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Novel Photochemical Reactions of Dibenzodisilacyclohexadiene with Ketones†,1)

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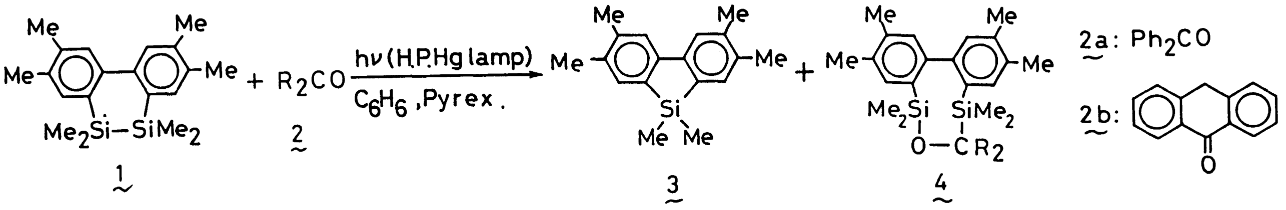
Dibenzodisilacyclohexadiene reacts with ketones and formaldehyde, under photolytic conditions, to give a variety of products depending on the nature of the ketones used. A compound having 2-sila-3-oxabicyclo[3.2.2]nona-6,8-diene structure was isolated as a result of intramolecular trapping of a cyclohexadienyl radical.

In prvious papers,2) we have reported several new photochemical reactions of dibenzodisilacyclohexadiene and derivatives. Herein an entirely new photochemical addition reaction of dibenzodisilacyclohexadiene with ketones will be reported.

Irradiation of a benzene solution of 13) in the presence of small excess benzophenone (2a) gave, in addition to the silylene extrusion product 3 (46%), a new compound 4a was obtained in 40% yield. A similar reaction of 1 with anthrone (2b) gave adducts 4b and 3 in 52 and 22% yields, respectively.4)



The possibility of an S_H2 reaction,5) that the Si-Si bond reacted with photochemically excited benzophenone, was ruled out by the fact that no reaction occurred at all by using a light of wavelength longer than 340 nm, by which benzophenone alone was excited. Therefore, photoaddition can be explained by the stepwise reactions initiated by homolysis of the Si-Si bond to give a biradical (5).2a) A silyl radical terminal of 5 adds to a ketone to give a key biradical (6), which affords eventually the adduct by intramolecular recombination.

On the other hand, the reaction of 1 with fluorenone (2c) gave a 1:2 adduct (7c, 14%) and 3 (16%), but the major product was an entirely new 1:1 adduct (8c) formed in 57% yield.6) No 1:1 adduct corresponding to 4 was obtained. A similar reaction occurred with 9-xanthenone (2d) to give 7d (15%), 8d (41%), and 3 (15%).7)

It is interesting to note that the benzene structure of 1 was destroyed in the photoproducts 8. This is a rare example of intramlecular trapping of a cyclohexadienyl radical. The structures of these compounds were identified on the basis of the spectroscopic data.8) The molecular structure of 8d was further confirmed by X-ray crystallographic analysis.8b)

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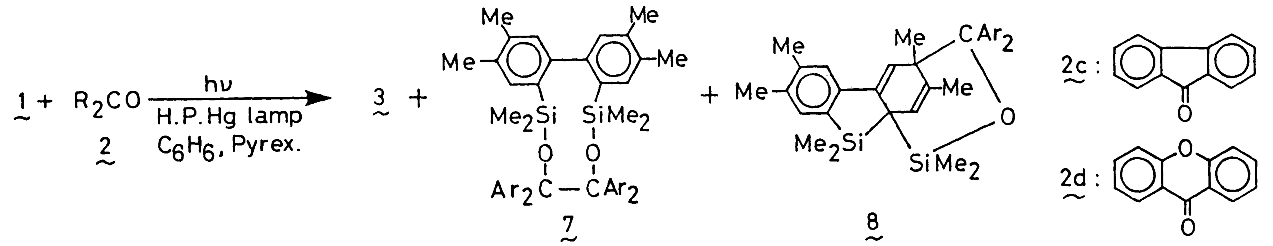
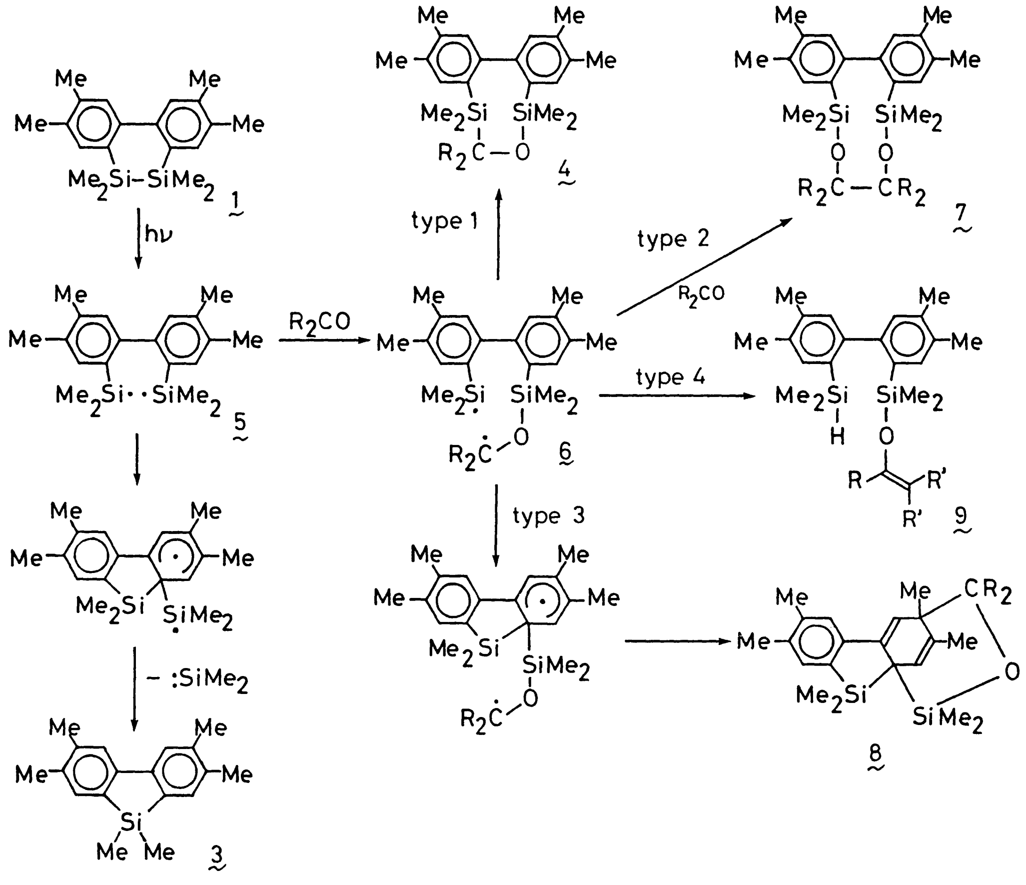
† Dedicated to the late Professor Ryozo Goto, the first Editor of this journal.



The formation of 8 provides evidence for the existence of an efficient ipso-silylation process involving 6. It has been previously suggested that the silylene elimination process includes also an intramolecular ipso-silylation process.9)

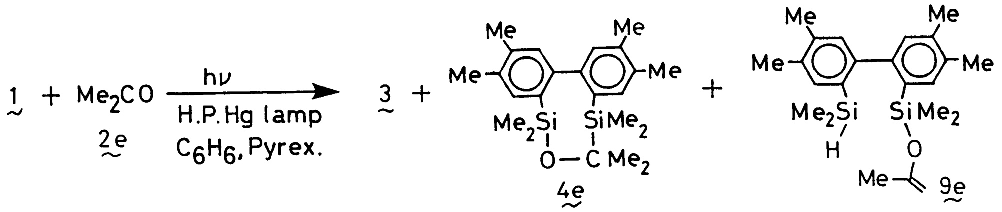
The formation of the products 7 and 8 can be explained by the stepwise mechanism involving the biradical 6 as a key intermediate as shown in Scheme 1. While biradicals 6 gave the adduct 4 in the reaction with benzophenone (2a) and anthrone (2b), it afforded a different type of adducts with fluorenone (2c) and 9-xanthenone (2d). The difference in the behavior of the intermediate radical 6 may be explained by longer life-time for 2c- and 2d-derived radicals.



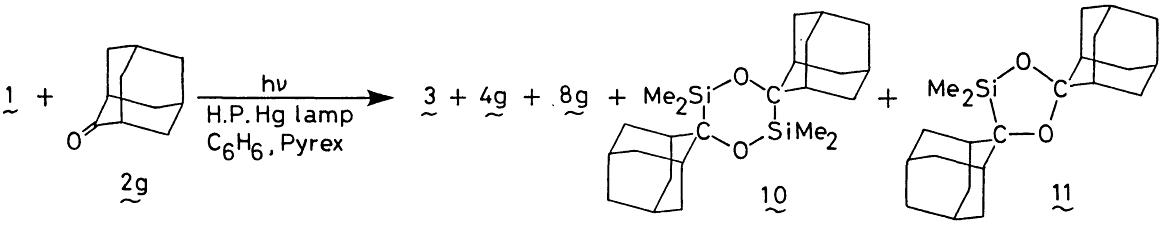
Scheme 1.

Photolysis of 1 in the presence of acetone (2e) gave the fourth type of adduct, 9e (43%), in addition to a 1:1 adduct (4e, 27%) and 3 (5%).10) The structure of 9e was determined by various spectroscopic data. A strong sharp absorption band at 2220 cm^{-1} due to Si-H stretching in an IR spectrum supports strongly the assigned structure.

The formation of 9e is explained by the intramolecular disproportionation of biradical 6e. Although hydrogen abstraction from hydrocarbon by a silyl radical is not favorable thermodynamically, intermolecular disproportionation of silyl radicals to afford hydrosilane and silaethene has been reported by several groups.[11] We also reported another example of intermolecular disproportionation.[12] The reaction of 1 with diisopropyl ketone (2f, R = Me_2CH-) gave the similar disproportionation product 9f (R = i-Pr, R' = Me) in 24% yield.[13] The direct recombination product similar to 4e was not detected in this case. Probably, large steric hindrance of two isopropyl groups may hinder recombination.



Photolysis of 1 in the presence of adamantanone (2g) gave 3, 4g, 8g, 10, and 11 in 30, 23, 5, 21, and 10% yields, respectively.[14] The formation of 8g is a result from the reduced rate of recombination of the biradical (6g) by large steric hindrance exerted by the adamantyl group. The compounds 10 and 11 were produced by the reaction of adamantanone with the dimethylsilylene formed from 1 as reported by Ando et al.[15]



Finally, the reaction of 1 with formaldehyde (2h), freshly prepared by a pyrolysis of paraformaldehyde in toluene, was examined. The isolated products were 3 and 4h (R = H) in 37 and 27% yields, respectively.

The photoreaction of 1 with ketones and formaldehyde are summarized in Scheme 1. Whereas photolysis of 1 gave 3 via an intramolecular ipso-silylation of 5 in the absence of ketone, the silyl radical terminal of 5 affords 6 when a carbonyl compound exists. Thus two reactions compete each other. The biradical 6 undergoes four types of reactions: recombination (type 1), further addition to the second ketone (type 2), intramolecular ipso-silylation followed by recombination (type 3), and intramolecular disproportionation (type 4).

References

1) Chemistry of Organosilicon Compounds 232.

2) a) M. Kira, K. Sakamoto, and H. Sakurai, J. Am. Chem. Soc., 105, 7469 (1983); b) H. Sakurai, K. Sakamoto, and M. Kira, Chem. Lett., 1984, 1213; c) H. Sakurai, K. Sakamoto, and M. Kira, ibid., 1984, 1379.

3) The tetramethyl derivative (1), instead of unsubstituted one, is used in this paper because of easiness of preparation from o-xylene: mp 184 °C.

4) 4a: white crystals; mp 185 °C; ^1H NMR (CCl_4, δ) -0.66 (s, 3H), -0.65 (s, 3H),

0.42 (s, 3H), 0.61 (s, 3H), 2.24 (bs, 12H), 6.9-7.4 (m, 14H); ^{29}Si NMR (CDCl$_3$, δ) -0.8, -2.6. 4b: white crystals; mp 218-220 °C; ^{1}H NMR (CCl$_4$, δ) -0.95 (s, 3H), -0.24 (s, 3H), 0.17 (s, 3H), 0.63 (s, 3H), 2.33 (s, 3H), 2.43 (s, 6H), 2.53 (s, 3H), 4.07 (bs, 2H), 6.68 (bs, 1H), 7.0-7.6 (s, 10H), 7.66 (bs, 1H).

5) A. Hosomi and H. Sakurai, J. Am. Chem. Soc., 94, 1385 (1972).

6) 7c: white crystals; mp > 280 °C; ^{1}H NMR (CCl$_4$, δ) -0.39 (s, 6H), 0.03 (s, 6H), 2.43 (bs, 12H), 5.68 (d, 2H, J = 7 Hz), 6.53 (t, 2H, J = 7 Hz), 6.7-7.5 (m, 16H); ^{29}Si NMR (CDCl$_3$, δ) 3.8. 8c: white crystals; mp 179 °C (dec.); ^{1}H NMR (CCl$_4$, δ) -0.18 (s, 3H), 0.22 (s, 3H),0.31 (s, 3H), 0.47 (s, 3H), 0.60 (s, 3H), 1.74 (d, 3H, J = 1.3 Hz), 2.31 (s, 3H), 2.38 (s, 3H), 6.09 (s, 1H), 6.39 (q, 1H, J = 1.3 Hz), 7.15-7.65 (m, 10H); ^{29}Si NMR (CDCl$_3$, δ) 7.0, -16.0.

7) 7d: white crystals; mp > 280 °C; ^{1}H NMR (CCl$_4$, δ) -0.27 (s, 6H), 0.20 (s, 6H), 2.46 (s, 6H), 2.48 (s, 6H), 5.8-7.7 (m, 20H). 8d: white crystals; mp 205 °C (dec.); ^{1}H NMR (CCl$_4$, δ) 0.07 (s, 3H), 0.32 (s, 3H),0.58 (s, 3H), 0.61 (s, 3H), 0.94 (s, 3H), 1.41 (d, 3H, J = 1.3 Hz), 2.24 (s, 3H), 2.48 (s, 3H), 5.67 (s, 1H), 6.32 (q, 1H, J = 1.3 Hz), 7.00-7.80 (m, 10H).

8) a) Satisfactory high-resolution MS and/or elemental analyses were obtained for all the new compounds. b) The X-ray structure of 8d will be reported later.

9) H. Sakurai, Y. Nakadaira, M. Kira, H. Sugiyama, K. Yoshida, and T. Takiguchi, J. Organomet. Chem., 184, C36 (1980).

10) 4e: colorless oil; ^{1}H NMR (CCl$_4$, δ) 0.1-0.2 (12H, m), 1.8 (3H, s), 2.20 (6H, s), 2.25 (6H, s), 4.00 (1H, bs), 4.05 (1H, bs), 4.15 (1H, septet, J = 6.8 Hz), 7.01 (1H, bs), 7.04 (1H, bs), 7.34 (1H, bs), 7.47 (1H, bs). 9e: colorless oil; ^{1}H NMR (CCl$_4$, δ) -0.66 (3H, s), -0.63 (3H, s), 0.24 (3H, s), 0.34 (3H, s), 1.17 (3H, s), 1.20 (3H, s), 2.30 (12H, s), 6.96 (2H, bs), 7.18 (1H, bs), 7.29 (1H, bs).

11) S. K. Tokach and R. D. Koob, J. Am. Chem. Soc., 102, 376 (1980); B. J. Cornett, K. Y. Choo, and P. P. Gaspar, ibid., 102, 377 (1980).

12) H. Sakurai, Y. Nakadaira, and H. Sakaba, Organometallics, 2, 1484 (1983).

13) 9f: colorless oil; ^{1}H NMR (CCl$_4$, δ) -0.04 (s, 3H), 0.06 (s, 3H), 0.09 (d, 3H, J = 3.5 Hz), 0.15 (d, 3H, J = 3.5 Hz), 1.00 (d, 3H, J = 6.8 Hz), 1.02 (d, 3H, J = 6.8 Hz), 1.48 (s, 3H), 1.68 (s, 3H), 2.32 (s, 3H), 2.35 (s, 3H), 2.38 (s, 3H), 2.41 (s, 3H), 2.83 (septet, 1H, J = 6.8 Hz), 4.10 (septet, 1H, J = 3.5 Hz), 6.92 (bs, 1H), 7.02 (bs, 1H), 7.23 (bs, 1H), 7.51 (bs, 1H).

14) 4g: white crystals; mp 184-185 °C; ^{1}H NMR (CCl$_4$, δ) -0.67 (3H, s), -0.60 (3H, s), 0.47 (3H, s), 0.52 (3H, s), 1.2-2.2 (m, 14H), 2.3-2.4 (12H, m), 6.96 (1H, bs), 6.99 (1H, bs), 7.20 (1H, bs), 7.23 (1H, bs). 8g: colorless oil; ^{1}H NMR (CCl$_4$, δ) 0.20 (s, 3H), 0.23 (s, 3H),0.38 (s, 3H), 0.43 (s, 3H), 0.90 (s, 3H), 1.2-2.1 (m, 14H), 1.90 (d, 3H, J = 1.5 Hz), 2.30 (s, 3H), 3.03 (s, 3H), 5.67 (s, 1H), 6.16 (q, 1H, J = 1.5 Hz), 6.70 (bs, 1H), 7.15 (bs, 1H). 4h: colorless oil; ^{1}H NMR (CCl$_4$, δ) -0.51 (3H, s), -0.50 (3H, s), 0.37 (3H, s), 0.41 (3H, s), 2.37 (6H, s), 2.41 (6H, s), 3.32 (1H, d, J = 14.4 Hz), 3.46 (1H, d, J = 14.4 Hz), 6.99 (2H, bs), 7.23 (1H, bs), 7.31 (1H, bs).

15) W. Ando, M. Ikeno, and A. Sekiguchi, J. Am. Chem. Soc., 100, 3613 (1978); W. Ando, Y. Hamada, and A. Sekiguchi, J. Chem. Soc., Chem. Commun., 1983, 952; W. Ando, Y. Hamada, and A. Sekiguchi, Tetrahedron Lett., 23, 5323 (1982).

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