopropylcyclotetrasilane (30%), in addition to the H-abstraction product, 1,1,2,2-tetraisopropylidisilane (5%).

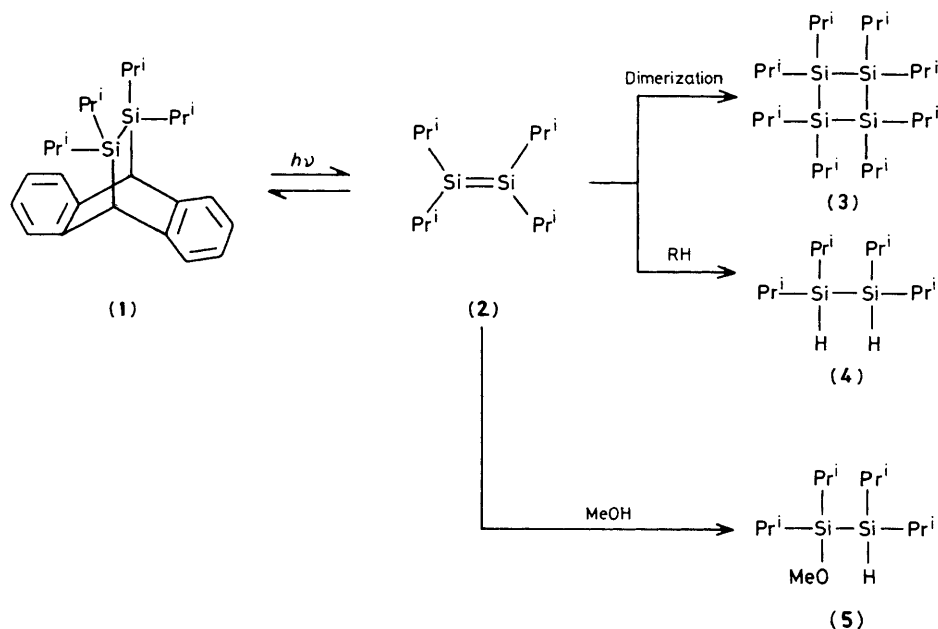
Quite recently, Chen and Gaspar reported the liquid-phase pyrolysis of methoxytris(trimethylsilyl)silane leading to the stable octakis(trimethylsilyl)cyclotetrasilane.<sup>1</sup> These workers suggested for the formation of the cyclotetrasilane a tempting mechanism which involves [2 + 2] cyclodimerization of the transient intermediate  $(\text{Me}_3\text{Si})_2\text{Si}=\text{Si}(\text{SiMe}_3)_2$ , as well as an alternative mechanistic hypothesis. However, to our knowledge, disilene dimerization has never been observed, although there is intense current interest in the chemistry of molecules containing the silicon-silicon (p-p) $\pi$  double bond.<sup>2-10</sup> For instance, photochemical or thermal retro-Diels-Alder reaction of 7,7,8,8-tetramethyl- or 7,7,8,8-tetraphenyl-7,8-disilabicyclo[2.2.2]octa-2,5-diene to generate tetramethyldisilene or tetraphenyldisilene was reported to result in the formation of a polysilane polymer.<sup>3,4†</sup> No description was given concerning the formation of a disilene dimerization product, *i.e.* a cyclotetrasilane.

† It might be presumed that the reaction would form a cyclotetrasilane (*e.g.*, octamethylcyclotetrasilane) initially which would then be converted to higher polysilanes. However, this presumption is hard to verify at the present time.

In an attempt to gain further evidence for the disilene dimerization, we decided to generate tetraisopropylidisilene from 2,3:5,6-dibenzo-7,7,8,8-tetraisopropyl-7,8-disilabicyclo[2.2.2]octa-2,5-diene (**1**) *via* a photochemical retrodiene process. This choice comes from our knowledge that the expected product, octaisopropylcyclotetrasilane, should be reasonably stable under the conditions employed.<sup>10,11</sup>

Synthesis of the desired photochemical precursor of the disilene (**2**) was accomplished by the reaction of 1,2-dichlorotetraisopropylidisilane with lithium and anthracene at room temperature (*ca.* 20 °C).‡ Thus, the disilane (6.90 g, 23.1 mmol) in dimethoxyethane (DME) (15 ml) was added dropwise to lithium anthracenide [prepared from anthracene

‡ The reaction temperature is critical. For example, the reaction at a lower temperature (*e.g.*, -78 °C), similar to that used earlier by Roark and Peddle for the synthesis of the 7,7,8,8-tetramethyl derivative,<sup>2</sup> was very sluggish and gave only a trace amount of (**1**) after 20 h. Further, although Masamune and coworkers reported that the reaction of dichlorodi-*t*-butylsilane with lithium naphthalenide gave 2,3-benzo-7,7,8,8-tetra-*t*-butyl-7,8-disilabicyclo[2.2.2]octa-2,5-diene,<sup>8</sup> the use of dichlorodi-isopropylsilane leading to (**1**) under similar conditions turned out to be unsuccessful.



(8.10 g, 45.6 mmol) and lithium (30% dispersion, 1.23 g, 55.5 mg-atom) in DME (45 ml) at room temperature in 6 h under argon. The mixture was stirred for an additional 14 h at room temperature and worked up to give a solid which, on recrystallization from ethanol, gave an analytically pure sample of (1) (1.92 g, 21%, m.p. 165.0–165.5 °C).§

Photolysis of (1) (50 mg, 0.12 mmol) in cyclohexane (4 ml) ( $3 \times 10^{-2} \text{ mol l}^{-1}$ ) with a 400 W high pressure mercury lamp at room temperature for 12 h gave octaisopropylcyclotetrasilane (3) (0.015 mmol, 30%), 1,1,2,2-tetraisopropylsilane (4) (0.005 mmol, 5%), anthracene, and dianthracene, together with the unreacted (1) (0.025 mmol, 20%).§

In view of the well-established mechanisms for the photolysis of 7,8-disilabicyclo[2.2.2]octa-2,5-dienes,<sup>3,5,8</sup> it is possible that the cyclotetrasilane (3) is formed through the [2+2] cycloaddition of the disilene (2). That the disilene (2) is indeed involved in this reaction is shown by the photolysis of (1) (0.10 g, 0.24 mmol) in cyclohexane (5 ml) containing methanol (40 mg, 1.25 mmol) under otherwise identical conditions which gave 1,1,2-tetraisopropylmethoxydisilane (5) (0.099 mmol), instead of the dimer (3).§ The result can be explained by postulating that methanol traps the disilene (2) so effectively that the concentration of the transient disilene species would be too low to undergo dimerization. The formation of the dihydrodisilane (4) is also in keeping with the disilene intermediate which is known to abstract hydrogen from the solvent.<sup>9</sup> It should also be noted that the preponderant formation of the tetrasilane (3) over (4) indicates that the disilene dimerization proceeds smoothly under the photolytic conditions employed.

The dimerization observed in this work is thus in accord with the previous suggestion advanced by Chen and Gaspar<sup>1</sup> and places emphasis on the view that the possibility of  $\pi$ -dimerization should be considered in any mechanistic discussions of disilene reactions.

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§ All compounds were characterized by i.r., n.m.r., and mass spectra. Satisfactory elemental analyses were obtained for new compounds.

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