

Photoreactions of 4,4'-Bis(pentamethyldisilanyl)biphenyl

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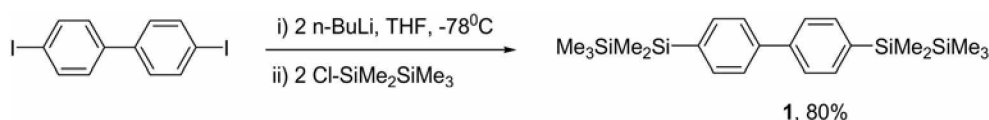
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It is well known that the photolysis of arylsilanes¹ gave the silenes containing Si=C bond as reaction intermediates since the earliest report on the photolysis of phenyl-pentamethyldisilane and (*p*-tolyl)pentamethyldisilane by Ishikawa *et al.*² in 1975. The silenes arising from the 1,3-trimethylsilyl radical shift of a terminal silyl group in the disilane moiety onto an *ortho* carbon atom in the aryl ring upon irradiation react with various substrates to give the various photoproducts.³⁻²⁵ In connection with the reactions of silene intermediates in the absence of trapping agents, Ishikawa and co-workers^{26,27} reported that the photolysis of 1,4-bis(pentamethyldisilanyl)benzene in hexane gave two isomeric dimers, 7,7,8,8-tetramethyl-3,12-bis(pentamethyldisilanyl)-13,14-bis(trimethylsilyl)-7,8-disilatricyclo[7.3.1.1^{2,6}]-tetradeca-3,5,9,11-tetraene and 7,7,8,8-tetramethyl-3,12-bis(pentamethyldisilanyl)-10,14-bis(trimethylsilyl)-7,8-disilatricyclo[7.3.1.1^{2,6}]-tetradeca-3,5,9(13),11-tetraene, in a ratio of 1:1 through head-to-head dimerization of silene intermediate. Very recently, I reported that the photoreaction

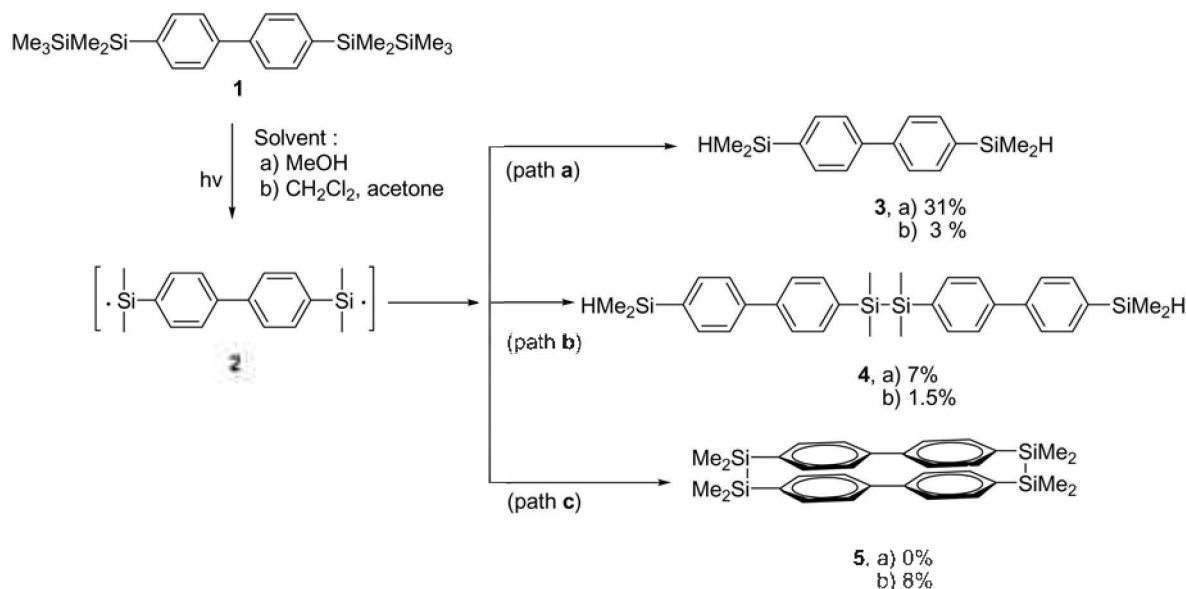
of (2-hydroxymethylphenyl)pentamethyldisilane in methanol provides a novel intramolecular photoproduct *via* silene intermediate arising from 1,3-migration of trimethylsilyl radical, which is formed *via* homolytic cleavage of silicon-silicon σ bond in the disilane moiety upon irradiation to the C₆ position of benzene ring.²⁸ In connection with my continuous studies for the utility of silacyclopropenes,²⁹⁻⁴³ 1-silaallenes, and silenes⁴⁴ as reaction intermediates in organic synthesis of silicon-containing heterocyclic compounds, the present author has now investigated the photochemistry of 4,4'-bis(pentamethyldisilanyl)biphenyl **1** expecting the formation of two silene intermediates in one molecule. In this paper, I would like to report the detailed photochemical study of 4,4'-bis(pentamethyldisilanyl)biphenyl.

The starting 4,4'-bis(pentamethyldisilanyl)biphenyl **1** was prepared by the reaction of 4,4'-diiodobiphenyl with chloropentamethyldisilane in 80% yield (Scheme 1).

In order to investigate whether or not the photolysis of **1** affords two silene intermediates and the photoproducts from



Scheme 1



Scheme 2

the reaction of the silene moiety thus formed with the trapping agent, methanol, the photolysis of **1** in the presence of methanol was performed.

Irradiation of **1** in deaerated methanol with 254 nm UV light afforded two photoproducts **3** and **4** (31 and 7% yield, respectively) along with some decomposition products of unknown structure as shown in Scheme 2, when 92% of **1** was photolyzed but the expected photoproducts from the reaction of the silene intermediate with methanol were not obtained, indicating that the photolysis of **1** did not give the silene intermediate in marked contrast to the photolysis of 1,4-bis(pentamethyldisilanyl)benzene^{26,27} which produces the two dimeric photoproducts *via* the silene intermediates. In connection with the formation of the compounds having the dimethylsilane moiety like **3** or **4**, Sakurai *et al.*⁴⁵ reported that the photolysis of 4-(trifluoromethyl)phenylpentamethyldisilane in ethanol-hexane mixture affords 4-(trifluoromethyl)phenyldimethylsilane, (trimethylsilyl)[(ethoxydimethyl)silyl](trifluoromethyl)cyclohexadienes, and 4-(trifluoromethyl)phenyl(ethoxydimethyl)silane in 24, 41, and 15% yields, respectively. In this reaction, it was concluded that 4-(trifluoromethyl)phenyldimethylsilane was formed through the nucleophilic attack of ethanol at the β -silicon atom of the disilane moiety. In the photolysis of **1**, the formation of **3** can be also explained by the nucleophilic attack of two methanol molecules at the two disilane moieties of **1** but the formation of **4** can not be explained because the silicon-silicon bond in **4** must be formed. Therefore, the existence of diradical species **2** as reaction intermediate was proposed in the photolysis of **1**. The formation of a photoproduct **3** may be understood in terms of the homolytic cleavage of two silicon-silicon σ bonds in the photoexcited state of **1** and then the hydrogen abstraction by the diradical species **2** thus formed in methanol solvent at both sides. The production of the photoproduct **4** was most likely explained by a mechanism involving the silyl radical-silyl radical coupling reaction of **2** at one side, followed by the hydrogen abstraction by the remaining radical part in methanol solvent.

The structures of the photoproducts **3** and **4** were determined by various physical methods, such as ¹H NMR, ¹³C NMR, UV, FT-IR, and high resolution mass spectrometry. The ¹H NMR spectra of **3** and **4** show septet resonances at δ 4.48 and 4.50 ppm, respectively, due to a Si-H proton of dimethylsilyl group. The ¹³C NMR spectrum of **3** reveals resonances due to four kinds of aromatic carbons at 126.8, 134.8, 136.7, and 142.1 ppm, dimethylsilyl carbon at -3.52 ppm and that of **4** shows resonances due to eight kinds of aromatic carbons at 126.7, 126.9, 133.8, 134.8, 136.6, 138.9, 142.1, and 142.2 ppm, two kinds of dimethylsilyl carbon at -3.48 and 1.2 ppm. The IR absorption spectra of **3** and **4** show characteristic absorptions at 2118.5 and 2117.8 cm⁻¹, respectively, due to the Si-H stretching mode in the dimethylsilyl group. The mass spectra of **3** and **4** show parent ions at *m/z* 270 and 538, respectively. These results are wholly consistent with the structures proposed for **3** and **4**.

In order to investigate the reactivity of acetone instead of

methanol as a trapping agent, the photolysis of **1** in the presence of acetone was carried out. Irradiation of **1** in a deaerated methylene chloride in the presence of acetone with 254 nm UV light afforded three compounds **3** (3% yield), **4** (1.5% yield), and **5** (8% yield) along with some decomposition products of unknown structure as shown in Scheme 2, when 88% of **1** was photolyzed but the expected photoproducts from the reaction of the photoexcited state of **1** with acetone were not obtained. In this reaction, the evidence for the formation of silene intermediate was not also detected. The formation of **3** and **4** can be also explained by the hydrogen abstraction by the diradical species **2** in the solvent cage the same as in methanol solvent. The formation of a novel photodimer **5** can be rationalized in terms of the initial formation of diradical species **2** upon irradiation, followed by the silyl radical-silyl radical coupling reactions of **2** in two sites to give the dimer of **2**. The photoproduct **5** was obtained only in a deaerated methylene chloride in the presence of acetone as solvent, indicating that diradical species **2** probably has the longer lifetime in the absence of silyl radical trapping agents than in methanol. The compound **5** was not obtained in the presence of silyl radical trapping agent, methanol, because **2** readily reacts with methanol to give the photoproducts **3** and **4**.

The photoreaction of **1** in a deaerated hexane with 254 nm UV light did not give any photoproduct in contrast to the photoreaction of **1** in the presence of methanol or acetone as solvent.

The structure of the photoproduct **5** was determined by various physical methods, such as ¹H NMR, ¹³C NMR, UV, FT-IR, and high resolution mass spectrometry. The ¹H NMR spectrum of **5** shows aromatic AB quartet at δ 7.06 and 7.17 ppm, due to para-disubstituted aromatic protons. The ¹³C NMR spectrum of **5** reveals resonances due to four kinds of aromatic carbons at 125.9, 133.5, 136.9, and 141.6 ppm, dimethylsilyl carbon at -0.069 ppm. The mass spectrum of **5** shows a parent ion at *m/z* 536, indicating that a compound **5** is the dimer of diradical species **2**. These results are wholly consistent with the structure proposed for **5**.

In conclusion, the photolysis of **1** in methanol provided **3** and **4** *via* diradical species **2** but the expected photoproducts from the reaction of the silene intermediate with methanol were not obtained. The photolysis of **1** in a deaerated methylene chloride in the presence of acetone provided a novel photoproduct **5** in addition to **3** and **4** *via* diradical species **2** but the expected photoproducts from the silene intermediate were also not obtained in this photoreaction.

Experimental

Synthesis of 4,4'-bis(pentamethyldisilanyl)biphenyl 1. A solution of 4,4'-diiodobiphenyl (1.0 g, 2.46 mmol) in THF (20 mL) was treated with *n*-BuLi (2.07 mL, 5.17 mmol) at -78 °C followed by chloropentamethyldisilane (1 mL, 5.17 mmol). The reaction mixture was warmed to room temperature and stirred for 5 hrs. After evaporation of solvent, the reaction mixture was extracted with ethyl acetate (3 × 20

mL), washed with water (3 × 20 mL), and dried with MgSO₄ and concentrated *in vacuo* to give the crude product. Flash column chromatography using *n*-hexane/ethyl acetate (100/1, v/v) as an eluent gave **1** (0.82 g, 80% yield); m.p. 35–36 °C. ¹H NMR (CDCl₃, 300 MHz) δ_H 0.10 (18H, s), 0.38 (12H, s), 7.54 (4H, d, *J* = 4.8 Hz, A part of AA'BB' spectrum), 7.60 (4H, d, *J* = 4.8 Hz, B part of AA'BB' spectrum); ¹³C NMR (CDCl₃, 75 MHz) δ_C –3.74, –2.00, 126.6, 134.5, 138.7, 141.2; UV (CH₂Cl₂) λ_{max} 279 nm; FT-IR (NaCl) 3065.3, 2951.5, 2893.6, 1594.2, 1485.6, 1245.7, 1109.6, 832.5, 796.3 cm⁻¹; MS (70 eV) *m/z* 414 (M⁺); MS *m/z* (%) 414 (M⁺, 26), 341 (100), 283 (79), 267 (13), 253 (14), 224 (9), 131 (17), 116 (35); HRMS (M⁺) calcd for C₂₂H₃₈Si₄ 414.2051, found 414.2079.

Irradiation of 4,4'-bis(pentamethyldisilyl)biphenyl 1 in methanol. A solution (3 × 10⁻² M) of 4,4'-bis(pentamethyldisilyl)biphenyl **1** (0.5 g) in methanol (40 mL) was deaerated by nitrogen purging for 30 min and irradiated in a Rayonet photochemical reactor, model RPR-208, equipped with RUL 254 nm lamps. After irradiation for 38 h, the resulting photoreaction mixture was concentrated *in vacuo*. The photoproducts **3** and **4** were isolated in 101 mg (31% yield) and 45.5 mg (7% yield), respectively, in addition to 8% (40 mg) of the starting compound **1** by column chromatography with *n*-hexane/ethyl acetate (100/1, v/v) as an eluent followed by normal phase HPLC using *n*-hexane/ethyl acetate (40/1, v/v) as an eluent.

3: ¹H NMR (CDCl₃, 300 MHz) δ_H 0.39 (12H, d, *J* = 3.9 Hz), 4.48 (2H, septet, *J* = 3.9 Hz), 7.60–7.64 (8H, m); ¹³C NMR (CDCl₃, 75 MHz) δ_C –3.52, 126.8, 134.8, 136.7, 142.1; UV (CH₂Cl₂) λ_{max} 265 nm; FT-IR (NaCl) 3065.7, 2957.3, 2924.9, 2118.5, 1594.9, 1381.2, 1249.3, 1117.0, 877.5, 807.7 cm⁻¹; MS (70 eV) *m/z* 270 (M⁺); MS *m/z* (%) 270 (M⁺, 7), 269 (27), 213 (16), 212 (100), 166 (8), 75 (9); HRMS (M⁺) calcd for C₁₆H₂₂Si₂ 270.1260, found 270.1221.

4: m.p. 54–56 °C, ¹H NMR (CDCl₃, 300 MHz) δ_H 0.40 (12H, d, *J* = 3.6 Hz), 0.41 (12H, s), 4.50 (2H, septet, *J* = 3.6 Hz), 7.61–7.65 (16H, m); ¹³C NMR (CDCl₃, 75 MHz) δ_C –3.48, 1.20, 126.7, 126.9, 133.8, 134.8, 136.6, 138.9, 142.1, 142.2; UV (CH₂Cl₂) λ_{max} 264 nm; FT-IR (NaCl) 3065.8, 2957.6, 2117.8, 1595.8, 1381.1, 1253.3, 1118.9, 1061.9, 880.5, 831.7, 789.0 cm⁻¹; MS (70 eV) *m/z* 538 (M⁺); MS *m/z* (%) 538 (M⁺, 4), 346 (10), 328 (100), 270 (70), 211 (9), 195 (30); HRMS (M⁺) calcd for C₃₂H₄₂Si₄ 538.2364, found 538.2327.

Irradiation of 4,4'-bis(pentamethyldisilyl)biphenyl 1 in methylene chloride in the presence of acetone. A solution (3 × 10⁻² M) of 4,4'-bis(pentamethyldisilyl)biphenyl **1** (0.5 g) and acetone (4 mL) in methylene chloride (40 mL) was deaerated by nitrogen purging for 30 min, and irradiated in a Rayonet photochemical reactor, model RPR-208, equipped with RUL 254 nm lamps. After irradiation for 38 h, the resulting photoreaction mixture was concentrated *in vacuo*. The photoproducts **3**, **4**, and **5** were isolated in (9.8 mg, 3% yield), (9.7 mg, 1.5% yield), and (51.8 mg, 8% yield), respectively, in addition to 12% (60 mg) of the starting material **1** by column chromatography with *n*-hexane/ethyl

acetate (100/1, v/v) as an eluent followed by normal phase HPLC using *n*-hexane/ethyl acetate (40/1, v/v) as an eluent.

5: m.p. 165–167 °C (decomposed). ¹H NMR (CDCl₃, 300 MHz) δ_H 0.43 (24H, s), 7.06 (8H, d, *J* = 7.8 Hz, A part of AA'BB' spectrum), 7.17 (8H, d, *J* = 7.8 Hz, B part of AA'BB' spectrum); ¹³C NMR (CDCl₃, 75 MHz) δ_C –0.069, 125.9, 133.5, 136.9, 141.6; UV (CH₂Cl₂) λ_{max} 260 nm; FT-IR (NaCl) 3059.0, 2960.0, 2917.0, 2849.1, 1559.0, 1379.7, 1275.2, 1260.9, 1046.4, 792.9, 764.2, 750.0 cm⁻¹; MS (70 eV) *m/z* 536 (M⁺); MS *m/z* (%) 536 (M⁺, 0.6), 342 (13), 328 (100), 270 (76), 212 (8), 196 (34), 149 (5); HRMS (M⁺) calcd for C₃₂H₄₀Si₄ 536.2207, found 536.2272.

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References

- (a) Patai, S.; Rappoport, Z. *The Chemistry of Organic Silicon Compounds*; Wiley: New York, 1989. (b) Rappoport, Z.; Apeloig, Y. *The Chemistry of Organic Silicon Compounds*; Wiley: New York, 1998; vol. 2. (c) Rappoport, Z.; Apeloig, Y. *The Chemistry of Organic Silicon Compounds*; Wiley: New York, 2001; vol. 3. (d) Brook, M. A. *Silicon in Organic, Organometallic, and Polymeric Chemistry*; Wiley: New York, 2000.
- Ishikawa, M.; Fuchikami, T.; Sugaya, T.; Kumada, M. *J. Am. Chem. Soc.* **1975**, *97*, 5923.
- Ishikawa, M.; Fuchikami, T.; Kumada, M. *J. Organomet. Chem.* **1976**, *118*, 155.
- Morkin, T. L.; Leigh, W. J. *Acc. Chem. Res.* **2001**, *34*, 129.
- Leigh, W. J.; Sluggett, G. W. *J. Am. Chem. Soc.* **1994**, *116*, 10468.
- Steinmetz, M. G. *Chem. Rev.* **1995**, *95*, 1527.
- Nate, K.; Ishikawa, M.; Ni, H.; Watanabe, H.; Saheki, Y. *Organometallics* **1987**, *6*, 1673.
- Ohshita, J.; Ohsaki, H.; Ishikawa, M.; Tachibana, A.; Kurosaki, Y.; Yamabe, T.; Minato, A. *Organometallics* **1991**, *10*, 880.
- Takaki, K.; Sakamoto, H.; Nishimura, Y.; Sugihara, Y.; Ishikawa, M. *Organometallics* **1991**, *10*, 888.
- Ohshita, J.; Ohsaki, H.; Ishikawa, M.; Tachibana, A.; Kurosaki, Y.; Yamabe, T.; Tsukihara, T.; Takahashi, K.; Kiso, Y. *Organometallics* **1991**, *10*, 2685.
- Ishikawa, M.; Nishimura, Y.; Sakamoto, H. *Organometallics* **1991**, *10*, 2701.
- Ishikawa, M.; Fuchikami, T.; Kumada, M. *J. Organomet. Chem.* **1977**, *133*, 19.
- Ohshita, J.; Niwa, H.; Ishikawa, M. *Organometallics* **1996**, *15*, 4632.
- Toll, N. P.; Leigh, W. J. *Organometallics* **1996**, *15*, 2554.
- Leigh, W. J.; Sluggett, G. W. *Organometallics* **1994**, *13*, 269.
- Ishikawa, M.; Fuchikami, T.; Kumada, M. *J. Organomet. Chem.* **1976**, *118*, 139.
- Ishikawa, M.; Fuchikami, T.; Kumada, M. *J. Organomet. Chem.* **1978**, *162*, 223.
- Ishikawa, M.; Sakamoto, H.; Kanetani, F.; Minato, A. *Organometallics* **1989**, *8*, 2767.
- Sakurai, H. *J. Organomet. Chem.* **1980**, *200*, 261.
- Guselnikov, L. E.; Nametkin, N. S. *Chem. Rev.* **1979**, *79*, 529.
- Ohshita, J.; Niwa, H.; Ishikawa, M.; Yamabe, T.; Yoshii, T.; Nakamura, K. *J. Am. Chem. Soc.* **1996**, *118*, 6853.
- Ishikawa, M.; Oda, M.; Miyoshi, N.; Fabry, L.; Kumada, M.; Yamabe, T.; Akagi, K.; Fukui, K. *J. Am. Chem. Soc.* **1979**, *101*, 4612.
- Ohshita, J.; Ohsaki, H.; Ishikawa, M. *Organometallics* **1991**, *10*,

- 2695.
24. Sakurai, H.; Nakadaira, Y.; Kira, M.; Sugiyama, H.; Yoshida, K.; Takiguchi, T. *J. Organomet. Chem.* **1980**, *184*, C36.
25. Ishikawa, M.; Fuchikami, T.; Kumada, M. *J. Organomet. Chem.* **1977**, *127*, 261.
26. Ishikawa, M.; Kikuchi, M.; Kunai, A.; Takeuchi, T.; Tsukihara, T.; Kido, M. *Organometallics* **1993**, *12*, 3474.
27. Ishikawa, M.; Kikuchi, M.; Watanabe, K.; Sakamoto, H.; Kunai, A. *J. Organomet. Chem.* **1993**, *443*, C3.
28. Park, S. K. *Bull. Korean Chem. Soc.* **2006**, *27*, 1305.
29. Shim, S. C.; Park, S. K. *Tetrahedron Lett.* **1998**, *39*, 6891.
30. Shim, S. C.; Park, S. K. *Bull. Korean Chem. Soc.* **1998**, *19*, 686.
31. Shim, S. C.; Park, S. K. *Bull. Korean Chem. Soc.* **1999**, *20*, 547.
32. Park, S. K.; Shim, S. C.; Seo, Y. W.; Shin, J. H. *Tetrahedron Lett.* **1999**, *40*, 4575.
33. Park, S. K.; Seo, K. H.; Shim, S. C. *J. Photochem. Photobiol. A: Chem.* **1999**, *127*, 67.
34. Shim, S. C.; Park, S. K. *J. Photosci.* **1999**, *6*, 13.
35. Park, S. K.; Shim, S. C. *J. Photochem. Photobiol. A: Chem.* **2000**, *136*, 219.
36. Park, S. K. *J. Photochem. Photobiol. A: Chem.* **2000**, *135*, 155.
37. Park, S. K. *J. Photochem. Photobiol. A: Chem.* **2001**, *144*, 167.
38. Park, S. K. *Bull. Korean Chem. Soc.* **2001**, *22*, 1202.
39. Park, S. K. *J. Photosci.* **2002**, *9*, 1.
40. Park, S. K.; Baek, D. J. *J. Photochem. Photobiol. A: Chem.* **2002**, *150*, 125.
41. Park, S. K.; Baek, D. J. *J. Photochem. Photobiol. A: Chem.* **2003**, *154*, 145.
42. Park, S. K.; Baek, D. J. *J. Photochem. Photobiol. A: Chem.* **2003**, *157*, 15.
43. Park, S. K.; Baek, D. J. *J. Photochem. Photobiol. A: Chem.* **2004**, *163*, 87.
44. Park, S. K. *J. Photochem. Photobiol. A: Chem.* **2005**, *173*, 29.
45. Kira, M.; Miyazawa, T.; Sugiyama, H.; Yamaguchi, M.; Sakurai, H. *J. Am. Chem. Soc.* **1993**, *115*, 3116.
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