# High-pressure Synthesis, Structure and Novel Photochemical Reactions of 7,7,8,8-Tetramethyl-7,8-disilabicyclo[2.2.2]octa-2,5-diene

**Akira Sekiguchi, Ikutaro Maruki, Keisuke Ebata, Chizuko Kabuto and Hideki Sakurai***

*Department of Chemistry and Organosilicon Research Laboratory, Faculty of Science, Tohoku University, Aoba-ku, Sendai 980, Japan*

7,7,8,8-Tetramethyl-7,8-disilabicyclo[2.2.2]octa-2,5-diene **1**, prepared by the high-pressure reaction (10 000 bar) of 1,1,2,2-tetramethyl-1,2-disilacyclohexa-3,5-diene and phenyl vinyl sulphoxide followed by elimination of benzenesulphenic acid, gave tetramethyldisilene ($Me_2Si{=}SiMe_2$) upon photolysis which underwent a photochemical [2 + 4] reaction with benzene at 10 K in an argon matrix to regenerate the precursor.

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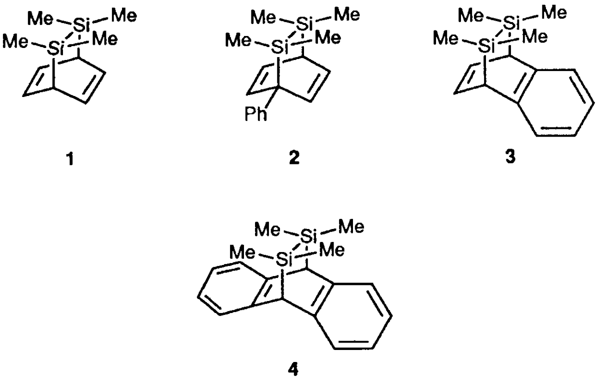
7,8-Disilabicyclo[2.2.2]octa-2,5-diene derivatives[1] such as **2**, **3** and **4** generate highly reactive tetramethyldisilene by either thermolysis[2] or photolysis.[3] These compounds thus behave as masked disilenes. Anionic polymerization of masked disilenes **2** to high-molecular weight polysilylenes has also been reported recently.[4]

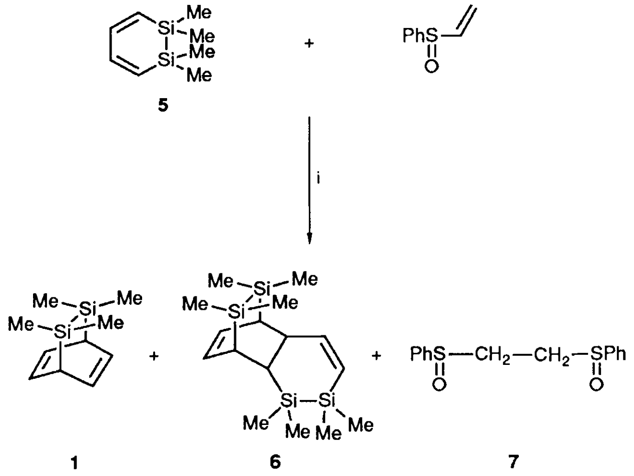
The parent compound **1** is of special interest in view of its highly symmetrical and simple structure, although the synthesis is not straightforward. We report herein the first successful preparation of 7,7,8,8-tetramethyl-7,8-disilabicyclo-[2.2.2]octa-2,5-diene **1**. Its molecular structure was determined by X-ray crystallography and unique photochemical reactions are reported as well.

The synthetic strategy for the preparation of **1** is based on the Diels–Alder reactions of 1,1,2,2-tetramethyl-1,2-disilacyclohexa-3,5-diene **5**[5] with alkynes. After several unsuccess-

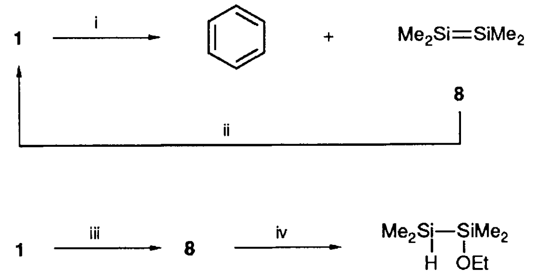


Scheme 1

ful attempts, we have found that the Diels–Alder reaction of **5** with phenyl vinyl sulphoxide followed by elimination of benzenesulphenic acid under ultra high pressure gave **1**. Thus, a diethyl ether solution of **5** (0.30 g, 1.79 mmol) and phenyl vinyl sulphoxide (0.59 g, 3.88 mmol) was heated at 100 °C for 12 h under a pressure of 10000 bar. Silica gel chromatography with hexane under argon followed by preparative gas chromatography afforded pure **1** (40 mg, 12%).† The dimer **6**‡ and 1,2-bis(phenylsulphinyl)ethane **7** were also formed. Application of ultra high pressure is essential in this reaction, since **1** is not formed under normal conditions.



**Scheme 2** *Reagents and conditions*: i, $Et_2O$, 100 °C, 10000 bar, 12 h



**Scheme 3** *Reagents and conditions*: i, $h\nu$ ($\lambda$ = 254 nm), Ar, 10 K; ii, $h\nu$ ($\lambda$ > 300 nm), Ar, 10 K; iii, $h\nu$ ($\lambda$ = 254 nm), EPA, 77K; iv, EtOH

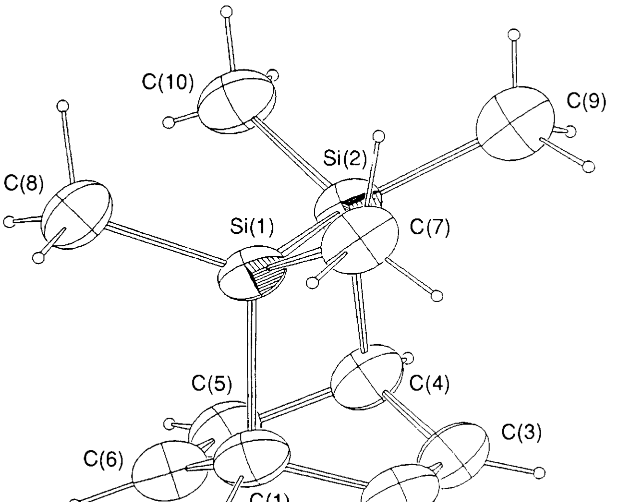


**Fig. 1** ORTEP drawing of **1**. Selected bond lengths (Å): Si(1)–Si(2) 2.363(2), Si(1)–C(1) 1.919(7), C(1)–C(2) 1.505(9), C(2)–C(3) 1.351(9), Si(1)–C(7) 1.872(7). Selected bond angles (°): C(1)–Si(1)–Si(2) 96.9(2), C(1)–C(2)–C(3) 118.3(7), C(2)–C(1)–C(6) 109.6(6). Dihedral angle (°): Si(1)–Si(2)–C(4)–C(1)/C(2)–C(3)–C(5)–C(6) 90.1.

Since no crystallographic structures have been reported for 7,8-disilabicyclo[2.2.2]octa-2,5-diene derivatives, the structure of **1** was determined by X-ray crystallography.§ Several interesting features of the structure can be pointed out. As shown in Fig. 1, the four alkenic carbons [C(2), C(3), C(5) and C(6)] are coplanar, while the bridged carbons [C(1) and C(4)] are located above the C(2)–C(3)–C(5)–C(6) plane. The dihedral angles between C(1)–C(2)–C(6) [or C(3)–C(4)–C(5)] and C(2)–C(3)–C(5)–C(6) planes are 33.8 ° (av.). The Si–Si bond (2.363 Å), parallel to the C(2)–C(3)–C(5)–C(6) plane, is slightly elongated. As a result, **1** was readily autoxidized to give mainly 2,2,4,4-tetramethyl-3-oxa-2,4-disilabicyclo-[3.2.2]nona-6,8-diene. The bridging Si–C bonds (av. 1.919 Å) are significantly lengthened and the bond angles around the bridged Si atoms (C–Si–Si av. 96.3°) are highly contracted. These structural features suggest the high reactivity of **1**.

The base peak is found at *m/z* 116 in the mass spectrum of **1**, and can be assigned to the cation radical of tetramethyldisilene

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† Compound **1**: air-sensitive colourless crystals; m.p. 43–44 °C; $^1$H NMR (300 MHz, $C_6D_6$) δ 0.07 (s, 12H, SiMe$_2$), 2.79–2.84 (m, 2H, C=C–CH), 5.77–5.79 (m, 4H, CH=CH); $^{13}$C NMR (75.5 MHz, $C_6D_6$) δ −3.33, 34.98, 126.20; $^{29}$Si NMR (59.6 MHz, $C_6D_6$) δ −25.0; UV (hexane) $\lambda_{max}$ 226 nm ($\epsilon$ 3500); MS (70 eV, rel. int.) *m/z* 194 ($M^+$ 2.7), 179 (1.7), 135 (6.2), 116 (100), 101 (34), 73 (73); high-resolution MS: calc. for $C_{10}H_{18}Si_2$: 194.0947; found 194.0943.

‡ Compound **6**: $^1$H NMR (300 MHz, $C_6D_6$) δ 0.08 (s, 3H), 0.11 (s, 3H), 0.12 (s, 3H), 0.14 (s, 3H), 0.17 (s, 3H), 0.18 (s, 6H), 0.28 (s, 3H), 1.35 (d, 1H, *J* 8 Hz), 1.88 (d, 1H, *J* 8 Hz), 2.01–2.04 (m, 1H), 2.82–2.87 (m, 1H), 5.81–5.88 (m, 2H), 5.98–6.03 (m, 1H), 6.36 (dd, 1H, *J* 14.5 and 3 Hz); $^{13}$C NMR (75.5 MHz, $C_6D_6$) δ −5.07 (2C), −3.83, −3.70, −3.53, −3.21, −2.59, −2.24, 25.3, 26.5, 36.5, 41.4, 127.5 (2C), 131.2, 155.5; $^{29}$Si NMR (59.6 MHz, $C_6D_6$) δ −36.9, −23.0, −20.6, −16.5; MS (70 eV) *m/z* 336 ($M^+$); high-resolution MS: calc. for $C_{16}H_{32}Si_4$: 336.1581; found: 336.1574.

§ The crystals for X-ray analysis were obtained from a methanol solution at 0 °C. A crystal of dimensions 0.2 × 0.4 × 0.5 mm was sealed in a capillary glass tube for data collection. A total of 2509 reflections within $2\theta$ = 128° were collected at −25 °C on a Rigaku-Denki AFC 5R four-circle diffractometer with graphite-monochromated Cu-K$\alpha$ radiation ($\lambda$ = 1.5418 Å) by the $2\theta$ − $\omega$ scan. *Crystal data*: $C_{10}H_{18}Si_2$, $M$ = 194.4, monoclinic, $a$ = 11.990(1), $b$ = 8.028(1), $c$ = 13.555(1) Å, $\beta$ = 112.90(1)°, $V$ = 1201.85(22) Å$^3$, space group $P2_1/c$, $Z$ = 4, $D_c$ = 1.075 g cm$^{-3}$. No absorption correction was applied. The final $R$ factor was 0.0849 ($R_w$ = 0.0807) for 1548 reflections with $F_o > 3\sigma(F_o)$. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

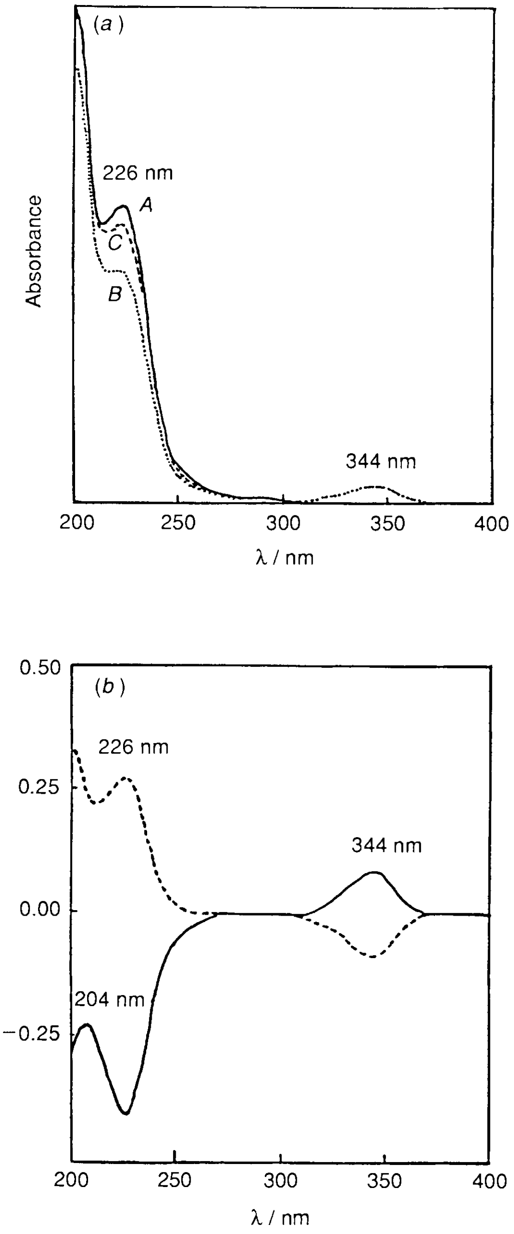

**Fig. 2** (*a*) UV spectra of **1** in Ar matrix at 10 K: *A*: before irradiation (——); *B*: after 90 sec irradiation ($\lambda$ = 254 nm) (··········); *C*: after additional irradiation ($\lambda > 300$ nm) of the above sample for 30 sec (- - - - -). (*b*) Differential spectra: *B* − *A* (——); *C* − *B* (- - - - -). **1**: 226 nm; $Me_2Si{=}SiMe_2$ **8**: 344 nm; benzene 204 nm.

formed by loss of benzene. The exact mass of the peak shows a composition of $C_4H_{12}Si_2$ consistent with the tetramethyldisilene (calc. 116.0478; found 116.0476). Thus, compound **1** could be a precursor of $Me_2Si{=}SiMe_2$. In fact, upon heating of **1** at 225 °C with anthracene in a sealed tube, a tetramethyldisilene adduct **4** was formed cleanly.

Of particular interest is the photochemical reaction of **1** to give tetramethyldisilene **8** and benzene. Argon-diluted **1**, deposited on a sapphire window cooled to 10 K,¶ was irradiated with 254 nm light, which resulted in a decrease of the UV absorption intensity at 226 nm of **1** with concurrent formation of a new band with a $\lambda_{max}$ at 344 nm. The same absorption band was observed in 3-methylpentane (3-MP) or EPA (a 5:5:2 mixture of diethyl ether, iso-pentane and ethanol) matrix at 77 K. On annealing the EPA matrix, a product of addition of ethanol to **8** was formed. Accordingly, the band at 344 nm can be assigned to that of tetramethyldisilene **8**.

Assignment of the UV absorption of tetramethyldisilene has been controversial until now. An absorption band near 350 nm was observed and assigned to tetramethyldisilene formed by dimerization of dimethylsilylene in a 3-MP or a 3-MP–isopentane matrix at 77 K;[6] on the basis of laser flash photolysis experiments, this absorption was assigned to dimethylsilylene.[7] Our experiment clearly shows that the absorption band at 344 nm is attributable to $Me_2Si{=}SiMe_2$.

Immediate disappearance of the band at 344 nm accompanied by simultaneous regeneration of the 226 nm band was observed by additional brief irradiation of the matrix of **8** with light of wavelength longer than 300 nm. This observation indicates that the disilene **8** reacts with benzene in the argon matrix at 10 K. It is likely that excitation of the disilene **8** results in π-bond breaking to form the diradical $Me_2Si{-}SiMe_2$ followed by the subsequent reaction with benzene in the matrix to regenerate **1**.

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¶ A Displex refrigerator (Air Products Inc.) was used for matrix isolation. The matrix-isolated sample was prepared by gas-phase deposition onto a sapphire window cooled to 10 K. The resulting matrix was irradiated with a mercury arc lamp through the quartz window.