

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

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Received March 23, 2007

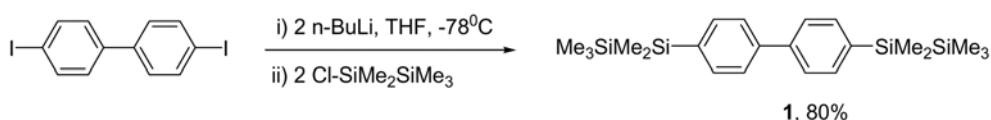
Key Words : 4,4'-Bis(pentamethyldisilanyl)biphenyl, Silene

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

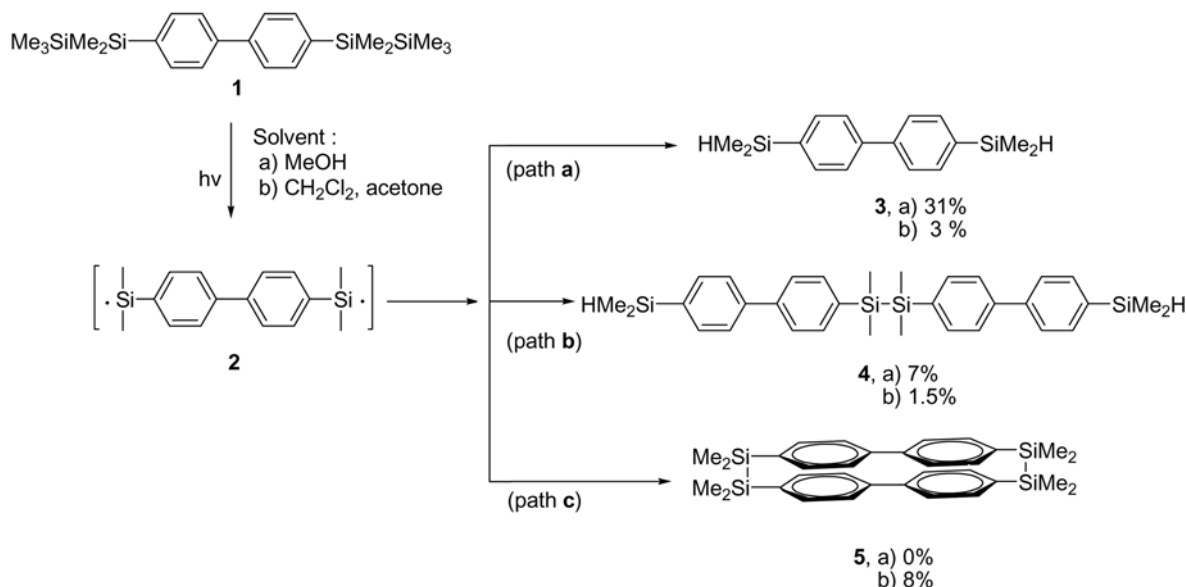
of (2-hydroxymethylphenyl)pentamethyldisilane in methanol provides a novel intramolecular photoproduct *via* silene intermediate arising from 1,3-migration of trimethylsilyl radical, which is formed *via* homolytic cleavage of silicon-silicon σ bond in the disilane moiety upon irradiation to the C₆ position 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 \times 20

mL), washed with water (3×20 mL), and dried with MgSO_4 , 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 (CDCl_3 , 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); ^{13}C NMR (CDCl_3 , 75 MHz) δ_{C} -3.74, -2.00, 126.6, 134.5, 138.7, 141.2; UV (CH_2Cl_2) 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 $\text{C}_{22}\text{H}_{38}\text{Si}_4$ 414.2051, found 414.2079.

Irradiation of 4,4'-bis(pentamethyldisilanyl)biphenyl 1 in methanol. A solution (3×10^{-2} M) of 4,4'-bis(pentamethyldisilanyl)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 (CDCl_3 , 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); ^{13}C NMR (CDCl_3 , 75 MHz) δ_{C} -3.52, 126.8, 134.8, 136.7, 142.1; UV (CH_2Cl_2) 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 $\text{C}_{16}\text{H}_{22}\text{Si}_2$ 270.1260, found 270.1221.

4: m.p. 54–56 °C, ^1H NMR (CDCl_3 , 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); ^{13}C NMR (CDCl_3 , 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 (CH_2Cl_2) 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 $\text{C}_{32}\text{H}_{42}\text{Si}_4$ 538.2364, found 538.2327

Irradiation of 4,4'-bis(pentamethyldisilanyl)biphenyl 1 in methylene chloride in the presence of acetone. A solution (3×10^{-2} M) of 4,4'-bis(pentamethyldisilanyl)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 (CDCl_3 , 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); ^{13}C NMR (CDCl_3 , 75 MHz) δ_{C} -0.069, 125.9, 133.5, 136.9, 141.6; UV (CH_2Cl_2) 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 $\text{C}_{32}\text{H}_{40}\text{Si}_4$ 536.2207, found 536.2272.

Acknowledgements. The author would like to thank Miss Su Yeon Gong at the university of Suwon for helping the preparation of compounds.

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