

PHOTOCHEMISTRY OF 1,4-DISILYLATED DIHYDRONAPHTHALENES¹

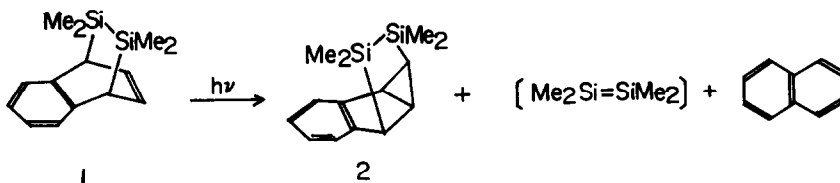
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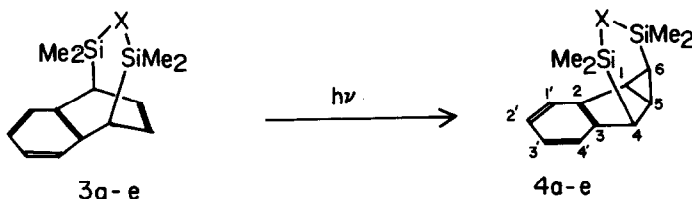
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Summary: Five 1,4-dihydronaphthalene derivatives bridged by a $-\text{SiMe}_2\text{XSiMe}_2-$ group ($\text{X}=\text{O}, \text{CH}_2, \text{CH}_2\text{CH}_2, \text{CH}_2\text{CH}_2\text{CH}_2, \text{SiMe}_2$) at 1,4-position were photolyzed to give isomers due to 1,2-silyl migration.

In a previous paper,² we have described the first photochemical 1,2-silyl migration together with generation of a disilene intermediate from 1.



Encouraged by this observation, we have investigated photochemical reactions of variously bridged 1,4-dihydronaphthalene derivatives (3), and have found that similar photochemical isomerization occurs very efficiently.

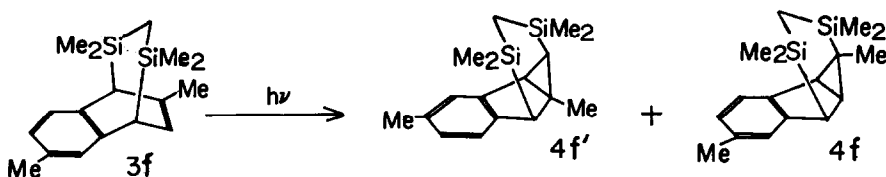


a, $\text{X}=\text{O}$; b, $\text{X}=\text{CH}_2$; c, $\text{X}=(\text{CH}_2)_2$; d, $\text{X}=(\text{CH}_2)_3$; e, $\text{X}=\text{SiMe}_2$.

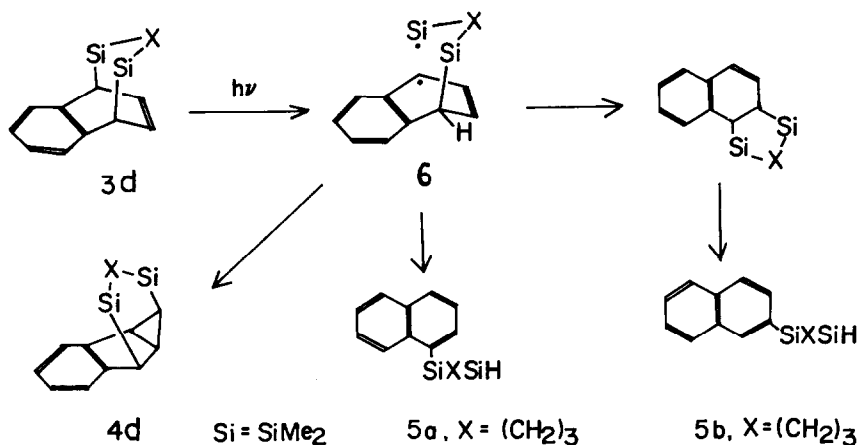
One interesting possibility that we have initially anticipated in the photochemistry of 3 was decomposition of 3 accompanied by the generation of di-radical and/or small-ring reactive intermediates, but no such decomposition to yield naphthalene was observed. Instead, irradiation of 3a,³ 3b,⁴ and 3c⁵ in n-hexane with a medium pressure mercury lamp through a quartz wall under argon

atmosphere afforded tricyclic compounds 4a, 4b, and 4c in 67, 58, and 52% yield, respectively. Table 1 lists the physical properties of the photo-products which are those expected from the photo-induced 1,2-silyl migration.

By the same labeling experiments described in the previous paper,² the 1,2-silyl migration was proved for 3b by the photolysis of 3f that gave two photo-products 4f' and 4f in 39 and 16% yield, respectively. The formation of these two products are only compatible with 1,2-silyl migration mechanism.²

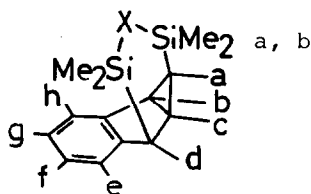


Interestingly, in the case of 3d⁶ containing a trimethylene bridge gave hydrosilanes 5a and 5b in 19 and 20% yield, respectively, along with the expected isomerization product 4d (12%). These hydrosilanes are presumed to arise from biradical intermediates such as 6. The hydrosilanes were identified with authentic samples prepared by the reaction with 1- and 2-naphthyl lithium with 1,3-bis(chlorodimethylsilyl)propane in ether followed by reduction with lithium aluminum hydride.⁷



On irradiation, 3e with a trisilanylene bridge afforded a new product 7 containing a hydroazulene ring in 23% yield along with 4e (23% yield). The structure of 7 was assigned on the basis of its spectroscopic properties coupled with the fact that it gave an azulene 8 upon exposure to air.⁸

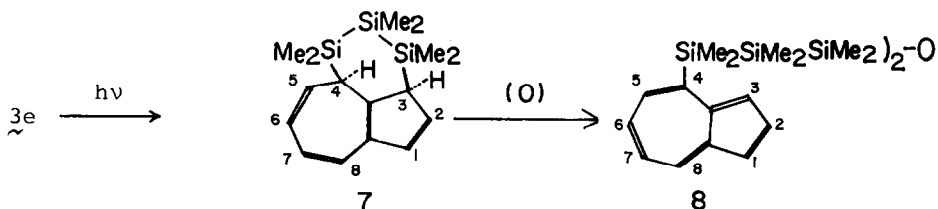
Table 1. Physical and Spectroscopic
Data of Photo-Products



- 4a (X=O): mp 43.5–45.5; NMR(CCl₄, δ ppm) -0.70(s, 3H, Si-CH₃), 0.05(t, 1H, J_{a-b}=J_{a-c}=8.5Hz, H_a), 0.15(s, 3H, Si-CH₃), 0.31(s, 3H, Si-CH₃), 0.36(s, 3H, Si-CH₃), 2.44(ddd, 1H, J_{a-c}=8.5, J_{b-c}=5.8, J_{c-d}=7.0Hz, H_c), 2.60(d, 1H, J_{c-d}=7.0Hz, H_d), 2.69(dd, 1H, J_{a-b}=8.5, J_{b-c}=5.8Hz, H_b), 7.0(m, 3H, Ar-H), 7.2(m, 1H, Ar-H); IR(CCl₄, cm⁻¹) 1250(Si-CH₃), 985(Si-O-Si); UV(n-hexane, λ_{max} nm (logε)) 273.5(3.12), 281.0(3.18); MS (m/e) M⁺, 260(26), 132(45), 117(100).
- 4b (X=CH₂): an oil; n_D²³=1.5481; NMR(CCl₄, δ ppm) -0.94(d, 1H, J_{HCH}=13.5Hz, CH₂), -0.49(d, 1H, J_{HCH}=13.5Hz, CH₂), -0.41(s, 3H, Si-CH₃), -0.04(t, 1H, J_{a-b}=J_{a-c}=9.0Hz, H_a), 0.14(s, 3H, Si-CH₃), 0.34(s, 3H, Si-CH₃), 0.35(s, 3H, Si-CH₃), 2.30(ddd, 1H, J_{a-c}=9.0, J_{b-c}=6.0, J_{c-d}=7.0Hz, H_c), 2.57(dd, 1H, J_{a-b}=9.0, J_{b-c}=6.0, Hz, H_b), 2.61(d, 1H, J_{c-d}=7.0Hz, H_d), 6.9(m, 3H, Ar-H), 7.2(m, 1H, Ar-H); IR(neat, cm⁻¹) 1245(Si-CH₃); UV(n-hexane, λ_{max} nm (logε)), 275.5(3.95), 283(3.17); MS (m/e) M⁺, 258(11), 130(100).
- 4c (X=CH₂CH₂): an oil; NMR(CCl₄, δ ppm) -0.84(s, 3H, Si-CH₃), -0.03(s, 3H, Si-CH₃), 0.06(dd, 1H, J_{a-b}=8.3Hz, J_{a-c}=9.0Hz, H_a), 0.0–1.0(m, 4H, -CH₂CH₂-), 0.25(s, 3H, Si-CH₃), 0.27(s, 3H, Si-CH₃), 2.18(ddd, 1H, J_{a-c}=9.0Hz, J_{c-d}=6.5Hz, J_{b-c}=5.6Hz, H_c), 2.78(dd, 1H, J_{a-b}=8.3Hz, J_{b-c}=6.5Hz, H_b), 2.83(d, 1H, J_{c-d}=6.5Hz, H_d), 7.3(m, 4H, Ar-H).
- 4d (X=CH₂CH₂CH₂): mp 70.0–71.0°; NMR(CCl₄, δ ppm) -0.34(s, 3H, Si-CH₃), 0.05(s, 3H, Si-CH₃), 0.05(dd, 1H, J_{a-b}=8.5, J_{a-c}=9.0Hz, H_a), 0.20(s, 3H, Si-CH₃), 0.45(s, 3H, Si-CH₃), 0.5–1.9(m, 6H, CH₂), 2.22(dt, 1H, J_{a-c}=9.0, J_{b-c}=7.0Hz, H_c), 2.62(dd, 1H, J_{a-b}=8.5, J_{b-c}=7.0Hz, H_b), 2.87(d, 1H, J_{c-d}=7.0Hz, H_d), 7.03(m, 3H, Ar-H), 7.28(m, 1H, Ar-H); IR(KBr, cm⁻¹) 1240(Si-CH₃); UV(n-hexane, λ_{max} nm (logε)) 275(3.00), 282.5(3.01); MS (m/e) M⁺, 286, 158(100).
- 4e (X=SiMe₂SiMe₂SiMe₂): an oil; NMR(CCl₄, δ ppm) -0.47(s, 3H, Si-CH₃), -0.42(s, 3H, Si-CH₃), 0.02(s, 3H, Si-CH₃), 0.02(t, 1H, J_{a-b}=J_{a-c}=8.8Hz, H_a), 0.11(s, 3H, Si-CH₃), 0.29(s, 3H, Si-CH₃), 0.41(s, 3H, Si-CH₃), 2.20(ddd, 1H, J_{a-c}=8.8, J_{b-c}=6.0, J_{c-d}=0.3Hz, H_c), 2.64(dd, 1H, J_{a-b}=8.8, J_{b-c}=6.0Hz, H_b), 2.75(d, 1H, J_{c-d}=6.3Hz, H_d), 6.9(m, 3H, Ar-H), 7.1(m, 1H, Ar-H); IR(neat, cm⁻¹) 1240(Si-CH₃); MS (m/e) M⁺, 302(5), 174(100).
- 4f (X=CH₂, a=f=Me): an oil; NMR(CCl₄, δ ppm) -0.92(d, 1H, J_{HCH}=13.5Hz, CH₂), -0.48(d, 1H, J_{HCH}=13.5Hz, CH₂), -0.24(s, 3H, Si-CH₃), 0.18(s, 3H, Si-CH₃), 0.36(s, 3H, Si-CH₃), 0.40(s, 3H, Si-CH₃), 1.09(s, 3H, Me_a), 2.00(t, 1H, J_{b-c}=J_{c-d}=6.5Hz, H_c), 2.22(d, 1H, J_{b-c}=6.5Hz, H_b), 2.39(s, 3H, Me_f), 2.70(d, 1H, J_{c-d}=6.5Hz, H_d), 6.8(m, 2H, H_e+H_g), 7.15(d, 1H, J_{g-h}=8.0Hz, H_h).
- 4f' (X=CH₂, c=g=Me): an oil; NMR(CCl₄, δ ppm) -0.92(d, 1H, J_{HCH}=13.5Hz, CH₂), -0.52(d, 1H, J_{HCH}=13.5Hz, CH₂), -0.52(d, 1H, J_{HCH}=13.5Hz, CH₂), 0.29(s, 3H, Si-CH₃), -0.02(d, 1H, J_{a-b}=9.0Hz, H_a), 0.18(s, 2H, Si-CH₃), 0.36(s, 3H, Si-CH₃), 0.40(s, 3H, Si-CH₃), 1.55(s, 3H, Me_c), 2.28(d, 1H, J_{a-b}=9.0Hz, H_b), 2.39(s, 3H, Me_g), 2.46(s, 1H, H_d), 6.8(m, 2H, H_e+H_f), 7.06(s, 1H, H_h); NOE (10%) between H_h and H_b was observed.

^a a–h stand for H, unless otherwise stated.

^b Correct elemental analyses were obtained for all compound.



The mechanism of the formation of 7 and the reason why only 3e gave this sort of product are not clear at this moment. The study on the mechanism of this novel photo-rearrangement is under way.

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References and Notes

- (1) Chemistry of Organosilicon Compounds, 148.
- (2) Y. Nakadaira, T. Otsuka, and H. Sakurai, *Tetrahedron Lett.*, accompanied paper.
- (3) T. J. Barton and J. A. Kilgour, *J. Am. Chem. Soc.*, **98**, 7746 (1976).
- (4) 3b; mp 79.5–81.0°C; NMR(CCl₄, δ ppm) -0.55(d, 1H), -0.33(d, 1H), -0.08(s, 6H), 0.13(s, 6H), 2.78(m, 2H), 5.93(m, 2H), 6.96(m, 4H). 3b was prepared by the reaction of lithium naphthalene with bis(dimethylchlorosilyl)methane in diglyme-THF.
- (5) R. Calas and J. Dunogués, *C. R. Acad. Sci., Ser. C*, 272, 554 (1971).
- (6) 3d; an oil, n_D^{16} =1.5656; NMR(CCl₄, δ ppm) 0.13(s, 6H), 0.18(s, 6H), 0.5(m, 4H), 1.4(m, 2H), 3.03(m, 2H), 5.77(m, 2H), 6.92(m, 4H).
- (7) 5a; an oil, bp 101–107°C/0.17 mmHg. NMR(CCl₄, δ ppm) 0.12(d, 6H), 0.58(s, 6H), 0.5–1.8(m, 6H), 3.98(m, 1H), 7.3–8.2(m, 7H); IR(neat, cm⁻¹) 2080(Si-H). 5b; an oil, n_D^{16} =1.5528; bp 105°C/0.2 mmHg; NMR(CCl₄, δ ppm), 0.21(d, 6H), 0.52(s, 6H), 0.7–1.9(m, 6H), 4.05(m, 1H), 7.3–8.2(m, 7H); IR(neat, cm⁻¹) 2070(Si-H).
- (8) 7; mp 75.0–77.0°C; NMR(CCl₄, δ ppm) -0.28(s, 3H), -0.10(s, 3H), 0.15(s, 6H), 0.22(s, 3H), 0.27(s, 3H), 2.89(bs, 1H, H₃), 2.91(dd, 1H, J_{4,6}=1.8, J_{4,5}=4.5Hz, H₄), 4.77(dd, 1H, J_{5,6}=9.0, J_{4,5}=4.5Hz, H₅), 5.84(ddd, 1H, J_{6,7}=5.5, J_{5,6}=9.0, J_{4,6}=1.8Hz, H₆), 5.87(m, 2H, H₁ and H₂), 6.24(dd, 1H, J_{7,8}=11.0, J_{6,7}=5.5Hz, H₇), 6.58(d, 1H, J_{7,8}=11.0Hz, H₈). 8; a blue solid; NMR(CDCl₃, δ ppm) -0.09(s, 12H), 0.04(s, 12H), 0.58(s, 12H), 7.12(dd, 1H, J_{6,7}=10.0, J_{7,8}=9.5Hz, H₇), 7.33(d, 1H, J_{5,6}=10.0Hz, H₅), 7.37(d, 1H, J_{2,3}=4.0Hz, H₃), 7.47(d, 1H, J_{1,2}=4.0Hz, H₁), 7.52(t, 1H, J_{5,6}=J_{6,7}=10.0Hz, H₆), 7.87(t, 1H, J_{1,2}=J_{2,3}=4.0Hz, H₂), 8.32(d, 1H, J_{7,8}=9.5Hz, H₈); UV(λ_{max} nm (logε)) 250(4.54), 283(4.80), 349(3.88), 363(3.46), 566(2.85), 592(2.92), 614(2.88), 646(2.83).

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