Tetrahedron Letters, Vol.22, No.25, pp 2417 - 2420, 1981
Printed in Great Britain

0040-4039/81/252417-04$02.00/0

PHOTOCHEMICAL GENERATION OF TETRAMETHYLDISILENE AND PHOTOINDUCED 1,2-SILYL-MIGRATION[1]

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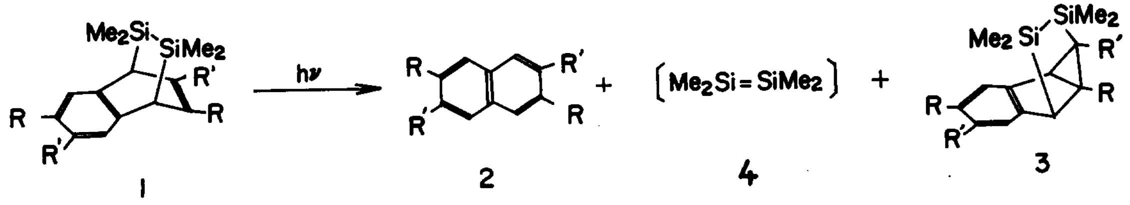
Summary: Described herein is the first clear evidence of the photochemical generation of tetramethyldisilene which can be efficiently trapped by dienes. An intriguing 1,2-photo-induced silyl migration is also reported.

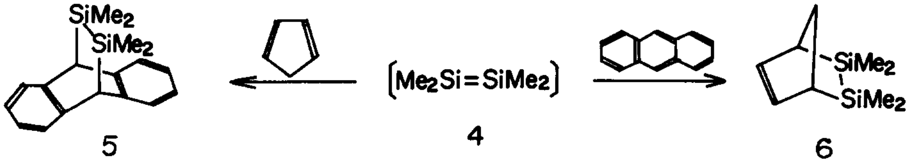
Roak and Peddle have demonstrated for the first time the transient existence of reactive tetramethyldisilene, $Me_2Si=SiMe_2$, produced by thermolysis of 7,7,8,8- tetramethyl-7,8-disilabicyclo[2.2.2]octa-2,5-diene derivatives.[2] In a recent publication,[3] we have proved the geometrical isomerism of thermally generated cis- and trans-1,2-dimethyl-1,2-diphenyldisilene which demonstrates clearly the double bond nature of disilene. Dimerization of silylenes to the corresponding disilene has also demonstrated.[4] However, there has been no report on the photochemical generation of disilene, which could be used for the low-temperature matrix isolation. We report the first clear photochemical reaction generating disilene[5] together with photo-induced 1,2-silyl migration.

Photolysis of 2,3-benzo-7,7,8,8-tetramethyl-7,8-disilabicyclo[2.2.2]octa-2,5-diene (1a)[2] in n-hexane through a quartz wall with a low pressure mercury lamp under Argon resulted in the formation of naphthalene (2a) (30%) and a rearranged product (3a) (20%).



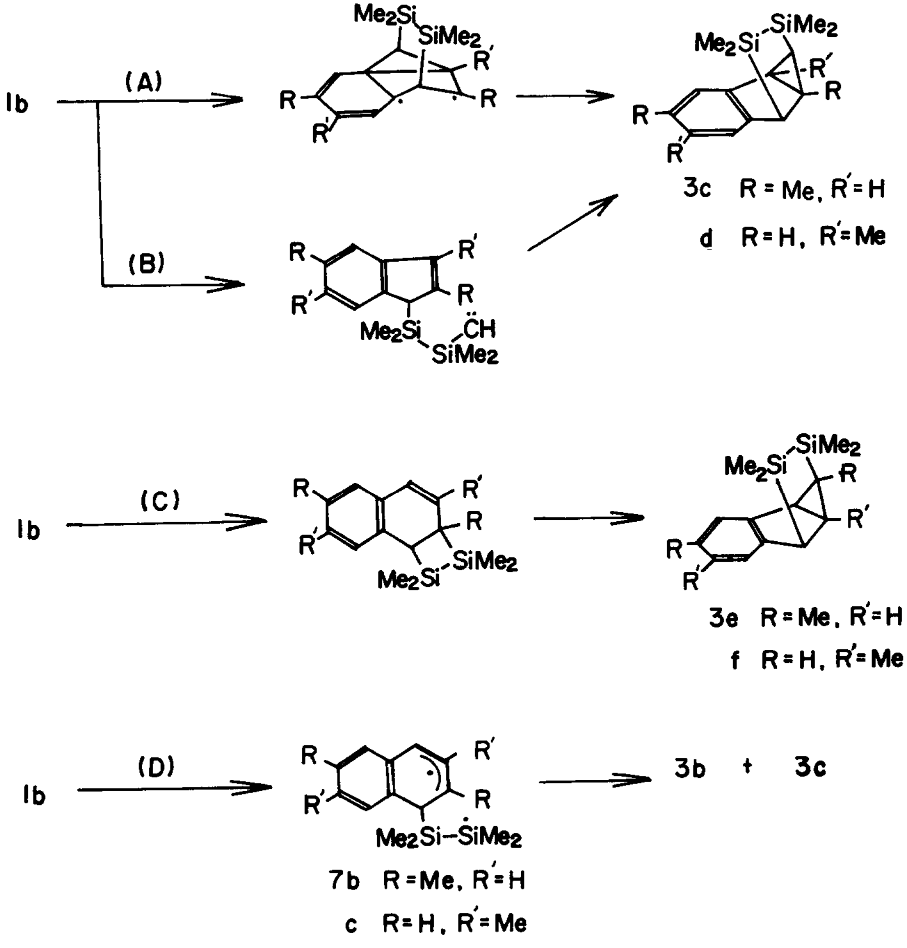
a. R=R'=H ; b. R=H, R'=Me ; c. R=Me, R'=H

This fact indicates that photolysis of 1a leads to the formation of tetramethyldisilene (4), which has been evidenced by the following trapping experiments. Irradiation of 1a in the presence of anthracene in benzene gave 5[2,3] in 20% yield. Photolysis of 1a in cyclopentadiene also gave an expected 5,5,6,6-tetramethyl-5,6-disilabicyclo[2.2.1]hept-2-ene (6).[6] Photolysis of a disilene generator (1b)[7] derived from 2,7-dimethylnaphthalene appeared to afford 4 more efficiently than 1a, since the adduct 5 was obtained in 52% yield.



5 4 6

The structure of 3a was assigned to 3,4-benzo-6,6,7,7-tetramethyl-6,7-disilatricyclo[3.3.0.0^{2,8}]octane by NMR and mass spectra.[8] Four possible reaction pathways can be described for this isomerization: (A) di-π-methane rearrangement;[9] (B) carbene mechanism;[10] (C) 1,3-silyl migration followed by ring opening and [2+4] ring closure;[11] and (D) 1,2-silyl migration followed by cyclization. The following scheme illustrates these four mechanisms with possible methyl-substitution patterns when products are derived from 1b.



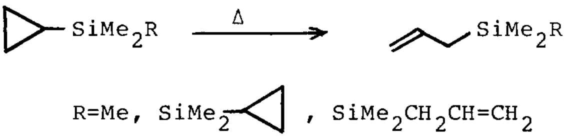
3c R = Me, R' = H
d R = H, R' = Me

3e R = Me, R' = H
f R = H, R' = Me

7b R = Me, R' = H
c R = H, R' = Me

Irradiation of 1b gave an isomeric mixture of 3b and 3c (1:2) in 15% yield together with 1,3-dimethylnaphthalene (75%).[12,13] The result can be accounted for only by the path D. Thus, both paths A and B may give the product 3c, but the combination of products 3b and 3c can arise only from the path D. Therefore, 1,2-silyl migration in the allylsilane system is responsible for the photoinduced isomerization.[14,15]

Previously, we have reported thermal isomerization of cyclopropyl-substituted silanes,[16] which should be a formally reverse process of the present photo-induced 1,2-silyl migration. Indeed, 3a isomerized to 1a on heating at ca.200°.



Acknowledgment: We thank Toshiba Silicone Co., Ltd., for a gift of chlorosilanes. The work was supported in part by the Takeda Science Foundation.

References and Notes

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(2) D. N. Roak and G. J. D. Peddle, J. Am. Chem. Soc., 94, 5837 (1972).

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(4) Y. Nakadaira, T. Kobayashi, T. Otsuka, and H. Sakurai, J. Am. Chem. Soc., 101, 486 (1979).

(5) Recently, generation of a disilene has been implied in the photolysis of octamethyl-1,2-disilacyclobutane by I. M. T. Davidson, N. A. Ostah, D. Seyferth, and D. P. Duncan, J. Organometal. Chem., 187, 297 (1980).

(6) 6, MS m/e M^+ 182(14), 116(100); uv λ_{max} (n-hexane) 210 nm (logε=4.08); NMR (CCl_4)δ, 0.20(s, 6H, SiMe), 0.37(s, 6H, SiMe), 1.79(ddd, 2H, $J_{1,7a}$=10.0, $J_{1,2}$=1.5, $J_{1,7b}$=0.5Hz, H_1), 2.26(m, 1H, $J_{7a,7b}$=6.0, $J_{1,7b}$=0.5, $J_{2,7b}$=0.5Hz, H_{7b}), 2.36(dt, 1H, $J_{1,7a}$=10.0, $J_{7a,b}$=6.0Hz, H_{7a}), 5.91(dd, 2H, $J_{1,2}$=1.5, $J_{2,7b}$=0.5Hz, H_2).

(7) 1b: mp 98.0-99.5°C; MS m/e (rel intensity), M^+ 272(19), 116(100); NMR (CCl_4)δ, -0.20(s, 6H, SiMe), 0.12(s, 3H, SiMe), 0.14(s, 3H, SiMe), 1.83(d, 3H, J=1.5Hz, MeC=), 2.27(s, 3H, ArMe), 3.03(s, 1H, CH), 3.10(d, 1H, J=6.0Hz, CH), 5.56(dq, 1H, J=6.0, 1,5Hz, HC=), 6.75(m, 3H, ArH).

(8) 3a: a colorless oil; n_D^{20}=1.5718; MS m/e (rel intensity) M^+ 244(5), 116(100); NMR(CCl_4)δ, -0.68(s, 3H, SiMe), 0.18(s, 3H, SiMe), 0.23(s, 3H, SiMe), 0.24 (s, 3H, SiMe), 0.37(dd, 1H, J=9.0, 7.8Hz, H_8), 2.54(dt, 1H, J=6.2, 7.8Hz, H_1), 2.80(dd, 1H, J=9.0, 7.8Hz, H_2), 2.84(d, 1H, J=6.2Hz, H_5), 6.9(m, 3H, ArH), 7.15(m, 1H, ArH).

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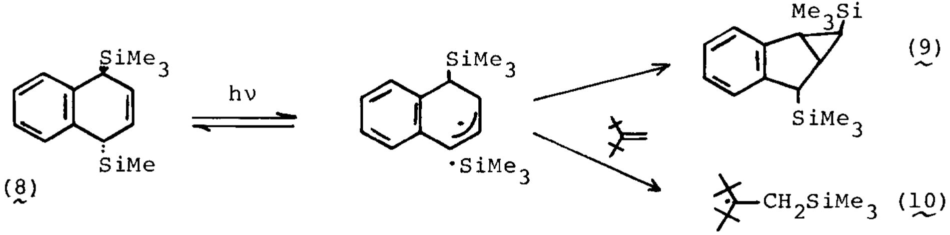
(12) Isomeric mixture of 3b and 3c: colorless oil; MS m/e (rel intensity), M^+ 272(77), 116(100). 3c: NMR(CCl_4)δ, -0.62(s, 3H, Si-Me), 0.21(s, 3H, Si-Me), 0.25(s, 3H, SiMe), 0.30(s, 3H, SiMe), 1.51(s, 3H, C-Me), 2.28(s, 3H, Ar-Me), 0.30(d, 1H, J=9.0Hz, H_8), 2.45(d, 1H, J=9.0Hz, H_2), 2.63(s, 1H, H_5), 6.7 (m, 2H, ArH), 6.98(s, 1H, $H_{1'}$). 3b: NMR(CCl_4)δ, -0.62(s, 3H, SiMe), 0.19 (s, 3H, SiMe), 0.25(s, 3H, SiMe), 0.28(s, 3H, SiMe), 1.21(s, 3H, C-Me), 2.28(s, 3H, ArMe), 2.11(t, 1H, J=6.5Hz, H_1), 2.39(d, 1H, J=6.5Hz, H_2), 2.61(d, 1H, J=6.5Hz, H_5), 6.7(m, 2H, ArH), 7.06(d, 1H, J=8.0Hz, $H_{1'}$).

(13) The methyl substitution patterns of 3b and 3c are based on the NMR evidence. Thus, in 3b the two signals due to H_2 and $H_{1'}$ appear as a doublet at 2.45 ppm and a singlet at 6.98 ppm, respectively, and NOE is observed between these two signals. In 3c, the most down-field signal due to $H_{1'}$ appears as a doublet at 7.06 ppm and because of a lack of the H_8 signal, three proton signals due to H_1, H_2, and H_5 are all observed separately with proper splittings.

(14) This does not necessarily mean a stepwise process. Concerted (2σa + 2πa) path will give formally the same result. However, preferential formation of 3c to 3b in the 1,2-silyl migration may be rationalized in terms of the relative stability of the possible diradical intermediates 7b and 7c.

(15) We strongly give support to the free-radical mechanism for the 1,2-silyl migration. A reason is the relative ratio of 3b to 3c. The second reason is the findings that trans-1,4-bis(trimethylsilyl)-1,4-dihydronaphthalene (8) gave a photo-product (9) similar to 3 and during the photolysis the trimethylsilyl radical was trapped by 1,1-di-t-butylethylene to give a relatively long-lived radical (10). Details will be reported in the due course with the result of the cis isomer of 8.



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(Received in Japan 28 March 1981)