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The First Preparation of Disilene via Reductive Dehalogenation of 1,2-Dichlorodisilane. The Formation of an Unusual Air-Oxidation Product, 1-Oxa-2-silacyclopent-3-ene Derivative

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The most air-stable disilene, tetrakis(2,4,6-triisopropylphenyl)disilene, again was obtained by the reaction of 1,2dichloro-1,1,2,2-tetrakis(2,4,6-triisopropylphenyl)disilane with lithium naphthalenide. The disilene afforded its air-oxidation product having 1-oxa-2-silacyclopent-3-ene framework which was determined by X-ray analysis.

Previously, we reported that tetrakis(2,4,6-triisopropylphenyl)disilene, the most air-stable disilene with half-life time of ca. one day in solid, could be produced by direct treatment of bis(2,4,6-triisopropylphenyl)dichlorosilane with lithium naphthalenide.¹⁾ However, there are no reports on the preparation of disilene via the reductive dehalogenation of tetra-substituted 1,2-dihalodisilane, although such reaction has been previously suggested by our group.²⁾ We should like to report here on the first synthesis and isolation of disilene from a 1,2dichlorodisilane bearing bulky substituents and on air-oxidation of the disilene. Thus, tetrakis(2,4,6-triisopropylphenyl)disilene (1) could be readily prepared in a good yield by the treatment of 1,2-dichloro-1,1,2,2-tetrakis(2,4,6-triisopropylphenyl)disilane (2)³⁾ with lithium naphthalenide.



Typically, a solution of 2 (0.50 g, 0.53 mmol) in dimethoxyethane (DME) (35 ml) was added dropwise with stirring over 5 min to a cold, dark green solution (-60 °C) of lithium naphthalenide prepared from lithium (15 mg, 2.2 mol) and naphthalene (0.14 g, 1.1 mmol) in DME (13 ml). The mixture was stirred for ca. 2 h at this temperature and then allowed to warm up to room temperature and the work-up for the reaction mixture was similar to that previously described.¹⁾ By the comparison of the spectral data with those of the authentic sample, the resulting yellow crystalline solid was identified to be compound 1 (0.23 g, 50%; mp 252-259 °C (sealed in Ar) (red-orange liquid); 295-300 °C (dec.; yellow liquid).

It is very interesting to investigate that what type of product can be formed from 1 via oxidation in air, since our disilene has much bulkier substituents around the Si=Si bond compared to other disilenes so far reported.⁴⁾ Thus, disilene 1 was left standing for two days in air and the resulting colorless solid was recrystallized from ethanol to give fine needles, mp 230-242 °C (sealed capillary) (71%). The structure of the molecule was determined by X-ray crystal analysis to be a 1-oxa-2-silacyclopent-3-ene derivative (3)⁵⁾ (Fig. 1), the framework of which is quite different from the expected 1,3-cyclodisiloxane structure (4) which, in turn, was reported to be derived from other analogous disilenes by air-oxidation.⁶⁾

In the crystal structure of 3, 7 the six bondings to the substituents around the Si-Si bond axis are arranged in gauche form with each other, and the four aryl groups are oriented so as to minimize the steric repulsions between them in a sim-





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Fig. 1. Molecular structure of compound 3 viewed down along the Si2-Si1 bond axis. Selected bond distance/Å: Si1-Si2, 2.390(7); Si2-O2, 1.74(1); O2-C13D, 1.45(2), C13D-C6D, 1.45(2); C6D-C1D, 1.41(2); C1D-Si2, 1.83(1). Selected bond angle/°: O2-Si2-C1D, 87.2(0.6); Si2-O2-C13D, 114.7(1.0); O2-C13D-C6D, 104.8(1.2); C13D-C6D-C1D, 115.1(1.2); C6D-C1D-Si2, 110.2(1.0).

ilar manner to that observed in the starting disilene.¹⁾ The Si-Si bond distance (2.39 Å) is close to normal single bond (2.35 Å), but the Si-O bond (1.74 Å) in the five-membered ring is longer than usual Si-O bonds (1.61–1.65 Å)⁸⁾ and also than that of tetramesityl-1,3-cyclodisiloxane (1.65 Å) reported by West et al.⁹⁾

The formation of both the five-membered ring system and Si-OH group from 1 is mechanistically of quite interest because of the unusual structure of compound 3 compared with compound 4.⁴⁾ It is worthwhile to note that in the unit cell of the crystal there exists a pair of enantiomers (d and l) with respect to the Si2 atom center, indicating that the oxidation proceeded through non-stereospecific manner. Thus, it is likely that the addition of O₂ to the Si=Si bond occurred to produce an intermediate, 5, which undergoes an intramolecular reaction between the O-O bond formed and an α -C-H bond of ortho isopropyl groups in aryl substituents, giving compound 3 with a retained Si-Si bonding. Further investigation of disilene 1 is currently in progress.

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- 1) H. Watanabe, K. Takeuchi, N. Fukawa, M. Kato, M. Goto, and Y. Nagai, Chem. Lett., <u>1987</u>, 1341.
- 2) H. Watanabe, read at 7th International Symposium on Organosilicon Chemistry, Abstracts, 5C0930, p. 144, Sept. 9-14, (1984), Kyoto; H. Watanabe and Y. Nagai, "Organosilicon and Bioorganosilicon Chemistry," ed by H. Sakurai, Ellis Horwood Limited, Chichester, West Sussex, England (1985), Chap. 9, pp. 107-114; H. Matsumoto, K. Takatsuna, M. Minemura, Y. Nagai, and M. Goto, J. Chem. Soc., Chem. Commun., <u>1985</u>, 1360.
- 3) HSiCl₃ $\xrightarrow{\text{ArLi}}$ HSiAr₂Cl $\xrightarrow{\text{Li}}$ HSi₂Si-SiAr₂H $\xrightarrow{\text{Cl}_2}$ 2 A B

- 4) S. Masamune, S. Murakami, J. T. Snow, H. Tobita, and D. J. Williams, Organometal., <u>3</u>, 333 (1984); M. J. Fink, M. J. Michalczyk, K. J. Haller, R. West, and J. Michl, J. Chem. Soc., Chem. Commun., <u>1983</u>, 1010; Organometal., <u>3</u>, 793 (1984).
- 5) Elemental analysis, Found: C, 79.76%; H, 10.24%. Calcd for $C_{60}H_{92}O_2Si_2$: C, 79.93%; H, 10.29%; UV λ_{max} 260 nm (ϵ 4800 dm³ mol⁻¹ cm⁻¹)(sh), 281 (3400)(sh) (c- C_6H_{12}); ¹HNMR (CDCl₃, TMS) δ (ppm) 0.25(d), 0.60(d), 1.08(d), 1.11(d), 1.25 (d), 1.61(s), 2.74(sept), 3.26(sept), 4.14(sept), 6.74(s), 6.81(s), 6.84(s), 7.01(s); IR (KBr) 3700 cm⁻¹ (vOH, unassociated); MW 900(MS) (Calcd 900).
- 6) M. J. Fink, D. J. De Young, and R. West, J. Am. Chem. Soc., <u>105</u>, 1070 (1983);
 M. J. Michalczyk, R. West, and J. Michl, ibid., <u>106</u>, 821 (1984); J. Chem. Soc., Chem. Commun., <u>1985</u>, 1525; M. J. Fink, K. J. Haller, R. West, and J. Michl, Organometal., <u>5</u>, 531 (1986).
- 7) Crystal data for 3: $C_{60}H_{92}O_2Si_2$; MW 901.574; Dimensions 0.2 mm x 0.2 mm x 0.3 mm; Triclinic a = 13.763(1), b = 13.066(2), c = 17.985(1) Å, $\alpha = 84.02(1)^{\circ}$, $\beta = 93.44(1)^{\circ}$, $\gamma = 110.99(2)^{\circ}$; V = 3002.2(3) Å³; Space group P1; Z = 2; $\rho_c = 0.997 \text{ g cm}^{-1}$; $\mu(Mo-K\alpha) 0.99 \text{ cm}^{-1}$. Data were collected on a Rigaku-Denki Model AFC-4 diffractometer with Mo-K α X-radiation (monochromated with graphite) using $\theta \sim 2\theta$ scans (scan rate, 4 °/min). The structure was solved by direct method and all non-hydrogen atoms were refined anisotropically to R = 0.129 as the preliminary result for 3332 observed reflections (numbers used for the calculations ($|F_{\circ}| > 3\sigma|(F_{\circ})|$) (total numbers collected: 10500, $2^{\circ} \leq 2\theta \leq 50^{\circ}$). Lists of the atomic co-ordinates and the other structural parameters are available from the authors as a supplementary material.
- 8) J. Kiss and G. Mencze, Acta Crystallogr., Sect. B, <u>31</u>, 1214 (1975).
- 9) M. J. Fink, K, J. Haller, R. West, and J. Michl, J. Am. Chem. Soc., <u>106</u>, 822 (1984).

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1346