

Synthesis, Structure, and Photochemistry of 2-Silyl- and 2-Disilyl-2-aryl-1,3-dithiane Derivatives

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A series of 2-silyl- and 2-disilyl-substituted 2-aryl-1,3-dithiane derivatives were prepared by the reactions of 2-aryl-2-lithio-1,3-dithianes with the corresponding chlorosilanes. Photolysis of 2-phenyl-2-(pentamethyldisilyl)-1,3-dithiane resulted in the intermediary formation of 1,1-dimethyl-2-phenyl-2-(trimethylsilyl)-1-silaethene.

The synthetic utility of 1,3-dithiane derivatives allow them to be used as carbonyl-protecting groups, masked-methylene compounds, and acyl-nucleophile synthons.¹ For example, 2-silyl-1,3-dithianes are frequently used as precursors of acylsilanes.^{2,3} However, there have not been any reports on the photochemistry of silyldithianes. We have synthesized a series of 2-silyl- and 2-disilyl-substituted 2-aryl-1,3-dithiane derivatives to study their spectroscopic properties and photochemical behavior.

Eight 2-aryl-2-silyl-1,3-dithiane derivatives (**1a–d** and **2a–d**) were prepared by the reactions of 2-aryl-2-lithio-1,3-dithianes with chlorosilanes as shown in Scheme 1.⁴ The yields and UV spectral data of **1** and **2** are summarized in Table 1.

Scheme 1.

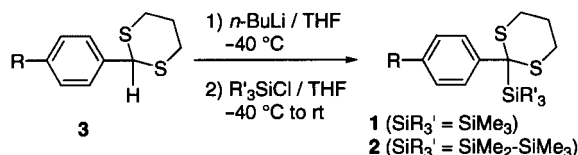


Table 1. Yields and UV spectral data of **1** and **2**

Compound	R	SiR' ₃	Yield / %	UV (hexane) λ _{max} /nm (ε)
1a ^a	H	SiMe ₃	63	230 (14800), 260 (2000)
1b	NC	SiMe ₃	58	244 (17300)
1c ^b	MeO	SiMe ₃	52	240 (20100), 280 (1700)
1d ^c	Me ₂ N	SiMe ₃	44	270 (24600), 309 (4000)
2a	H	Si ₂ Me ₅	58	242 (24300), 282 (1800)
2b	NC	Si ₂ Me ₅	54	257 (23400)
2c	MeO	Si ₂ Me ₅	51	241 (25500), 280 (4000)
2d	Me ₂ N	Si ₂ Me ₅	49	272 (28100), 310 (3000)

^a ref 2b. ^b ref 3a. ^c ref 3b

Figure 1 shows the UV-absorption spectra of **1a** and **2a**. Both compounds had a strong absorption band between 220–250 nm (La band) and a weak absorption band between 260–300 nm (Lb band). The UV spectra of **1** and **2** did not show any solvatochromism. On the La band, we noted that the wavelength of absorption maximum of disilane **2a** (242 nm) was much longer than that of monosilane **1a** (230 nm) and 2-

phenyl-1,3-dithiane (**3a**, 233 nm). Because such a red shift was not observed between benzyltrimethylsilane (**5**, 222 nm)⁵ and benzylpentamethyldisilane (**6**, 225 nm),⁵ we can conclude there is substantial interaction between the disilanyl group and the 2-phenyl-1,3-dithiane moiety. As shown in Table 1, the red-shift was significant not for the electron-donating aryl derivatives (**1c–2c** and **1d–2d**) but for the electron-withdrawing cyano derivatives (**1b–2b**). Therefore, the interaction would be homo-hyperconjugation between disilane and aryl moieties.

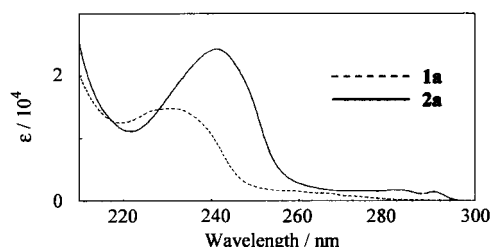


Figure 1. UV spectra of **1a** and **2a** in hexane.

Figure 2 shows ORTEP drawings for **2a** and **2d**.^{6,7} It reveals that the six-membered rings are in chair forms. The aryl groups are in axial positions and the silyl groups are in equatorial positions in both compounds. The bond lengths and angles of **2a** and **2d** were in the standard range. Although their absorption was different in solution, there were no specific structural changes between **2a** and **2d** in the solid state. Thus, the red-shifted absorptions mentioned above are responsible only for the electronic effects of substituents.

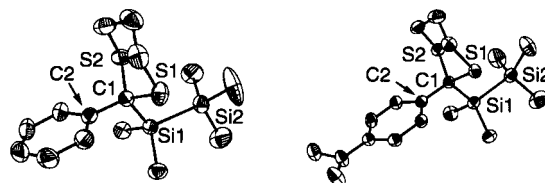

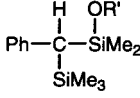


Figure 2. ORTEP drawings of **2a** (left) and **2d** (right). Thermal ellipsoids are drawn at a 30% probability level. Hydrogen atoms have been omitted for clarity.

As shown in Table 2, irradiation (254 nm) of **1a** in hexane and isopropyl alcohol gave benzyltrimethylsilane (**5**) in 7% and 34% yields, respectively. Thus, the 1,3-dithiane moiety is reduced to methylene under photochemical conditions. This photochemical reduction was accelerated by the silyl substituents because photolysis of 2-ethyl-2-phenyl-1,3-dithiane (**4a**) resulted in only 6% and 7% yields of *n*-propylbenzene (**7**) in hexane and isopropyl alcohol (Table 2), respectively.

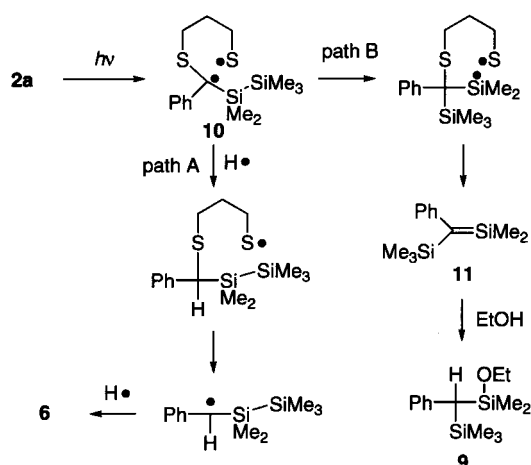
Table 2. Photolysis of dithiane derivatives in various solvents

	Solvent (Hexane or R'OH)	Products (Yield/%) ^a	
		PhCH ₂ R	
1a (R = SiMe ₃)	hexane	5 (7)	-
1a (R = SiMe ₃)	<i>i</i> -PrOH	5 (34)	-
2a (R = Si ₂ Me ₅)	hexane	6 (18)	-
2a (R = Si ₂ Me ₅)	<i>i</i> -PrOH	6 (28)	8 (7)
2a (R = Si ₂ Me ₅)	EtOH	6 (46)	9 (5)
4a (R = Et)	hexane	7 (6)	-
4a (R = Et)	<i>i</i> -PrOH	7 (7)	-

^aDetermined by GLC.

Interestingly, photolysis⁸ of **2a** in isopropyl alcohol gave phenyl(trimethylsilyl)(isopropoxydimethylsilyl)methane (**8**) in 7% yield along with a simple reduction product, benzylpentamethyldisilane (**6**, 28%). Photolysis of an ethanolic solution of **2a** produced ethoxy-derivative **9**¹⁰ and **6** in 5% and 46% yields, respectively, whereas photolysis of **2a** in hexane gave only **6** (18%) as a volatile product.

It is well-known that methyl migration of (trimethylsilyl)-carbene occurs easily,¹¹ however, no methyl-migrated compound was found in the photoproducts. Therefore, phenyl-(silyl)carbene [Ph(R₃Si)C:] was not considered as a common intermediate of the reaction. The results showed that silene is formed during the photolysis of **2a**, even though its yield is low. The plausible mechanism of the photoreaction of **2a** is shown in Scheme 2. The first step should be the cleavage of a C–S bond to give biradical **10**. The simple reduction to produce benzyl-disilane **6** would then take place through path A and would include intermolecular and/or intramolecular hydrogen abstraction. However, the 1,2-migration of trimethylsilyl moiety followed by a second C–S bond cleavage gives silene **11** as an intermediate (path B). Silene **11** reacts with alcohol to form the corresponding adduct. Formation of **9-d** in the photolysis of an EtOD solution of **2a** supports the existence of **11**. However, the *d*-content was only about 50% determined by GC–MS. The result showed other pathway should be included in the formation mechanism of **9**.

Scheme 2.

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References and Notes

- a) D. Seebach, *Synthesis*, **1969**, 17. b) B. T. Grobel and D. Seebach, *Synthesis*, **1977**, 357. c) R. K. Olsen and J. O. Currie, "The Chemistry of the Thiol Group," ed. by S. Patai, Wiley, New York (1974), p.519. d) H. Hauptman and W. F. Walter, *Chem. Rev.*, **62**, 347 (1962).
- a) A. G. Brook, J. M. Duff, P. F. Jones, and N. R. Davis, *J. Am. Chem. Soc.*, **18**, 431 (1967). b) E. J. Corey, D. Seebach, and R. Freedman, *J. Am. Chem. Soc.*, **18**, 434 (1967).
- a) A. F. Patrocínio, I. R. Correa, Jr., and P. J. S. Moran, *J. Chem. Soc., Perkin Trans. 1*, **21**, 3133 (1999). b) K. Yamamoto, A. Hayashi, S. Suzuki, and J. Tsuji, *Organometallics*, **6**, 979 (1987).
- Satisfactory elemental analyses and spectral data were obtained for compounds **1b** and **2a-d**. For example, **2a**: colorless crystals; mp 55.5 °C; ¹H NMR (CDCl₃, δ) 0.01 (s, 6H), 0.08 (s, 9H), 1.8–2.1 (m, 2H), 2.3–2.5 (m, 2H), 2.6–2.9 (m, 2H), 7.0–7.2 (m, 1H), 7.25–7.35 (m, 2H), 7.75–8.0 (m, 2H); ¹³C NMR (CDCl₃, δ) –5.8, –0.9, 25.2, 25.4, 47.5, 125.1, 128.3, 129.4, 141.0; ²⁹Si NMR (CDCl₃, δ) –17.8, –6.0; MS (70 eV) *m/z* 326 (M⁺); Anal. Calcd for C₁₅H₂₆S₂Si₂: C, 55.15; H, 8.02%. Found: C, 55.04; H, 7.99%. **2d**: pale yellow crystals; mp 101 °C; ¹H NMR (CDCl₃, δ) 0.01 (s, 6H), 0.10 (s, 9H), 1.8–2.1 (m, 2H), 2.3–2.5 (m, 2H), 2.7–3.05 (m, 2H), 2.94 (s, 6H), 6.72 (d, *J* = 9 Hz, 2H), 7.68 (d, *J* = 9 Hz, 2H); ¹³C NMR (CDCl₃, δ) –5.7, –0.8, 25.2, 25.4, 40.6, 47.0, 112.4, 128.3, 130.0, 148.1; ²⁹Si NMR (CDCl₃, δ) –18.1, –6.6; MS (70 eV) *m/z* 369 (M⁺); Anal. Calcd for C₁₇H₃₁NS₂Si₂: C, 55.22; H, 8.45; N, 3.79%. Found: C, 54.80; H, 8.20; N, 3.91%.
- H. Sakurai, M. Kira, and M. Ochiai, *Chem. Lett.*, **1972**, 87.
- Crystal data for **2a**: colorless prisms, C₁₅H₂₆S₂Si₂, monoclinic, space group P2₁/n, *a* = 14.525(2) Å, *b* = 9.0510(13) Å, *c* = 15.146(2) Å, β = 107.771(3)°, *V* = 1896.2(5) Å³, *Z* = 4, fw 326.66, *D*_{calcd} = 1.144 g/cm³, absorption coefficient = 0.395 mm^{–1}, F(000) = 704, Mo Kα, λ = 0.71073 Å, T = 296 K, Bruker AXS/CCD diffractometer, crystal size 0.1 × 0.1 × 0.5 mm³, 2θ_{max} = 50°, 9670 reflections collected, 3336 [R(int) = 0.0401] independent reflections, 172 parameters, GOF = 0.875, *R*₁ = 0.0427, *wR*₂ = 0.0945 for 1838 unique reflections observed (*I* > 2σ(*I*)) and *R*₁ = 0.0928, *wR*₂ = 0.1097 for all 3336 unique reflections. Selected lengths (Å) and bond angles (°): Si1–Si2 = 2.341(1), Si1–C1 = 1.925(3), Si1–C1 = 1.810(3), Si2–C1 = 1.818(3), C1–C2 = 1.526(4), C1–Si1–Si2 = 113.9(1), C2–C1–Si1 = 113.6(2), C2–C1–Si2 = 112.8(2), Si1–C1–Si2 = 109.8(1).
- Crystal data for **2d**: a pale yellow prisms, C₁₇H₂₇NS₂Si₂, monoclinic, space group P2₁/n, *a* = 9.1874(12) Å, *b* = 10.1539(14) Å, *c* = 22.852(3) Å, β = 92.283(2)°, *V* = 2130.2(5) Å³, *Z* = 4, fw 365.70, *D*_{calcd} = 1.140 g/cm³, Absorption coefficient = 0.360 mm^{–1}, F(000) = 784, Mo Kα, λ = 0.71073 Å, T = 296 K, Bruker AXS/CCD diffractometer, crystal size 0.1 × 0.3 × 0.5 mm³, 2θ_{max} = 50°, 10862 reflections collected, 3739 [R(int) = 0.0408] independent reflections, 199 parameters, GOF = 0.901, *R*₁ = 0.0470, *wR*₂ = 0.1029 for 2279 observed unique reflections (*I* > 2σ(*I*)) and *R*₁ = 0.0887, *wR*₂ = 0.1150 for all 3739 unique reflections. Si1–Si2 = 2.351(1), Si1–C1 = 1.926(3), Si1–C1 = 1.822(3), Si2–C1 = 1.829(3), C1–C2 = 1.520(4), C1–Si1–Si2 = 113.8(1), C2–C1–Si1 = 113.2(2), C2–C1–Si2 = 112.7(2), Si1–C1–Si2 = 109.2(2).
- Products **8** and **9** were isolated by gel permeation chromatography eluting with chloroform and characterized by ¹H, ¹³C, and ²⁹Si NMR, and MS spectroscopic data. The yields of **5–9** were determined by GLC, using decane as an internal standard.
- 8**: a colorless oil, ¹H NMR (CDCl₃, δ) 0.01 (s, 9H), 0.02 (s, 3H), 0.08 (s, 3H), 1.08 (d, *J* = 6 Hz, 3H), 1.11 (d, *J* = 6 Hz, 3H), 1.54 (s, 1H), 3.93 (sept, *J* = 6 Hz, 1H), 6.9–7.05 (m, 3H), 7.1–7.2 (m, 2H); ¹³C NMR (CDCl₃, δ) –0.21, –0.16, 0.3, 25.76, 25.81, 30.7, 65.0, 123.2, 127.9, 129.0, 142.2; ²⁹Si NMR (CDCl₃, δ) 1.5, 11.5; HRMS *m/z* found 265.1426, calcd for C₁₅H₂₈OSi₂–Me, 265.1443.
- N. Shimizu, C. Kinoshita, E. Osajima, F. Hayakawa, and Y. Tsuno, *Bull. Chem. Soc. Jpn.*, **64**, 3280 (1991).
- G. Maas, "The Chemistry of Organic Silicon Compounds Vol. 2," ed. by Z. Rappoport and Y. Apeloig, Wiley, New York (1998), p.703.