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Photochemistry of Disilanylcyclohexenones. ESR Detection of a Novel Silatrimethylenemethane Intermediate†,1)

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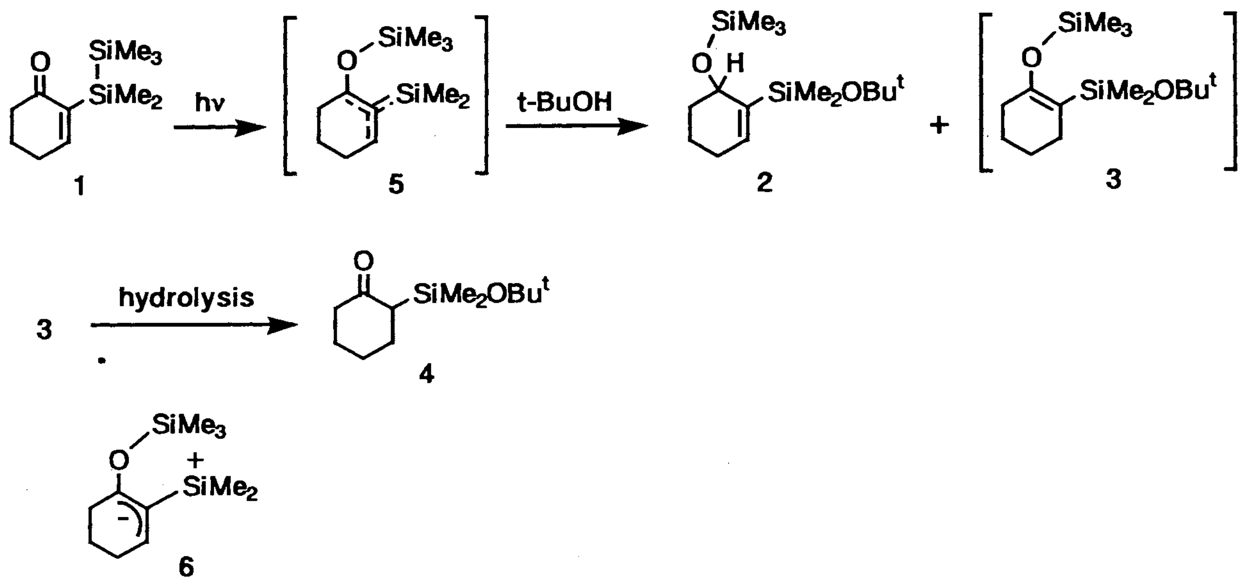
Irradiation of 2-pentamethyldisilanyl-2-cyclohexenone in a *t*-butyl alcohol-benzene mixed solvent gave 2-*t*-butoxydimethylsilyl-3-trimethylsilyloxycyclohexene and 1-trimethylsilyloxy-2-(*t*-butoxydimethylsilyl)cyclohexene. Silatrimethylenemethane was detected by UV and ESR spectra. Irradiation of 2-pentamethyldisilanyl-3-methyl-2-cyclohexenone afforded 1-trimethylsilyloxy-3-methyl-3-(*t*-butyldimethylsilyl)hexene through methylenesilacyclopropane.

Photochemical reactions of organosilicon compounds involving intramolecular charge transfer interactions have received considerable attention. In a recent paper,2) we reported photochemistry of disilanylbenzoquinones as an example of such a system involving the formation of sila-*m*-quinomethane intermediates which were trapped by alcohols and ketones. Spectroscopic evidence of the formation of the sila-*m*-quinomethane intermediates was also indicated. Herein we report the photochemical reactions of 2-pentamethyldisilanyl-2-cyclohexenones in which both electron-donating (Si-Si) and electron-accepting (enone) groups are connected directly. A silatrimethylenemethane intermediate is postulated and detected by UV and ESR spectra.



Scheme 1.

[†] Dedicated to celebrate 80th birthday of Professor Emeritus Osamu Simamura of The University of Tokyo.

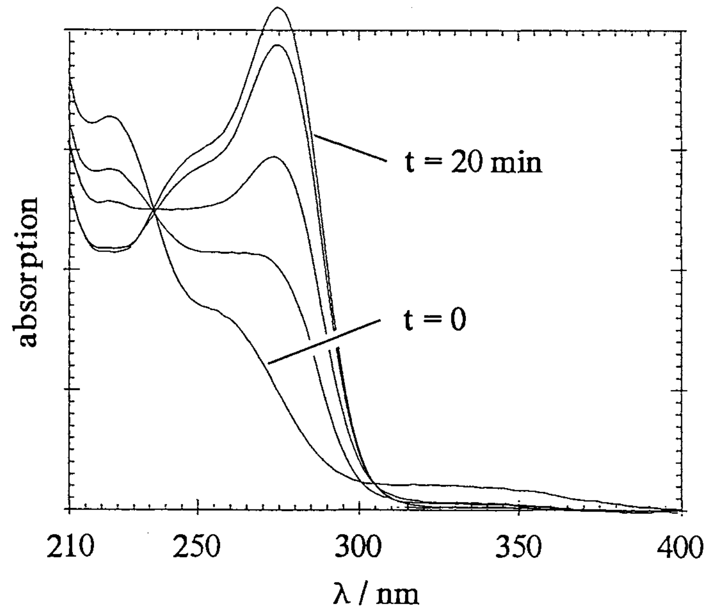


Fig. 1. UV spectral change during the reaction of **1** in 3–MP matrix at 77 K. Time intervals are 5 min.

2–Pentamethyldisilanyl–2–cyclohexenone (**1**)3) has UV maxima at 258 (ε 3500) and 350 (ε sh 100) nm. Irradiation of **1** with a light of wave length longer than 300 nm in a mixed *t*–butyl alcohol–benzene solvent gave two adducts, **2** (15%) and **4** (15%).4) Compound **3** may be the primary product but extremely hygroscopic and identified as a hydrolysis product **4**.

A 3–MP matrix of **1** was irradiated ($\lambda>300$ nm) at 77 K. As shown in Fig. 1, a new strong peak centered at 274 nm appeared along the progress of the reaction. By annealing the matrix, the peak disappeared.

Photolysis of **1** in a 3–MP matrix containing a small amount of *t*–butyl alcohol at 77 K showed a similar spectral change and products **2** and **4** were obtained after annealing. Therefore, the species with the peak at 274 nm should be attributed to the intermediate developed during the photolysis. Next, a degassed 3–MP matrix containing **1** (0.4 M) was irradiated ($\lambda>300$ nm) for 10 min. Interestingly, the matrix containing the intermediate gave ESR spectra which were characteristic of a randomly oriented triplet state spectrum consisting of strong absorptions centered at near 3330 G and weak absorptions at 1650 G. The former is expected as a six–line spectrum but appears as three–line with shoulders due to overlap and/or poor resolution. The latter can be ascribed to the half–field ($\Delta m = 2$) transition. The zero field splitting parameters for **5** are evaluated to be $|D| = 0.027$ cm^{-1} and $|E| = 0.007$ cm^{-1} by simulating the ESR spectral line shape at near 3330 G ($\Delta m = 1$ transition). We postulate silatrimethylenemethane **5** as the intermediate.

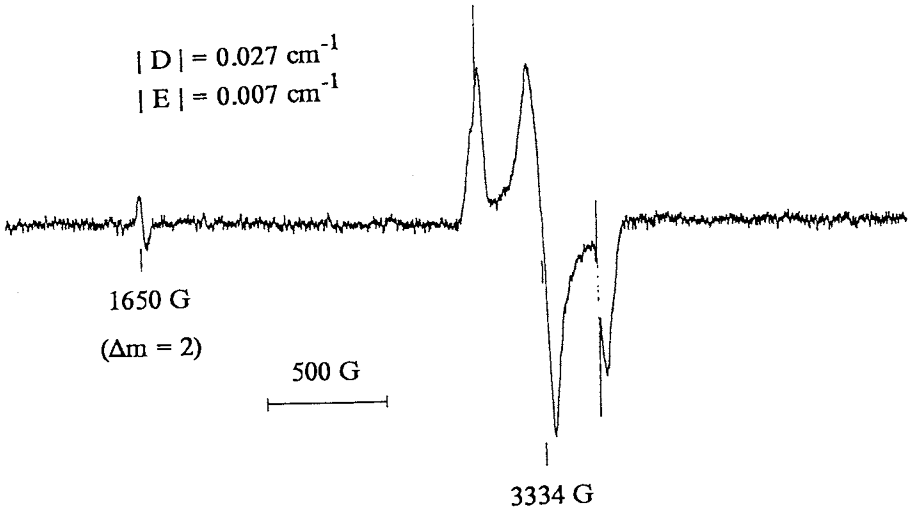
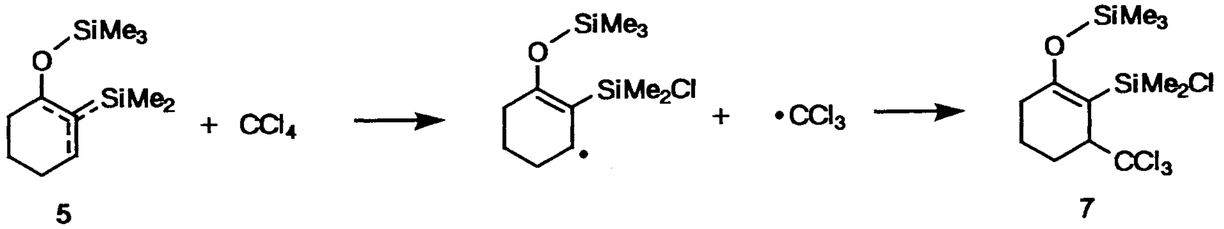


Fig. 2. Triplet ESR spectra observed after the photolysis of **1** in 3–MP at 77 K.

Free silatrimethylenemethane has been an elusive entity among reactive organosilicon intermediates. Ando has suggested the intermediacy of a silatrimethylenemethane during the course of the photochemical formation of methylenecyclopropane.5) More recently, metal complexes of silatrimethylenemethanes have been reported by Ando et al.6) Therefore, it is extremely interesting that the silatrimethylenemethane could be detected by spectroscopic methods. Comparison of these data with the reported values of the trimethylenemethane,7) $|D| = 0.025\ \mathrm{cm}^{-1}$ and $|E| = 0\ \mathrm{cm}^{-1}$, suggests a distorted structure of the π electron system of **5** from the D_{3h} symmetry.

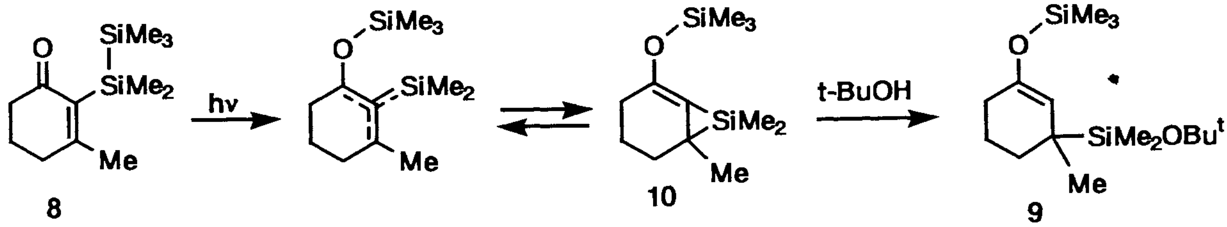
The products **2** and **4** may be derived from an ionic intermediate **6** (the singlet state of **5**). However, it is still unclear at this moment that the observed triplet is the ground state or thermally accessible species, although the energy difference between triplet and singlet species should be small. Photolysis of **1** in carbon tetrachloride gave an adduct **7** in 60% yield.8) Abstraction of chlorine from carbon tetrachloride followed by addition of the trichloromethyl radical explains the formation of **7**.9)



Scheme 2.

Irradiation of **1** resulted in the formation of a charge-separated zwitter ionic species by intramolecular charge transfer (OICT).10) The half-filled Si–Si σ orbital should lie on the same plane of the π system to avoid back electron transfer and hence to facilitate 1,4-trimethylsilyl migration.

Substitution of **1** by a methyl group at the 3-position changes the course of the photochemical reaction dramatically. Thus, irradiation of 2-pentamethyldisilanyl-3-methyl-2-cyclohexenone (**8**)11) in *t*-butyl alcohol afforded 1-trimethylsilyloxy-3-methyl-3-(*t*-butoxydimethylsilyl)cyclohexene (**9**) exclusively in higher yield than 70%.12) No triplet ESR signal was detected for **8** under the same reaction conditions as **1**. An interpretation of the reaction is illustrated in Scheme 3. The formation of the silatrimethylenemethane from **8** is probably disfavored due to the steric repulsion between two methyl groups on both silicon and ring and a methylenesilacyclopropane intermediate **10** may be formed instead. Alcoholysis of the intermediate resulted in the formation of the product **9**.



Scheme 3.

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References

1) Chemistry of Organosilicon Compounds. 295
2) K. Sakamoto and H. Sakurai, *J. Am. Chem. Soc.*, **113**, 1466 (1991).
3) Compound **1**: Colorless oil; ^{1}H NMR (C_6D_6, 300 MHz) δ 0.23 (s, 9H), 0.27 (s, 6H), 1.44 (tt, J = 6.0 Hz, 6.5 Hz, 2H), 1.71 (dt, J = 4.0 Hz, 6.0 Hz, 2H), 2.11 (t, J = 6.5 Hz, 2H), 6.74 (t, J = 4.0 Hz, 1H); ^{13}C NMR (C_6D_6, 75 MHz) δ −3.9, −1.6, 23.0, 27.3, 38.5, 142.2, 156.9, 201.0; ^{29}Si NMR (C_6D_6, 59 MHz) δ −24.1, −18.5; UV (hexane) λ_{max}/nm (ε) 258 (3500), 350 (sh, 100); MS (70 eV) m/e (%) 226 (M^+, 0.3), 211 (100), 153 (50), 133 (95), 73 (37); HRMS m/e obsd 226.1217, calcd for $C_{11}H_{22}OSi_2$ 226.1209.
4) Compound **2**: Colorless oil; ^{1}H NMR (C_6D_6, 300 MHz) δ 0.18 (s, 9H), 0.39 (s,3H), 0.40 (s, 3H), 1.27 (s, 9H), 1.59−1.89 (m, 6H), 4.52−4.56 (m, 1H), 6.28−6.30 (m, 1H); ^{13}C NMR (C_6D_6, 75 MHz) δ 1.0, 2.5, 2.6, 19.4, 26.8, 32.3, 33.2, 69.3, 72.2, 138.6, 143.2; ^{29}Si NMR (C_6D_6, 59 MHz) δ −3.4, 13.5; MS (70 eV) m/e (%) 300 (M^+, 7), 227 (18), 169 (19), 147 (29), 75 (100), 73 (30); HRMS m/e obsd 300.1923, calcd for $C_{15}H_{32}O_2Si_2$ 300.1941. Compound **4**: Colorless oil; ^{1}H NMR (C_6D_6, 300 MHz) δ −0.02 (s, 6H), 1.10 (s, 9H), 0.91−2.42 (m, 9H); ^{13}C NMR (C_6D_6, 75 MHz, DEPT) δ −0.9, 25.7, 29.3 (C2), 29.5$_7$, 29.5$_8$, 32.0, 42.0 (C5), 72.2, 209.5; ^{29}Si NMR (C_6D_6, 59 MHz) δ 5.8; MS (70 eV) m/e (%) 228 (M^+, 1), 172 (37), 171 (38), 155 (28), 75 (100); HRMS m/e obsd 228.1568, calcd for $C_{12}H_{34}O_2Si$ 228.1546.
5) W. Ando and H. Saso, *Tetrahedron Lett.* **27**, 5625 (1986).
6) W. Ando, T. Yamamoto, H. Saso, and H. Kabe, *J. Am. Chem. Soc.*, **113**, 2791 (1991).
7) P. Dowd, *J. Am. Chem. Soc.*, **88**, 2587 (1966); P. Dowd, *Acc. Chem. Res.*, **5**, 242 (1972).
8) Compound **7**: Colorless oil; ^{1}H NMR (C_6D_6, 300 MHz) δ 0.08 (s, 9H), 0.59 (s, 3H), 0.61 (S, 3H), 1.40−2.00 (m, 6H), 3.73 (dd, J = 3.0 Hz, 6.0 Hz, 1H); ^{13}C NMR (C_6D_6, 75 MHz) δ 1.2, 3.7, 4.0, 18.8, 25.9, 29.9, 55.7, 86.8, 161.2, 168.0; ^{29}Si NMR (C_6D_6, 59 MHz) δ 18.4, 18.8; MS (70 eV) m/e (%) 382 (M^+, 2), 380 (M^+, 4), 378 (M^+, 3), 261 (53), 153 (100), 93 (45), 73 (31); HRMS m/e obsd 377.9953, calcd for $C_{12}H_{22}OSi_2{}^{35}Cl_4$ 377.9963.
9) H. Sakurai, "Free Radicals," ed by J. K. Kochi, Wiley-Interscience, New York, N. Y. (1973), Chap. 25.
10) For charge separation by σ−π OICT, see H. Sakurai, "Silicon Chemistry," ed by J. Y. Corey, E. G. Corey, P. P. Gaspar, Ellis Horwood, Chichester, U. K. (1988), Chap. 16; H. Sakurai, H. Sugiyama, and M. Kira, *J. Phys. Chem.*, **94**, 1837 (1990); K. A. Horn and A. A. Whitenack, *J. Phys. Chem.*, **92**, 3879 (1988); K. A. Horn, R. B. Grossman, J. R. G. Thorne, and A. A. Whitenack, *J. Am. Chem. Soc.*, **111**, 4809 (1988).
11) Compound **8**: Colorless oil; ^{1}H NMR (C_6D_6, 300 MHz) δ 0.30 (s, 9H), 0.40 (s, 6H), 1.40 (tt, J = 6.0 Hz, 6.5 Hz, 2H), 1.64 (s, 3H), 1.67 (t, J = 6.0 Hz, 2H), 2.07 (t, J = 6.5 Hz, 2H); ^{13}C NMR (C_6D_6, 75 MHz) δ −1.0, −0.5, 22.3, 24.3, 34.4, 37.5, 136.6, 168.6, 201.7; ^{29}Si NMR (C_6D_6, 59 MHz) δ −25.3, −17.2; UV (hexane) λ_{max}/nm (ε) 237 (6000), 338 (100); MS (70 eV) m/e (%) 240 (M^+, 0.1), 225 (58), 167 (52), 133 (100), 73 (42); HRMS m/e obsd 240.1383, calcd for $C_{12}H_{24}OSi_2$ 240.1366.
12) Compound **9**: Colorless oil; ^{1}H NMR (C_6D_6, 300 MHz) δ 0.12 (s, 3H), 0.13 (s, 3H), 0.21 (s, 9H), 1.10 (s, 3H), 1.17 (s, 9H), 1.56−2.08 (m, 6H), 4.95 (s, 1H); ^{13}C NMR (C_6D_6, 75 MHz) δ −1.4, −1.3, 0.6, 19.3, 23.5, 24.7, 30.3$_6$, 30.4$_0$, 32.1, 71.9, 110.7, 149.6; ^{29}Si NMR (C_6D_6, 59 MHz) δ 6.6, 14.9; MS (70 eV) m/e (%) 314 (M^+, 9), 241 (43), 183 (100), 75 (58), 73 (42); HRMS m/e obsd 314.2088, calcd for $C_{16}H_{34}O_2Si_2$ 314.2097.

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