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

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A series of 2-silyl- and 2-disilanyl-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-(pentamethyldisilanyl)-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-disilanyl-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.

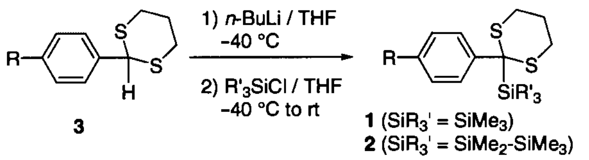


Table 1. Yields and UV spectral data of **1** and **2**

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_2N	$SiMe_3$	44	270 (24600), 309 (4000)
2a	H	Si_2Me_5	58	242 (24300), 282 (1800)
2b	NC	Si_2Me_5	54	257 (23400)
2c	MeO	Si_2Me_5	51	241 (25500), 280 (4000)
2d	Me_2N	Si_2Me_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.

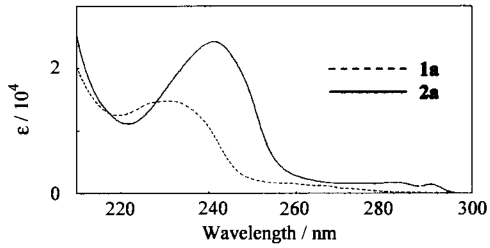


Figure 1. UV spectra of **1a** and **2a** in hexane.

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.

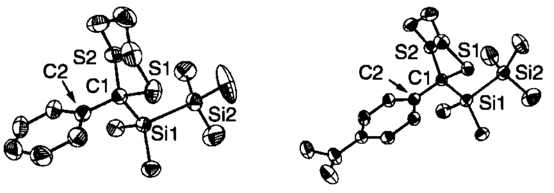
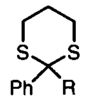
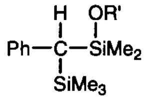


Figure 2. ORTEP drawings of **2a** (left) and **2d** (right). Thermal ellipsoids are drawn at a 30% probability level. Hydrogen atoms have been omitted for clarity.

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

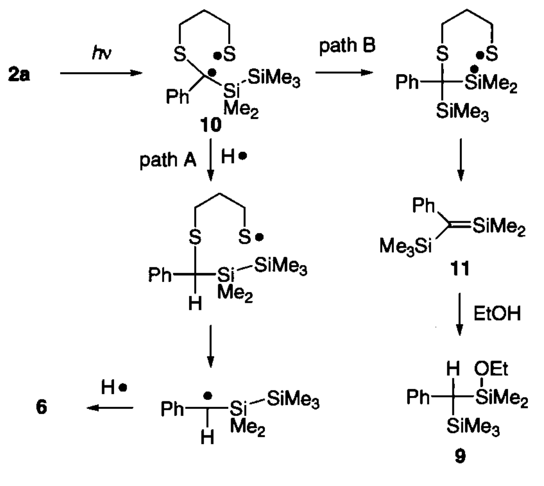
	Solvent (Hexane or R'OH)	Products (Yield/%)[a]	
		$PhCH_2R$	 $Ph-C(H)(SiMe_3)-SiMe_2(OR')$
1a (R = $SiMe_3$)	hexane	**5** (7)	-
1a (R = $SiMe_3$)	*i*-PrOH	**5** (34)	-
2a (R = Si_2Me_5)	hexane	**6** (18)	-
2a (R = Si_2Me_5)	*i*-PrOH	**6** (28)	**8** (7)
2a (R = Si_2Me_5)	EtOH	**6** (46)	**9** (5)
4a (R = Et)	hexane	**7** (6)	-
4a (R = Et)	*i*-PrOH	**7** (7)	-

[a]Determined by GLC.

Interestingly, photolysis[8] of **2a** in isopropyl alcohol gave phenyl(trimethylsilyl)(isopropoxydimethylsilyl)methane (**8**[9]) in 7% yield along with a simple reduction product, benzylpentamethyldisilane (**6**, 28%). Photolysis of an ethanol 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 [$Ph(R_3Si)C:$] 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 benzyldisilane **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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4 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 ($CDCl_3$, 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); ^{13}C NMR ($CDCl_3$, δ) –5.8, –0.9, 25.2, 25.4, 47.5, 125.1, 128.3, 129.4, 141.0; ^{29}Si NMR ($CDCl_3$, δ) –17.8, –6.0 ; MS (70 eV) *m/z* 326 (M^+); Anal. Calcd for $C_{15}H_{26}S_2Si_2$: C, 55.15; H, 8.02%. Found: C, 55.04; H, 7.99%. **2d**: pale yellow crystals; mp 101 °C; ^1H NMR ($CDCl_3$, 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); ^{13}C NMR ($CDCl_3$, δ) –5.7, –0.8, 25.2, 25.4, 40.6, 47.0, 112.4, 128.3, 130.0, 148.1; ^{29}Si NMR ($CDCl_3$, δ) –18.1, –6.6; MS (70 eV) *m/z* 369 (M^+); Anal. Calcd for $C_{17}H_{31}NS_2Si_2$: C, 55.22; H, 8.45; N, 3.79%. Found: C, 54.80; H, 8.20; N, 3.91%.

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6 Crystal data for **2a**: colorless prisms, $C_{15}H_{26}S_2Si_2$, monoclinic, space group $P2_1/n$, a = 14.525(2) Å, b = 9.0510(13) Å, c = 15.146(2) Å, β = 107.771(3)°, V = 1896.2(5) $Å^3$, Z = 4, fw 326.66, D_{calcd} = 1.144 g/cm^3, 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 mm^3, $2\theta_{max}$ = 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 ($I > 2\sigma(I)$) 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), S1–C1 = 1.810(3), S2–C1 = 1.818(3), C1–C2 = 1.526(4), C1–Si1–Si2 = 113.9(1), C2–C1–S1 = 113.6(2), C2–C1–S2 = 112.8(2), S1–C1–S2 = 109.8(1).

7 Crystal data for **2d**: a pale yellow prisms, $C_{17}H_{27}NS_2Si_2$, monoclinic, space group $P2_1/n$, a = 9.1874(12) Å, b = 10.1539(14) Å, c = 22.852(3) Å, β = 92.283(2)°, V = 2130.2(5) $Å^3$, Z = 4, fw 365.70, D_{calcd} = 1.140 g/cm^3, 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 mm^3, $2\theta_{max}$ = 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 ($I > 2\sigma(I)$) and R_1 = 0.0887, wR_2 = 0.1150 for all 3739 unique reflections. Si1–Si2 = 2.351(1), Si1–C1 = 1.926(3), S1–C1 = 1.822(3), S2–C1 = 1.829(3), C1–C2 = 1.520(4), C1–Si1–Si2 = 113.8(1), C2–C1–S1 = 113.2(2), C2–C1–S2 = 112.7(2), S1–C1–S2 = 109.2(2).

8 Products **8** and **9** were isolated by gel permeation chromatography eluting with chloroform and characterized by ^1H, ^{13}C, and ^{29}Si NMR, and MS spectroscopic data. The yields of **5–9** were determined by GLC, using decane as an internal standard.

9 **8**: a colorless oil, ^1H NMR ($CDCl_3$, 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, 3 H), 1.54 (s, 1H), 3.93 (sept, *J* = 6Hz, 1H), 6.9–7.05 (m, 3H), 7.1–7.2 (m, 2H); ^{13}C NMR ($CDCl_3$, δ) –0.21, –0.16, 0.3, 25.76, 25.81, 30.7, 65.0, 123.2, 127.9, 129.0, 142.2; ^{29}Si NMR ($CDCl_3$, δ) 1.5, 11.5; HRMS *m/z* found 265.1426, calcd for $C_{15}H_{28}OSi_2$–Me, 265.1443.

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