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

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It is well known that the photolysis of aryldisilanes\(^1\) gave the silenes containing Si=C bond as reaction intermediates since the earliest report on the photolysis of phenylpentamethyldisilane and (p-tolyl)pentamethyldisilane by Ishikawa \textit{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 \(\sigma\) bond in the disilane moiety upon irradiation to the C\(_6\) position of benzene ring.\(^28\) In connection with my continuous studies for the utility of silacycloprenenes,\(^29-43\) 1-silaallenes, and silenes\(^44\) 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
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 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. reported that the photolysis of 4-(trifluoromethyl)phenylpentamethyldisilane in ethanol-hexane mixture affords 4-(trifluoromethyl)phenylpentamethyldisilane, (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)phenylpentamethyldisilane 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 spectrum 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 0.10 (18H, s), 0.38 (12H, s), 7.54 (4H, d, J = 4.8 Hz, A part of AA’BB’ spectrum), 5.60 (2H, d, J = 4.8 Hz, B part of AA’BB’ spectrum); 13C NMR (CDCl3, 75 MHz) δC -3.74, -2.00, 126.6, 134.5, 138.7, 141.2; UV (CH2Cl2) λmax 279 nm; FT-IR (NaCl) 3025.0, 1657.0, 1594.9, 1381.2, 1249.3, 1117.0, 1061.9, 877.5, 807.7 cm\(^{-1}\); MS (70 eV) m/z 536 (M+); MS m/z (%) 538 (M+, 0.6), 342 (10), 270 (3), 247 (4), 223 (5), 195 (11), 171 (15), 153 (19), 135 (22), 117 (26), 99 (29), 81 (32), 63 (35), 45 (38), 27 (41), 19 (44), 11 (47), 5 (50), HRMS (M+) calcd for C16H22Si2 228.0904, found 228.0903.

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, 4, and 5 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 (40/1, v/v) as an eluent followed by normal phase HPLC using n-hexane/ethyl acetate (40/1, v/v) as an eluent.

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 (9.7 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.