

Photoreactions of (2-Acetoxyphenyl)pentamethyldisilane[†]

Seung Ki Park* and Hyun A Kim

Department of Chemistry, College of Natural Sciences, The University of Suwon, Suwon 445-743, Korea

*E-mail: skpark@suwon.ac.kr

Received February 25, 2011, Accepted April 6, 2011

Key Words : (2-Acetoxyphenyl)pentamethyldisilane, Silene

It is well known that the photoreactions of aryldisilanes show four reaction patterns¹ since the first report on the photolysis of phenylpentamethyldisilane and (*p*-tolyl)pentamethyldisilane by Ishikawa *et al.*² in 1975 : (path a) formation of a silene compound *via* elimination of a trimethylsilane³, (path b) formation of a silene compound arising from 1,3-shift of trimethylsilyl radical, which is formed *via* homolytic cleavage of silicon-silicon bond⁴⁻⁹, (path c) formation of a trimethylsilyl compound *via* elimination of a silylene^{10,11}, (path d) formation of a direct solvolysis compound *via* elimination of a trimethylalkoxysilane or pentamethylalkoxydisilane.^{12,13}

Silenes having the C=Si moiety are regarded as highly interesting intermediates. Consequently the synthesis and reactions of silenes as useful intermediates have been extensively investigated.^{14,15} The intermolecular reactions between highly unstable silenes and the compounds containing functional groups such as OH¹⁶⁻²², C=O²³⁻²⁶, and C=C²⁷⁻³¹ bonds resulted in the formation of the addition products.

In connections with the photolysis of aryldisilanes, we recently disclosed the intramolecular reactions between the silene intermediates resulted from the photoreactions of *ortho*-substituted aryldisilanes and *ortho*-substituents to give the novel silicon-containing heterocyclic compounds such as the photoinduced intramolecular reactions of (2-substituted-phenyl)pentamethyldisilanes³², (2-alkoxymethylphenyl)pentamethyldisilanes³³, 2-(pentamethyldisilanyloxy)phenylpentamethyldisilane³⁴ and (2-hydroxyethoxyphenyl)pentamethyldisilane.³⁵ We have also investigated the synthesis of silicon-containing heterocyclic compounds through the intramolecular reactions of silacyclopentene or 1-silaallene moiety with *ortho*-substituents in *ortho*-substituted-phenylethynylpentamethyldisilanes³⁶.

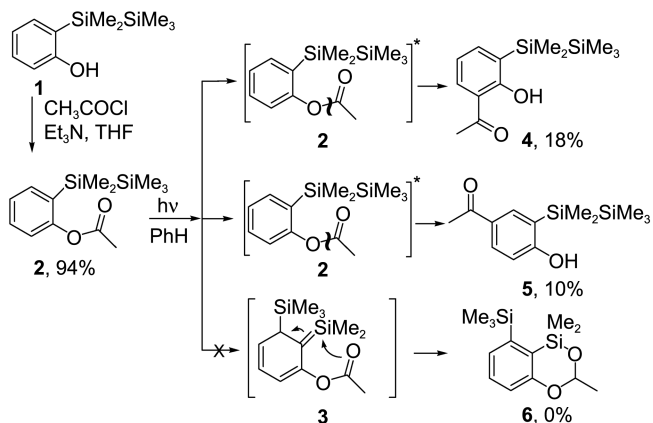
As a part of our continuous studies utilizing the silenes as reaction intermediates for the synthesis of silicon-containing heterocyclic compounds, we investigated the photoreactions of (2-acetoxyphenyl)pentamethyldisilane which has the acetoxy group as *ortho* substituent to phenylpentamethyldisilane because it was expected that the novel photoproducts could be formed from the intramolecular reaction of *ortho*-substituted acetoxy group with the silene intermediate. In this note, we would like to report the detailed photochemical study of (2-acetoxyphenyl)pentamethyldisilane.

The starting (2-acetoxyphenyl)pentamethyldisilane **2** was prepared from the reaction of (2-hydroxyphenyl)pentamethyldisilane **1**³⁵ with acetyl chloride using triethylamine as base in tetrahydrofuran at room temperature (Scheme 1).

In order to investigate a possibility that the C=O bond as *ortho* substituent in **2** reacts intramolecularly with a silene, the photolysis of **2** was performed.

Irradiation of **2** in deaerated benzene with 254nm UV light afforded two photo-Fries rearrangement products **4** (18% yield) and **5** (10% yield) along with some decomposition products of unknown structure as shown in Scheme 1.^{37,38}

However, when 90% of **2** was photolyzed the expected reaction of the C=O bond in *o*-acetoxy group with C=Si bond of silene intermediate in **3** arising from 1,3-migration of trimethylsilyl radical *via* homolytic cleavage of silicon-silicon bond in the pentamethyldisilanyl group of the photo-excited state of **2** to the C₆ position of benzene ring to give the compound **6** was not observed in this photoreaction. In relation to the photolysis of *ortho*-substituted aryldisilane, we found that the photoreaction of (2-allyloxyphenyl)pentamethyldisilane³² in benzene gave a novel intramolecular photoproduct through the reaction between the silene intermediate and *ortho*-substituent, allyloxy group. The photolysis of (2-hydroxymethylphenyl)pentamethyldisilane³³ and (2-acetoxymethylphenyl)pentamethyldisilane³³ also afforded a novel intramolecular photoproducts *via* silene intermediates. In contrast to the photoreaction of (2-allyloxyphenyl)pentamethyldisilane or (2-hydroxymethylphenyl)pentamethyldisilane, desired product **6** *via* the silene intermediate was not



Scheme 1

[†]This paper is dedicated to Professor Eun Lee on the occasion of his honourable retirement.

detected in the photolysis of **2** in deaerated benzene. This observation clearly indicated that the photo-Fries rearrangement reaction is faster than the silene formation in this photoreaction.

The structures of these photoproducts **4** and **5** were determined by various physical methods. The photoproducts **4** and **5** can be distinguished by the proton resonances in the phenyl region and OH peak in $^1\text{H-NMR}$. The $^1\text{H-NMR}$ spectrum of **4** shows the 1,2,3-trisubstituted benzene structure and OH peak at 12.53 ppm, but **5** shows the 1,3,4-trisubstituted benzene structure and OH peak at 1.26 ppm. Appearing at 12.53 ppm is a result of the intramolecular hydrogen bonding between the carbonyl group and the hydroxyl group in **4**.

Irradiation of **2** in deaerated methanol with 254 nm UV light gave three photoproducts **7**, **1**, and **8** (9, 18, and 21% yield, respectively) along with some decomposition products as shown in Scheme 2. When 97% of **2** was photolyzed the expected photoproducts from the reaction of the silene intermediate with the C=O bond as *ortho*-substituent were not obtained, indicating that the photolysis of **2** did not give the silene intermediate in methanol solvent.

Compound **7** was probably formed from the nucleophilic attack at β silicon atom of pentamethyldisilanyl group in the photoexcited state of **2** by methanol and the photo-Fries rearrangement of the acetyl group in **2** to the C₅ position of benzene ring. Compound **1** was formed from the methanolysis of the acetoxy group as *ortho*-substituent group in **2**. The formation of phenol **8** was explained by α silicon atom attack of pentamethyldisilanyl group in the photoexcited state of **2** by methanol and the methanolysis of the acetoxy group in **2**.

The $^1\text{H-NMR}$ and IR absorption spectra of **7** show a septet resonance at 4.50 ppm and a characteristic absorption at 2112.6 cm^{-1} , respectively, due to a Si-H proton and a Si-H stretching mode in the dimethylsilyl group of **7**.

In contrast to the photolysis of **2** in a deaerated benzene, the photolysis of **2** in a deaerated methanol provided more methanolysis products **1** and **8** than the photo-Fries rearrangement product **7**, indicating that the methanolysis reaction about the acetoxy group in **2** is much more reactive than the

photo-Fries rearrangement reaction in methanol solvent.

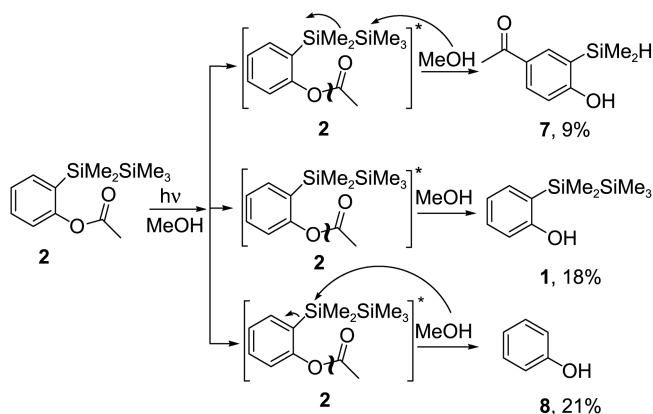
In conclusion, the photoreaction of **2** in a deaerated benzene provided **4** and **5** via a photo-Fries rearrangement reaction but the expected photoproduct from the intramolecular reaction between the C=Si moiety and *ortho*-substituent, C=O group was not obtained. The photolysis of **2** in a deaerated methanol gave a photoproduct **7** via β silicon atom attack of pentamethyldisilanyl group by methanol and the photo-Fries rearrangement and compounds **1** and **8** but the expected photoproducts from the silene intermediate was also not obtained in this photoreaction.

Experimental

Synthesis of (2-Acetoxyphenyl)pentamethyldisilane 2. Triethylamine (0.46 mL, 3.3 mmol) was added to a solution of (2-hydroxyphenyl)pentamethyldisilane **1** (0.5 g, 2.2 mmol) in tetrahydrofuran (20 mL) at 0 °C under nitrogen atmosphere. Acetyl chloride (0.3 mL, 4.4 mmol) was added dropwise to the resulting solution and the mixture was stirred at room temperature for 2 h. Water (30 mL) was added to the solution and extracted with ethyl acetate (3 \times 10 mL). The combined ethyl acetate solution was washed with water (20 mL), brine (20 mL) and dried (MgSO_4). The solvent was evaporated in vacuo to give the crude product. Flash column chromatography with *n*-hexane/ethyl acetate (5/1, v/v) as an eluent gave **2** (0.56 g, 94% yield) as a colorless oil; $^1\text{H-NMR}$ (CDCl_3 , 300 MHz) δ_{H} 0.09 (9H, s), 0.35 (6H, s), 2.32 (3H, s), 7.08 (1H, dd, $J=7.5, 1.5$ Hz), 7.22 (1H, td, $J=7.5, 1.5$ Hz), 7.38 (1H, td, $J=7.5, 1.5$ Hz), 7.44 (1H, dd, $J=7.5, 1.5$ Hz); $^{13}\text{C-NMR}$ (CDCl_3 , 75 MHz) δ_{C} -3.35, -1.78, 21.8, 122.1, 125.7, 130.1, 130.9, 135.6, 155.6, 169.7; UV (CH_2Cl_2) λ_{max} 274 nm; FT-IR (NaCl) 3066.1, 2952.4, 2895.4, 1768.1, 1246.8, 1179.5, 1074.5, 834.1 cm^{-1} ; MS (70 eV) m/z 266 (M^+); MS m/z (%) 266 (M^+ , 1.3), 251(30), 227 (15), 209 (50), 193 (100), 151 (14), 73 (16); HRMS (M^+) calcd for $\text{C}_{13}\text{H}_{22}\text{O}_2\text{Si}_2$ 266.1158, found 266.1182.

Irradiation of (2-Acetoxyphenyl)pentamethyldisilane 2 in benzene. A solution (5×10^{-4} M) of (2-acetoxyphenyl)pentamethyldisilane **2** (133 mg) in benzene (1 L) 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 2.5 h, the resulting photoreaction mixture was concentrated in vacuo. The photoproducts **4** and **5** were isolated in 24 mg (18% yield) and 13 mg (10% yield), respectively, in addition to 13 mg (10% yield) of the starting compound **2** by column chromatography with *n*-hexane/ethyl acetate (5/1, v/v) as an eluent followed by normal phase HPLC using *n*-hexane/ethyl acetate (3/1, v/v) as an eluent.

4: $^1\text{H-NMR}$ (CDCl_3 , 300 MHz) δ_{H} 0.053 (9H, s), 0.33 (6H, s), 2.63 (3H, s), 6.88 (1H, t, $J=7.5$ Hz), 7.53 (1H, dd, $J=7.5, 1.5$ Hz), 7.72 (1H, dd, $J=7.5, 1.5$ Hz), 12.53 (1H, s); $^{13}\text{C-NMR}$ (CDCl_3 , 75 MHz) δ_{C} -3.77, -1.72, 29.8, 118.9, 129.4, 131.5, 137.1, 142.3, 166.8, 204.9; UV (CH_2Cl_2) λ_{max} 257, 335 nm; FT-IR (NaCl) 3456.1, 2952.5, 2926.5, 1634.4, 1410.7, 1242.9, 835.1 cm^{-1} ; MS (70 eV) m/z 266 (M^+); MS



Scheme 2

m/z (%) 266 (M^+ , 23), 265 (93), 251 (66), 211 (23), 193 (68), 149 (100), 131 (15), 73 (14); HRMS (M^+) calcd for $C_{13}H_{22}O_2Si_2$ 266.1158, found 266.1104.

5: 1H -NMR ($CDCl_3$, 300 MHz) δ_H 0.065 (9H, s), 0.37 (6H, s), 1.26 (1H, s), 2.55 (3H, s), 6.74 (1H, d, $J=8.4$ Hz), 7.85 (1H, dd, $J=8.4, 2.4$ Hz), 7.97 (1H, d, $J=2.4$ Hz); ^{13}C -NMR ($CDCl_3$, 75 MHz) δ_C -3.28, -1.31, 26.8, 114.5, 126.1, 130.4, 132.1, 137.2, 165.5, 198.2; UV (CH_2Cl_2) λ_{max} 269 nm; FT-IR (NaCl) 3327.6, 2956.3, 1657.5, 1576.5, 1252.5, 832.1 cm^{-1} ; MS (70 eV) m/z 266 (M^+); MS m/z (%) 266 (M^+ , 28), 265 (100), 249 (14), 225 (23), 193 (42), 149 (21), 73 (9); HRMS (M^+) calcd for $C_{13}H_{22}O_2Si_2$ 266.1158, found 266.1131.

Irradiation of (2-Acetoxyphenyl)pentamethyldisilane 2 in methanol. A solution (5×10^{-4} M) of (2-acetoxyphenyl)pentamethyldisilane **2** (133 mg) in methanol (1 L) 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 1h, the resulting photoreaction mixture was concentrated in *vacuo*. The photoproducts **7**, **1** and **8** (phenol) were isolated in 9 mg (9% yield), 20 mg (18% yield) and 10 mg (21% yield), respectively, in addition to 4 mg (3% yield) of the starting compound **2** by column chromatography with *n*-hexane/ethyl acetate (5/1, v/v) as an eluent followed by normal phase HPLC using *n*-hexane/ethyl acetate (3/1, v/v) as an eluent.

7: 1H -NMR ($CDCl_3$, 300 MHz) δ_H 0.39 (6H, d, $J=3.6$ Hz), 1.25 (1H, s), 2.58 (3H, s), 4.50 (1H, septet, $J=3.6$ Hz), 6.82 (1H, d, $J=8.7$ Hz), 7.91 (1H, dd, $J=8.7, 2.1$ Hz), 8.07 (1H, d, $J=2.1$ Hz); ^{13}C -NMR ($CDCl_3$, 75 MHz) δ_C -3.92, 26.5, 114.5, 123.4, 129.8, 132.6, 137.5, 165.5, 198.1; UV (CH_2Cl_2) λ_{max} 267 nm; FT-IR (NaCl) 3674.7, 3120.3, 2962.1, 2112.6, 1649.8, 1561.1, 1353.8, 1260.3, 881.3 cm^{-1} ; MS (70 eV) m/z 194 (M^+); MS m/z (%) 194 (M^+ , 19), 193 (100), 169 (9), 149 (13), 135 (17); HRMS (M^+) calcd for $C_{10}H_{14}O_2Si$ 194.0763, found 194.0711.

References

- Kira, M.; Miyazawa, T.; Sugiyama, H.; Yamaguchi, M.; Sakurai, H. *J. Am. Chem. Soc.* **1993**, *115*, 3116.
- Ishikawa, M.; Fuchikami, T.; Sugaya, T.; Kumada, M. *J. Am. Chem. Soc.* **1975**, *97*, 5923.
- Nate, K.; Ishikawa, M.; Ni, H.; Watanabe, H.; Saheki, Y. *Organometallics* **1987**, *6*, 1673.
- Ishikawa, M.; Fuchikami, T.; Kumada, M. *J. Organomet. Chem.* **1976**, *118*, 139.
- Ishikawa, M.; Fuchikami, T.; Kumada, M. *Tetrahedron Lett.* **1976**, 1299.
- Ishikawa, M.; Fuchikami, T.; Kumada, M. *J. Organomet. Chem.* **1978**, *162*, 223.
- 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.; Tachibana, A.; Kurosaki, Y.; Yamabe, T.; Minato, A. *Organometallics* **1991**, *10*, 880.
- Ohshita, J.; Ohsaki, H.; Ishikawa, M. *Organometallics* **1991**, *10*, 2695.
- Ishikawa, M. *Pure Appl. Chem.* **1978**, *50*, 11.
- Kira, M.; Sakamoto, K.; Sakurai, H. *J. Am. Chem. Soc.* **1983**, *105*, 7469.
- Okinoshima, H.; Weber, W. P. *J. Organomet. Chem.* **1978**, *149*, 279.
- Park, S. K. *Bull. Korean Chem. Soc.* **2007**, *28*, 1045.
- Park, S. K.; Gong, S. Y. *Bull. Korean Chem. Soc.* **2010**, *31*, 731.
- Ishikawa, M.; Fuchikami, T.; Kumada, M. *J. Organomet. Chem.* **1977**, *127*, 261.
- 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.
- 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.
- Tolft, N. P.; Leigh, W. J. *Organometallics* **1996**, *15*, 2554.
- Leigh, W. J.; Sluggett, G. W. *Organometallics* **1994**, *13*, 269.
- Ishikawa, M.; Sakamoto, H.; Kanetani, F.; Minato, A. *Organometallics* **1989**, *8*, 2767.
- Sakurai, H. *J. Organomet. Chem.* **1980**, *200*, 261.
- Gusel'nikov, 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.
- Sakurai, H.; Nakadaira, Y.; Kira, M.; Sugiyama, H.; Yoshida, K.; Takiguchi, T. *J. Organomet. Chem.* **1980**, *184*, C36.
- Park, S. K. *J. Photochem. Photobiol. A: Chem.* **2005**, *173*, 29.
- Park, S. K. *Bull. Korean Chem. Soc.* **2006**, *27*, 1305.
- Park, S. K. *Bull. Korean Chem. Soc.* **2008**, *29*, 1018.
- Park, S. K.; Seong, W. J. *Bull. Korean Chem. Soc.* **2009**, *30*, 1331.
- Park, S. K.; Baek, D. J. *J. Photochem. Photobiol. A: Chem.* **2004**, *163*, 87 and references cited therein.
- Anderson, J. C.; Reese, C. B. *Proc. Chem. Soc.* **1960**, 217.
- Anderson, J. C.; Reese, C. B. *J. Chem. Soc.* **1963**, 1781.