Molecular Structure and Photochemical Reactions of Trimethylsilylmethyl-Substituted Masked Disilene[1]

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(Trimethylsilylmethyl)trimethyldisilene was generated photochemically from 1-phenyl-7-trimethylsilylmethyl-7,8,8-trimethyl-7,8-disilabicyclo[2.2.2]octa-2,5-diene (masked disilene). UV spectrum and regioselectivity of the addition reaction of phenols to the disilene were discussed. The molecular structure of the masked disilene was also determined by single-crystal X-ray diffraction.

Masked disilenes play an important role in the chemistry of reactive disilenes[2,3] and polysilanes.[4] Facile 1,2-addition of alcohols to the Si=Si double bond is of particular interest as one of the fundamental reactions of disilenes.[3] The regioselectivity induced by the functional group bound to the Si=Si double bond is quite interesting for the understanding of the reaction mechanism. We have reported previously that the alcohol addition to $PhMeSi{=}SiMe_2$ is highly regioselective to form 1-alkoxy-2-phenyl-1,1,2-trimethyldisilane.[5] On the basis of the regio and diastereochemical results, we have concluded the involvement of the rate-determining nucleophilic step to form a four-membered intermediate where an incipient silyl anion is stabilized by phenyl group (Figure 1, **a**).

More recently, we have reported that alcohol addition reactions of $(t\text{-BuO})MeSi{=}SiMe_2$ and $(Et_2N)MeSi{=}SiMe_2$ proceed in an extremely highly regioselective fashion and the major direction of the addition is completely opposite to $PhMeSi{=}SiMe_2$,[2,6] the rate-determining proton transfer being proposed as the reaction mechanism to explain the regioselectivity (Figure 1, **b**). Apeloig and Nakash have reported recently an interesting crossover of the mechanism from nucleophilic to electrophilic in the addition of substituted phenols to tetramesityldisilene depending on the substituents.[7] However, their conclusion was based on the kinetics and no regiochemistry was reported. It is thus interesting to examine the reaction of disilene with a moderately electron releasing substituent because of the possible competition of both mechanisms.

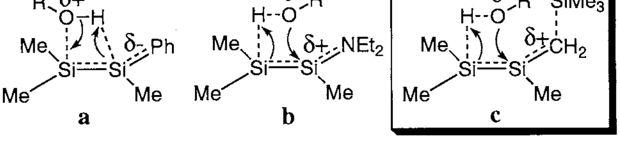
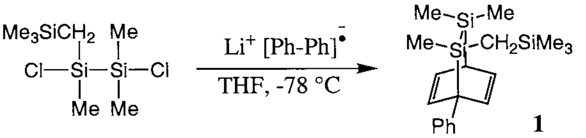


Figure 1. Intermediates of alcohol addition to disilenes via rate-determining nucleophilic step (**a**) or proton transfer (**b** and **c**).

In this paper, authors wish to report synthesis, molecular structure, and reactions of new trimethylsilylmethyl-substituted masked disilene, 1-phenyl-7-trimethylsilylmethyl-7,8,8-trimethyl-7,8-disilabicyclo[2.2.2]octa-2,5-diene (**1**). The substituent effect of the trimethylsilylmethyl (Me_3SiCH_2) group on the Si=Si double bond was estimated by UV spectrum of (trimethylsilylmethyl)trimethyldisilene, $(Me_3SiCH_2)MeSi{=}SiMe_2$ (**2**) generated by the photolysis of **1**.

Masked disilene (**1**) was prepared in 28% yield by the reaction of the corresponding 1,2-dichlorodisilane with lithium biphenylide in THF at -78 °C (Eq. 1).[8] The 1-phenyl-7,8-disilabicyclo[2.2.2]octa-2,5-diene derivatives are highly reactive, to serve not only as the precursors for the disilenes,[9] but also as good monomers of the highly ordered alternating polysilylene copolymers.[10] Regiospecific attack of nucleophiles to the 7-Si atom is one of the characteristic features in the anionic polymerization of masked disilenes. Then, its molecular structures are very interesting. Because **1** was obtained as colorless crystals, we have first characterized the molecular structure of 1-phenyl-7,8-disilabicyclo[2.2.2]octa-2,5-diene derivatives (Figure 2).[11]



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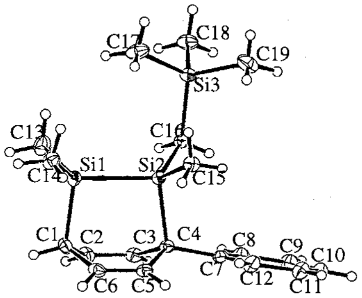


Figure 2. ORTEP drawing of **1**. Selected bond lengths (Å): Si1-Si2 2.344(6), Si1-C1 1.919(2), Si2-C4 1.960(2), C1-C2 1.509(3), C2-C3 1.324(3), C4-C7 1.519(3), C7-C8 1.398(3). selected bond angles (°): Si2-Si1-C1 96.3(1), Si1-Si2-C4 97.8(1), Si1-C1-C2 104.5(1), Si2-C4-C3 104.2(1), Si2-C4-C7 109.1(1), C1-C2-C3 119.5(2), C2-C1-C6 108.3(2), C3-C4-C5 107.5(1), C3-C4-C7 116.2(1), C8-C7-C12 116.8(2).

Around the bridging moiety, the Si(1)-Si(2) bond (2.344 Å) remains a regular Si-Si single bond length, but the Si-C bonds (av. 1.940 Å) and the Si-Si-C bond angles (av. 97.1 °) are significantly distorted from normal values, respectively. The 1,4-cyclohexadiene part is also remarkably bent to form a boat conformation where the dihedral angles of C(2)-C(1)-C(6)-C(5) and C(3)-C(4)-C(5)-C(6) are 38.3(2) ° and -38.3(2) °, respectively. These structural features around the bridging moiety were also observed in the parent masked disilene, 7,7,8,8-tetramethyl-7,8-disilabicyclo[2.2.2]octa-2,5-diene.[12] On the other hand, the C(7)-C(12) ring is an ordinary phenyl ring except for the C(8)-C(7)-C(12) angle. Interestingly, the bond angle of C(8)-C(7)-C(12) adjacent to the 1,4-cyclohexadiene is somewhat narrowed from a normal hexagonal structure (116.8 °). The phenyl group is coplanar to the diene moiety in the crystal structure but rotates freely as judged by NMR spectra. Thus the phenyl group protects sterically the Si(2) atom effectively against the nucleophilic attack.

Irradiation of **1** (254 nm) in 3-MP glass at 77 K gave a new UV absorption at 360 nm, which is the evidence for the formation of the disilene (**2**). The absorption maximum is 16 nm longer than that of $Me_2Si{=}SiMe_2$,[12] but somewhat shorter than other substituted trimethyldisilenes (Table 1).[2,5] This moderate red shift of **2** suggests that the substituent effect of the Me_3SiCH_2 group is smaller than phenyl, alkoxy and amino groups for the Si=Si double bond. Interestingly, a plot of $\Delta\nu$ (cm^{-1}) (except for $PhMeSi{=}SiMe_2$) against the σ_p^+ constants of the substituent groups gave a good linear relationship (Eq. 2).

Table 1. UV Absorption Maxima of $RMeSi{=}SiMe_2$

R	σ_p^+	λ_{max}/nm	$\Delta\nu$/cm^{-1a}
CH_3^{b}	-0.26^e	344	0
Me_3SiCH_2 (**2**)	-0.66^f	360	1290
t-BuO^c	-0.99^g	373	2260
Ph^d	-0.085^e	386	3160
Et_2N^c	-1.7^h	395	3750

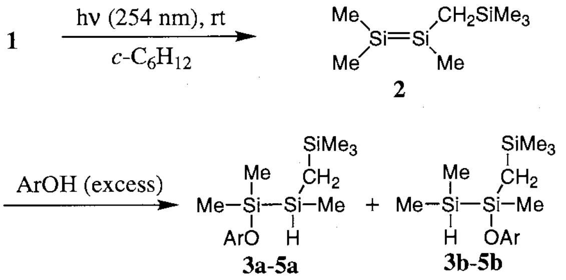
^{a} Difference of frequencies from that of tetramethyldisilene. ^{b} Ref.12. ^{c} Ref.2. ^{d} Ref.5. ^{e} Ref.13. ^{f} Ref.14. ^{g} Value of i-PrO. Ref.13. ^{h} Ref.15.

$$\Delta\nu\ (\mathrm{cm^{-1}}) = -5.0\times10^2 - 2.6\times10^3\ \sigma_p^+ \quad (r = -0.993) \qquad (2)$$

The exception of $PhMeSi{=}SiMe_2$ may be attributed to the difference in the substituent effect of the phenyl group in that the phenyl group is a π-conjugative whereas other groups are σ- (or n-) donors. In fact, the regiochemistry of alcohol addition is quite different for $PhMeSi{=}SiMe_2$ as compared with other donor-substituted disilenes (*vide infra*).

The relationship (Eq. 2) suggests that these electron-donating groups may facilitate the proton transfer in the alcohol addition where a cationic silicon should be stabilized corresponding to the values of σ_p^+ constants. In these cases, electrophilic rate determining step is dominant. Indeed, $(Et_2N)(t\text{-}BuO)MeSi\text{-}SiHMe_2$ was obtained exclusively in the reaction of $(Et_2N)MeSi{=}SiMe_2$ with t-butyl alcohol, whereas $(t\text{-}BuO)MeSi{=}SiMe_2$ gave $(t\text{-}BuO)(RO)MeSi\text{-}SiHMe_2$ and $(t\text{-}BuO)(H)MeSi\text{-}Si(RO)Me_2$ in a ratio of 93/7 with t-butyl alcohol and 98/2 with more acidic 2,6-dimethylphenol.[2,6] Although the rate-determining electrophilic proton transfer is overwhelming, the rate-determining nucleophilic alkoxy (phenoxy) oxygen attack cannot be excluded in the latter. Since the Brown-Okamoto's σ_p^+ constant of the Me_3SiCH_2 group is in between the methyl and alkoxy groups, the Me_3SiCH_2 group should exert a moderate electron-donating effect to the Si=Si double bond (Figure 1, **c**) and then both nucleophilic and electrophilic attack should compete each other. We have thus investigated the regioselectivity in the addition reaction of phenols to **2** (Eq. 3).

Irradiation of a c-C_6H_{12}/C_6H_5-OH solution of **1** gave a mixture of **3a**:**3b** (63:37). Predominant formation of **3a** suggests that the rate-determining nucleophilic step is important in the addition reaction. The reaction with more acidic phenol, 4-CF_3-C_6H_4-OH gave a mixture of **4a**:**4b** (58:42). The relative yield of **4b** increased in comparison with the case of C_6H_5-OH, indicating increased importance of the electrophilic process, although the nucleophilic process is still predominant. In the case of 2,6-$(CH_3)_2$-C_6H_3-OH, the relative yield of **5b** increased furthermore (**5a**:**5b** = 53:47). We explain the results as follows. The rate-determining nucleophilic addition should be subjected by stronger steric hindrance than the electrophilic process due to the two *ortho*-methyl groups. Then nucleophilic process was suppressed and electrophilic process became relatively important. Further works are in progress.



$$\mathbf{1} \xrightarrow[c\text{-}C_6H_{12}]{h\nu\ (254\ nm),\ rt} Me_2Si{=}Si(Me)CH_2SiMe_3\ \ \mathbf{2}$$

$$\xrightarrow{ArOH\ (excess)} Me(ArO)HSi\text{-}Si(H)(Me)CH_2SiMe_3\ \ \mathbf{3a\text{-}5a} + Me(H)_2Si\text{-}Si(OAr)(Me)CH_2SiMe_3\ \ \mathbf{3b\text{-}5b} \qquad (3)$$

2

3a-5a **3b-5b**

(3)

3: Ar = C_6H_5 **3a**:**3b** = 63:37
4: Ar = 4-$CF_3C_6H_4$ **4a**:**4b** = 58:42
5: Ar = 2,6-$(CH_3)_2C_6H_3$ **5a**:**5b** = 53:47

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References and Notes

1 Chemistry of Organosilicon Compounds. 356.
2 H. Sakurai, in "The Chemistry of Organic Silicon Compounds", S. Patai and Z. Rappoport, Eds.; Part 3, John Wiley & Sons, Chichester, UK, in press.
3 For a recent review on kinetically stabilized disilenes, see: R. Okazaki and R. West, *Adv. Organomet. Chem.*, **39**, 231 (1996).
4 H. Sakurai, in "Macromolecular Design of Polymeric Materials," K. Hatada, T. Kitayama, and O. Vogl, eds., Marcel Dekker, Inc., New York, 1997, chapt. 27.
5 A. Sekiguchi, I. Maruki, and H. Sakurai, *J. Am. Chem. Soc.*, **115**, 11460 (1993).
6 H. Sakurai, K. Sakamoto, and M. Yoshida, submitted.
7 Y. Apeloig and M. Nakash, *J. Am. Chem. Soc.*, **118**, 9798 (1996).
8 **1**: mp 88-89 °C; ^{1}H NMR ($CDCl_3$) δ -0.39 (d, 1H), -0.38 (d, 1H), -0.13 (s, 9H), -0.06 (s, 3H), 0.12 (s, 3H), 0.18 (s, 3H), 3.00 (t, 1H), 5.9 (m, 2H), 6.13 (d, 1H), 6.18 (d, 1H), 7.20-7.40 (m, 5H); ^{13}C NMR ($CDCl_3$) δ -3.22, -3.18, -2.6, -1.4, 1.3, 34.8, 48.1, 124.2, 125.4, 126.2, 126.6, 127.8, 128.1, 128.5, 142.2; ^{29}Si NMR ($CDCl_3$) δ -18.7, -16.3, 0.7; MS (70 eV), m/z (%): 342 (M^+, 2), 188 (75), 173 (100), 129 (35), 73 (80).
9 D. N. Roark and G. J. D. Peddle, *J. Am. Chem. Soc.*, **94**, 5837 (1972).
10 K. Sakamoto, K. Obata, H. Hirata, M. Nakajima, and H. Sakurai, *J. Am. Chem. Soc.*, **111**, 7641 (1989).
11 Crystal data for **1** (150 K): colorless crystals; formula $Si_3C_{19}H_{30}$, fw = 342.7; monoclinic, space group $P2_1/n$ (# 14), a = 9.536(2) Å, b = 13.604(1) Å, c = 16.253(2) Å; β = 103.66(1)°, V = 2048.99(6) Å^3, Z = 4, D_{calc} = 1.111 g/cm^3. A total of reflection 3615, 3055 (I > 3.00σ(I)) were used in refinement: R = 0.031, R_w = 0.034. The reflection intensities were collected on a Rigaku AFC5R diffractometer with a rotating anode (45 kV, 200 mA) using graphite monochromated CuKα (λ = 1.54178 Å). All calculations were performed using the teXsan crystallographic software package of Molecular Structure Corporation.
12 A. Sekiguchi, I. Maruki, K. Ebata, C. Kabuto, and H. Sakurai, *J. Chem. Soc., Chem. Commun*, **1991**, 341.
13 C. G. Swain and E. C. Lupton, Jr., *J. Am. Chem. Soc.*, **90**, 4328 (1968).
14 W. Hanstein, H. J. Berwin, and T. G. Traylor, *J. Am. Chem. Soc.*, **92**, 829 (1970).
15 H. C. Brown and Y. Okamoto, *J. Am. Chem. Soc.*, **80**, 4979 (1958).