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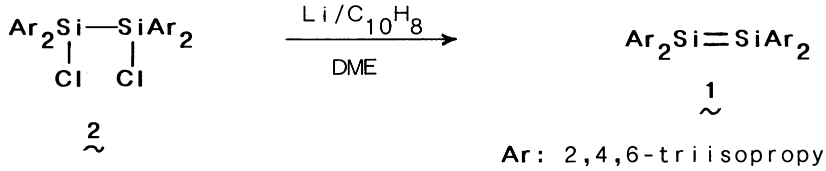
The most air-stable disilene, tetrakis(2,4,6-triisopropylphenyl)disilene, again was obtained by the reaction of 1,2-dichloro-1,1,2,2-tetrakis(2,4,6-triisopropylphenyl)disilane with lithium naphthalenide. The disilene afforded its air-oxidation product having 1-oxa-2-silacyclopent-3-ene framework which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



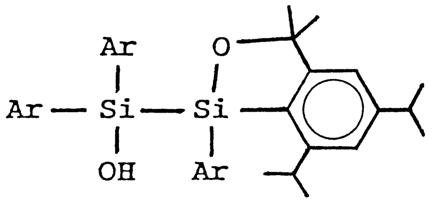
$$\underset{\mathbf{2}}{\mathrm{Ar_2Si(Cl)\!-\!Si(Cl)Ar_2}} \xrightarrow[\text{DME}]{\mathrm{Li/C_{10}H_8}} \underset{\mathbf{1}}{\mathrm{Ar_2Si{=}SiAr_2}}$$

Ar: 2,4,6-triisopropylphenyl

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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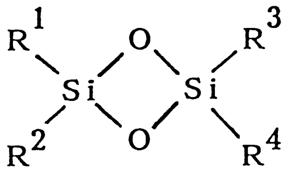

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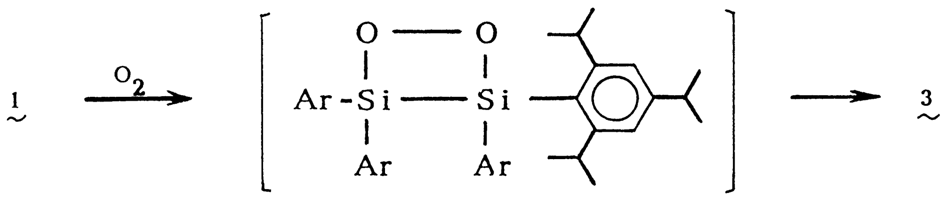
R^1, R^2, R^3, R^4 = mesityl, etc.



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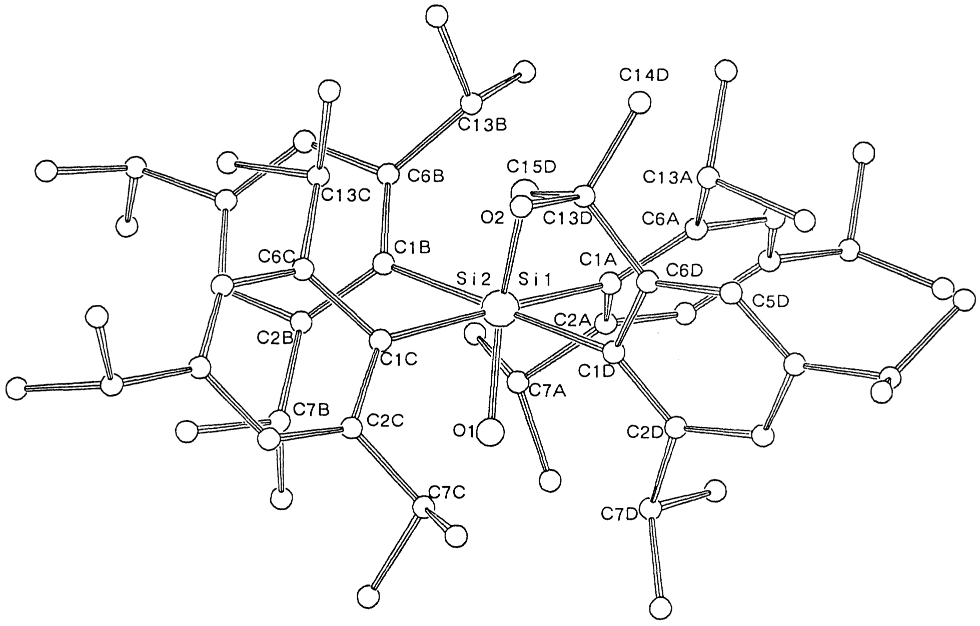

Fig. 1. Molecular structure of compound **3** viewed down along the Si2-Si1 bond axis. Selected bond distance/Å: Si1-Si2, 2.390(7); Si2-O2, 1.74(1); O2-C13D, 1.45(2), C13D-C6D, 1.45(2); C6D-C1D, 1.41(2); C1D-Si2, 1.83(1). Selected bond angle/°: O2-Si2-C1D, 87.2(0.6); Si2-O2-C13D, 114.7(1.0); O2-C13D-C6D, 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 O_2 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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References

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3) $HSiCl_3 \xrightarrow{ArLi} \underset{\mathbf{A}}{HSiAr_2Cl} \xrightarrow{Li} \underset{\mathbf{B}}{HSi_2Si\text{-}SiAr_2H} \xrightarrow{Cl_2} \mathbf{2}$

A: 35%; bp 197-201 °C/3 Torr (Torr, 133.32 Pa); MW 470(MS) (Calcd 470); IR (neat) 2170 cm^{-1} (νSiH). **B**: 43%; mp 219.0-222.0 °C; MW 870(MS) (Calcd 870); IR (KBr) 2140 cm^{-1} (νSiH). **2**: 84%; mp 254.0-255.0 °C; ^{1}HNMR ($CDCl_3$, TMS) δ(ppm) −0.06(d), 0.11(d), 1.10(d), 1.18(d), 1.36(d), 1.46(d), 2.85(sept), 3.67(sept), 6.91(s), 7.00(s), 7.16(s); Analysis, Found: C, 76.58%; H, 9.74%. Calcd for $C_{60}H_{92}Cl_2Si_2$: C, 76.63%; H, 9.86%.

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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 $dm^3\ mol^{-1}\ cm^{-1}$)(sh), 281 (3400)(sh) ($c\text{-}C_6H_{12}$); ^{1}HNMR ($CDCl_3$, 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} (νOH, unassociated); MW 900(MS) (Calcd 900).

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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, α =84.02(1)°, β = 93.44(1)°, γ = 110.99(2)°; V = 3002.2(3) $Å^3$; Space group $P\bar{1}$; Z = 2; ρ_c = 0.997 g cm^{-1}; μ(Mo-Kα) 0.99 cm^{-1}. Data were collected on a Rigaku-Denki Model AFC-4 diffractometer with Mo-Kα 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 ($|F_o| > 3\sigma|(F_o)|$) (total numbers collected: 10500, $2° \leqq 2\theta \leqq 50°$). Lists of the atomic co-ordinates and the other structural parameters are available from the authors as a supplementary material.

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