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PHOTOCHEMISTRY OF DIBENZO-1,1,2,2,3,3 -HEXAMETHYL-1,2,3-TRISILACYCLOHEPTA-4,6-DIENE AND THE GERMANIUM ANALOG. GENERATION OF TETRAMETHYLDISILENE BY FREE-RADICAL DISPROPORTIONATION AND THE FIRST SPECTROSCOPIC DETECTION OF DIMETHYLGERMYLENE1)

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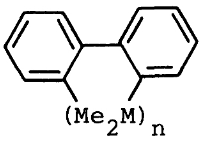
Photolysis of the title compound afforded silafluorene and dibenzo-1,2-disilacyclohexadiene as primary photoproducts. Two reactive intermediates, tetramethyldisilene and dimethylsilylene, were detected by trapping. The dimethylgermylene, derived from the germanium analog, was first observed by electronic spectra.

In a prévious paper,2) we reported photoreactions of dibenzo-1,2-disilacyclohexadiene (3) and its germanium analog (4) to give 1 and 2 accompanied by the generation of dimethylsilylene and dimethylgermylene, respectively. The extention of the work to higher members, 5 and 6, revealed interesting consequences.

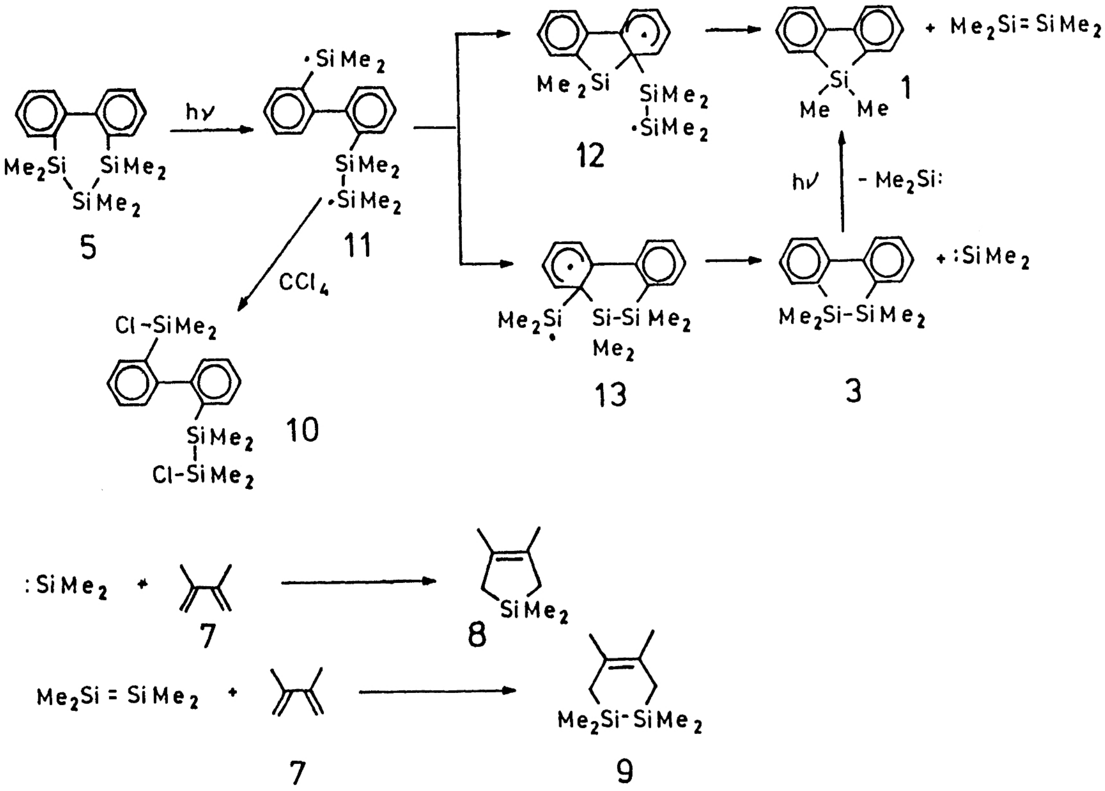


1: M=Si, n=1; 2: M=Ge, n=1;
3: M=Si, n=2; 4: M=Ge, n=2;
5: M=Si, n=3; 6: M=Ge, n=3

The title trisilacycloheptadiene (5)3) gave silafluorene (1) in 70-90% yield upon irradiation with a 450 W high-pressure Hg lamp at room temperature under argon in benzene or in hexane. In order to detect possible reactive intermediates, a hexane solution of 5 and 20 molar excess 2,3-dimethylbutadiene (7) was similarly irradiated for 1 h. The starting 5 disappeared completely and 1 (90%), 1,2,4,4-tetramethyl-4-silacyclopentene (8, 82%),4) and 1,2,4,4,5,5-hexamethyl-4,5-disilacyclohexene (9, 38%)5) were obtained. The most straightforward explanation for the formation of 9 is a [2+4] cycloaddition of tetramethyldisilene derived directly from 56) with 7. Tetramethyldisilene can be formed also by the dimerization of the dimethylsilylene.7) However the dimerization process cannot compete with cycloaddition of dimethylsilylene with 7 to form 8 in the presence of large excess 7.7)

Stepwise loss of dimethylsilylene from 5 should yield 3 which actually detected by GC-MS at the very early stage of the reaction. However under the conditions as reported previously,2) photodecomposition of 3 proceeds very rapidly to give 1 and dimethylsilylene which eventually affords 8. Then it is reasonable to assume that the half amount of 8 (41%) is derived by the dimethylsilylene which comes from the latter indirect path. The yield of the primary products, 8 and 9, is therefore altogether 79%. It also means that the trapping efficiency of dimethylsilylene and tetramethyldisilene by 7 under the conditions is as high as 88% relative to 1.

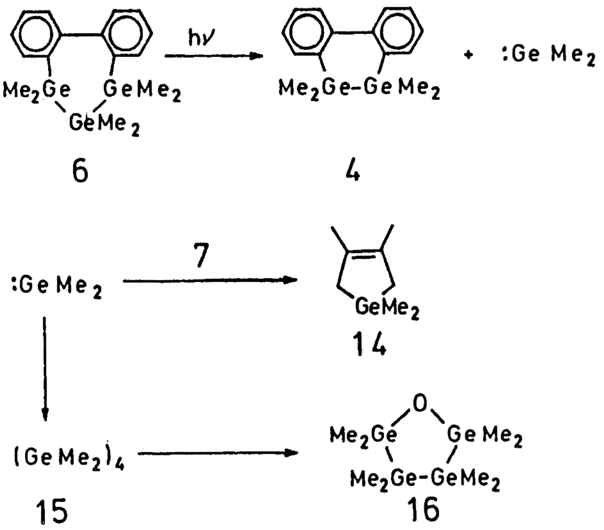
Similar to the photolysis of 3,2) irradiation of 5 in carbon tetrachloride with a Pyrex filter gave a dichloride (10) in 75% yield. The result suggests strongly the formation of the diradical (11) as a key intermediate. The diradical may undergo ipso substitution to form either 12 or 13 which eliminates tetramethyldisilene or dimethylsilylene as shown in Scheme 1. The relative rate of the formation of 12 to 13 is thus 41/38 ≃ 1.



Scheme 1.

Photolysis of 6[8)] in the presence of 7 in benzene for 1 h gave 4 (99%) and 1,2,4,4-tetramethyl-4-germacyclopentene (14, 72%). Since the rate of photolysis of 4 is much slower than 3,[2)] 4 can survive reasonably under the conditions. A strikingly different behavior of 6 from those of 3, 4, and 5 was observed at the low temperature photolysis. 3, 4, and 5 are completely inert towards photolysis in a 3-methylpentane glass matrix at 77 K in accordance with the proposed free-radical mechanism[2)] that the radical pairs cannot undergo ipso substitution at low temperature and only return to the starting materials by coupling. However, 6 yields 4 and a yellow substance even under the conditions of glass matrix. The electronic spectra of the yellow substance is shown in Fig. 1. The broad absorption maximum at 430 nm resembles to that of the dimethylsilylene at 450 nm[9)] so that the yellow color can be ascribed most reasonably to the dimethylgermylene.[10)]

The color disappeared as temperature rised and octamethylcyclotetragermane (15)[11)] was detected by GC-MS. Efforts of isolating 15 failed so far, but octamethylcyclotetragermoxane (16),[12)] an oxidation product, was obtained. Yellow color did not develop in the photolysis of 6 in the presence of 7 under the same conditions. Instead, 14 was detected by GC-MS. Therefore, cycloaddition of the dimethylgermylene with 7 proceeds even at 77 K in the matrix. (Scheme 2) The very intriguing photochemistry of these compounds is actively in progress.



Scheme 2.

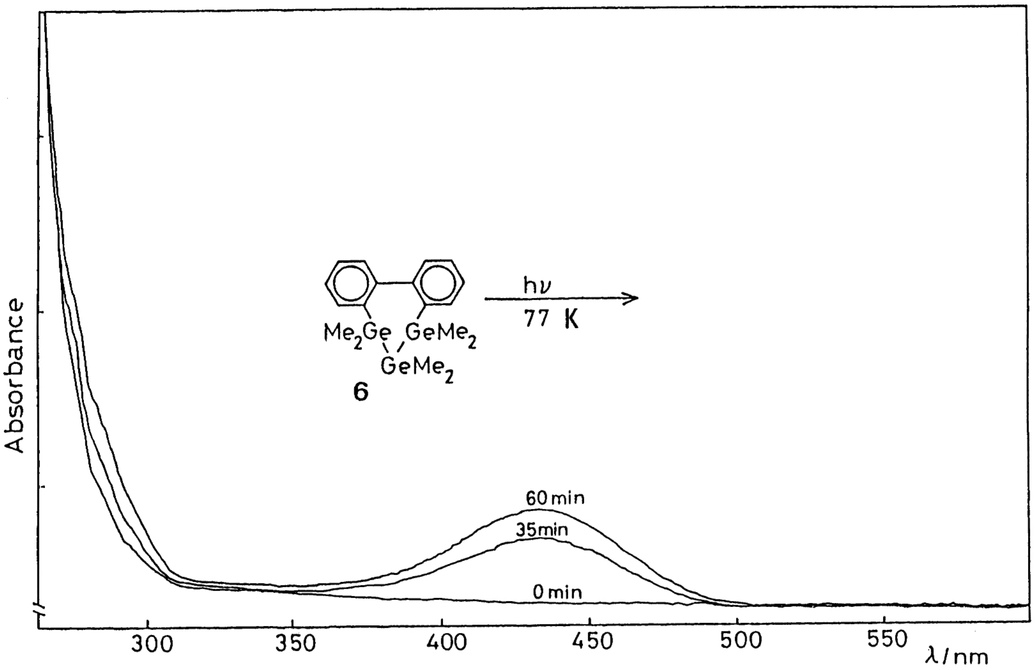
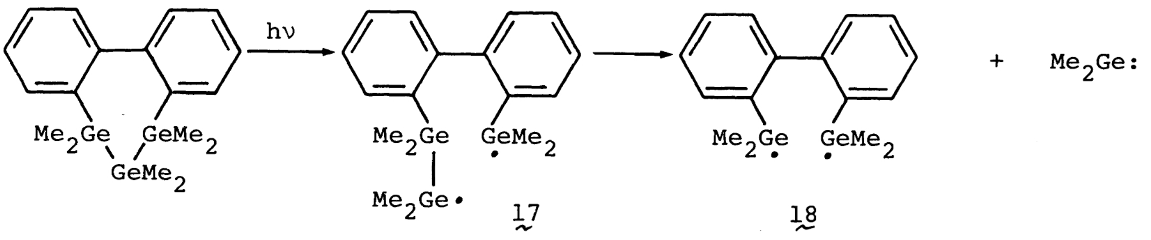


Fig. 1. Absorption spectra of dibenzo-1,1,2,2,3,3-hexamethyl-1,2,3-trigermacyclohepta-4,5-diene during irradiation at 77 K in 3-methylpentane glass matrix. The absorbance is in an arbitrary unit.

We thank Professor Y. Ikegami for low-temperature electronic spectra of dimethylgermylene. We also thank Toshiba Silicone Co., Ltd., for gifts of chlorosilanes.

References

1) Chemistry of Organosilicon Compounds 189.
2) M. Kira, K. Sakamoto, and H. Sakurai, J. Am. Chem. Soc., 106, 7469 (1984).
3) **5** was obtained as a low yield byproduct in the preparation of **3**.[2)] Independent preparation by the reaction of 2,2'-dilithiobiphenyl and 1,3-difluorohexamethyltrisilane gave **5** in 9.3% yield: mp 94 °C; ^{1}H NMR (CCl_4) δ -0.55 (6H, s), 0.10 (6H, s), 0.38 (6H, s), 7.00-7.45 (8H, m); ^{13}C NMR ($CDCl_3$) δ -7.90, -4.11, 126.45, 128.47, 130.36, 133.23, 138.26, 150.27; ^{29}Si NMR ($CDCl_3$) δ -20.57, -41.39; MS (m/e %) 326 (M^+, 6), 211 (48), 195 (53), 116 (100); UV (hexane) 220 nm (sh, ε 28000), 250 nm (ε 9300); High Resolution MS Found: 326.1362. Calcd for $C_{18}H_{26}Si_3$: 326.1342. Found: C, 65.97; H, 8.19%. Calcd for $C_{18}H_{26}Si_3$: C, 66.18; H, 8.02%.
4) W. H. Atwell and D. R. Weyenberg, J. Am. Chem. Soc., 90, 3438 (1968).
5) D. N. Roark and G. J. D. Peddle, J. Am. Chem. Soc., 94, 5837 (1972).
6) It is interesting to note that tetramethyldisilene is the base peak in MS of **5**.[3)]
7) R. T. Conlin and P. P. Gaspar, J. Am. Chem. Soc., 98, 868 (1976); Y. Nakadaira, T. Kobayashi, T. Otsuka, and H. Sakurai, ibid., 101, 486 (1979).
8) **6** was obtained as a low-yield byproduct in the preparation of **4**:[2)] mp 100-101 °C; ^{1}H NMR (CCl_4) δ -0.33 (6H, s), 0.34 (6H, s), 0.51 (6H, s), 7.00-7.50 (8H, m); ^{13}C NMR ($CDCl_3$) δ -6.85, -4.31, -3.46, 126.18, 127.68, 130.55, 132.31, 141.06, 149.62; UV (hexane) 225 nm (sh, ε 25000), 250 nm (ε 10000); High resolution MS Found: 459.9640. Calcd for $C_{18}H_{26}{}^{72}Ge_2{}^{74}Ge$: 459.9688. Found: C, 46.82; H, 5.78%. Calcd for $C_{18}H_{26}Ge_3$: C, 46.82; H, 5.69%.
9) T. J. Drahnak, J. Michl, and R. West, J. Am. Chem. Soc., 101, 5427 (1979).
10) Although it may be premature to discuss the mechanism of germylene extrusion, we like to suggest that the dimethylgermane may be formed from the digermanyl radical moiety of **17** by the unzipping reaction. The resulting diradical (**18**) undergoes coupling to form **4**. Strictly speaking, we cannot exclude the possibility that the yellow color can also be ascribed to tetramethyldigermene, since S. Masamune, Y. Hanzawa, and D. J. Williams, J. Am. Chem. Soc., 104, 6136 (1982), reported that tetrakis(2,6-dimethylphenyl)digermene had an absorption maximum at around 400 nm. However, the available data suggest strongly the formation of dimethylgermylene.



11) **15**: MS (m/e %) four M^+ at 414 (49), 412 (66), 410 (66), 408 (53) (isomer ratio calcd for $C_8H_{16}Ge_4$ is 52:69:68:46), 221 (42), 119 (100), 117 (71), 115 (51).
12) **16**: MS (m/e %) four M^+ at 430 (7), 428 (8), 426 (8), 424 (6), 412 (22), 412 (28), 410 (27), 408 (21), 223 (24), 117 (73), 115 (55), 89 (30), 87 (22).

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