



ELSEVIER

Available online at www.sciencedirect.com

SCIENCE @ DIRECT®

Journal of Organometallic Chemistry 685 (2003) 162–167

Journal
of Organo
metallic
Chemistrywww.elsevier.com/locate/jorganchem

Silicon–carbon unsaturated compounds. 68. Reactions of silenes produced thermally and photochemically from acylpolysilanes with diketones

Akinobu Naka, Mitsuo Ishikawa *

Department of Chemistry and Bioscience, Kurashiki University of Science and the Arts, 2640 Nishinoura, Tsurajima-cho, Kurashiki, Okayama 712-8505, Japan

Received 15 November 2002; received in revised form 25 February 2003; accepted 5 March 2003

Abstract

The reactions of the silenes produced thermally from $(\text{Me}_3\text{Si})_3\text{SiCOR}$ (**1a–1d**; R = *t*-Bu, Ad, Ph, and Mes) with benzil in a sealed glass tube at 140 °C gave the respective five-membered cyclic compounds, 2,5-dioxa-1-silacyclopent-3-enes (**2a–2d**) in high yields. The silenes from **1a–d** also reacted with 4,4'-dimethylbenzil to give the 2,5-dioxa-1-silacyclopent-3-ene derivatives. The photolysis of **1a** and **1b** in the presence of benzil in a benzene solution gave the respective products, 3,6-dioxa-1-silacyclohex-4-enes (**3a** and **3b**) arising from [2+4] cycloaddition in high yields. The thermolysis of **3a** and **3b** in a sealed tube at 140 °C afforded **2a** and **2b**, respectively, in quantitative yields.

© 2003 Elsevier Science B.V. All rights reserved.

Keywords: Silenes; Acylpolysilanes; Thermolysis; Photolysis; Diketones

1. Introduction

In the past decade, we have studied the thermal reactions of acylpolysilanes and found that the thermolysis of these compounds proceeds cleanly to give the silenes, which react readily with alkenes, dienes, alkynes, and diynes [1,2]. The reactions of silenes produced from pivaloyl- and adamantoyl-tris(trimethylsilyl)silane with alkenes and dienes afforded the adducts arising from formal [2+2] and [2+4] cycloaddition, respectively, together with the ene-type adducts [2a]. While with alkynes and diynes, the silacyclobutene derivatives were obtained as a result of [2+2] cycloaddition of the silenes to a triple bond [2c,2d,2e,2f].

The silenes also reacted with ketones to give various types of the products depending upon the structure of the ketones used [2b]. With acetone, the silenes gave the cyclopropane derivatives and silyl enol ethers, respectively. The formation of both types of compounds can

be best understood in terms of isomerization of the siloxetanes formed from formal [2+2] cycloaddition of the silenes to a carbonyl group in acetone. Similar reactions with benzophenone afforded the silyl enol ethers and cyclohepta-2,4,6-triene derivatives originated from the [2+2] and [2+4] adducts.

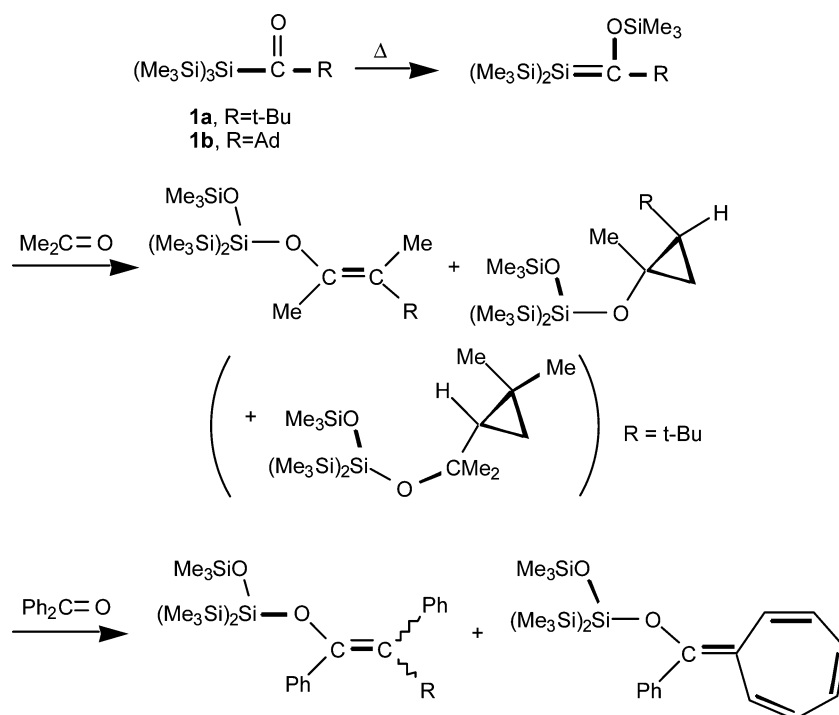
In order to learn more about chemical behavior of the silenes produced thermally from acylpolysilanes toward carbonyl compounds, we investigated the co-thermolysis of the acylpolysilanes with diketones. In this paper we report the thermolysis of pivaloyl-, adamantoyl-, benzoyl-, and mesitoyl-tris(trimethylsilyl)silane with benzil and 4,4'-dimethylbenzil.

2. Results and discussion

When the co-thermolysis of pivaloyl-tris(trimethylsilyl)silane (**1a**) with benzil was carried out in a sealed tube at 140 °C for 12 h, 1-[(*tert*-butyl)bis(trimethylsilyl)methyl]-3,4-diphenyl-1-trimethylsiloxy-2,5-dioxa-1-silacyclopent-3-ene (**2a**) was obtained in 67% yield, along with an 18% recovery of the starting compound

* Corresponding author. Tel.: +81-864401086; fax: +81-864401062.

E-mail address: mishika@chem.kusa.ac.jp (M. Ishikawa).

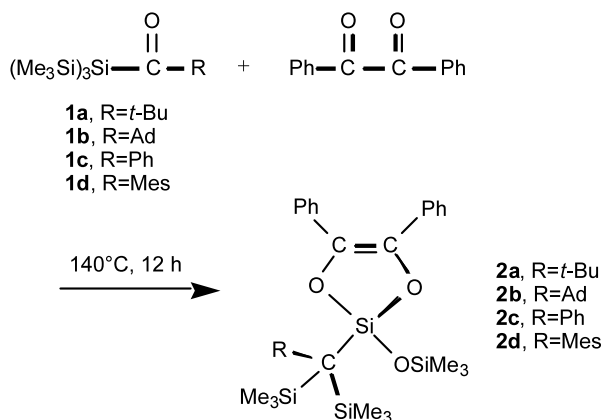


1a (Scheme 1). The $^1\text{H-NMR}$ spectrum of **2a** shows the presence of three resonances at δ 0.12, 0.34, and 1.34 ppm, due to two kinds of trimethylsilyl protons and *tert*-butyl protons, as well as multiple resonances in the phenyl region. The $^{13}\text{C-NMR}$ spectrum of **2a** reveals resonances attributed to two kinds of trimethylsilyl carbons, one quaternary sp^3 carbon, a single resonance of olefinic carbons, two resonances of *tert*-butyl carbons, and four resonances of phenyl carbons. Its $^{29}\text{Si-NMR}$ spectrum indicates the presence of three kinds of silicon atoms at -31.5 , -0.6 , and 12.7 ppm. These results are wholly consistent with the structure proposed

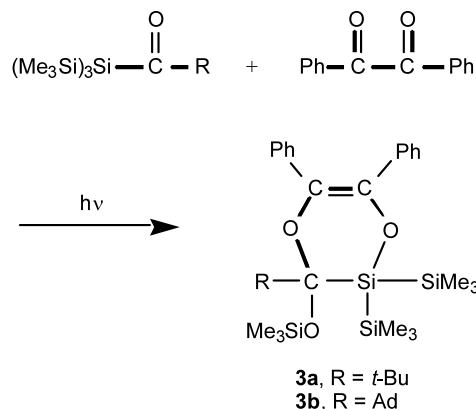
for **2a**. Similar reaction of adamantoyltris(trimethylsilyl)silane (**1b**) with benzil proceeded cleanly to give a product analogous to **2a**, 1-[(adamantyl)bis(trimethylsilyl)methyl]-3,4-diphenyl-1-trimethylsiloxy-2,5-dioxolane-2-ene (**2b**) in 90% isolated yield. No other volatile products were detected in the reaction mixture.

The reaction of benzoyltris(trimethylsilyl)silane (**1c**) with benzil proceeded in the same fashion as those of acylpolysilanes **1a** and **1b** to give an adduct. Thus, the thermolysis of **1c** with benzil at 140°C for 24 h afforded 3,4-diphenyl-1-[(phenyl)bis(trimethylsilyl)methyl]-1-trimethylsiloxy-2,5-dioxolane-2-ene (**2c**) in 66% yield. Again, no other isomers were detected by spectroscopic analysis of the reaction mixture. Mesityltris(trimethylsilyl)silane (**1d**) also reacted with benzil under the same conditions to give 1-[(mesityl)bis(trimethylsilyl)methyl]-3,4-diphenyl-1-trimethylsiloxy-2,5-dioxolane-2-ene (**2d**) in 44% yield as the sole product, in addition to 42% of the starting compound **1d**.

In order to get more information concerning the formation of products **2a–2d**, we investigated the photolysis of **1a** and **1b** with benzil. In marked contrast to the thermal reaction of the acylpolysilanes with benzil, in which 2,5-dioxolane-2-enes are formed, photochemically generated silene gives six-membered cyclic compound, arising from [2+4] cycloaddition. Thus, irradiation of **1a** in the presence of



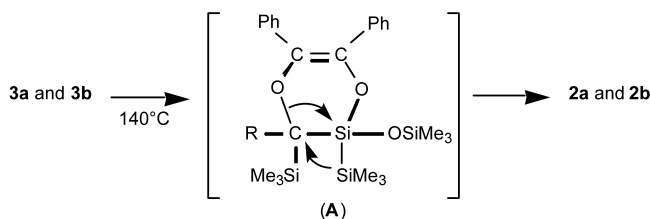
Scheme 1.



Scheme 2.

benzil in benzene-*d*₆ afforded 2-*tert*-butyl-4,5-diphenyl-2-trimethylsilyloxy-1,1-bis(trimethylsilyl)-3,6-dioxo-1-silacyclohex-4-ene (**3a**) in 91% yield (Scheme 2). The ¹H-NMR spectrum of **3a** shows three resonances at 0.23, 0.28, and 0.29 ppm due to two kinds of trimethylsilyl protons and one trimethylsilyloxy protons, as well as protons attributed to the *tert*-butyl and phenyl groups. The ¹³C-NMR spectrum of **3a** reveals resonances due to three trimethylsilyl carbons, two *tert*-butyl carbons, one sp³ ring carbon, in addition to phenyl and olefinic carbons. Its ²⁹Si-NMR spectrum indicates the presence of four nonequivalent silicon atoms at -24.9, -21.0, 3.2, and 10.4 ppm. These results are wholly consistent with the structure proposed for **3a**. Similar photolysis of **3b** under the same conditions again gave a [2+4] cycloadduct, 3,6-dioxo-1-silacyclohex-4-ene (**3b**) in 93% yield. The structure of **3b** was verified by spectrometric analysis, as well as elemental analysis.

To our surprise, when **3a** and **3b** were heated in a sealed glass tube at 140 °C for 12 h, isomerized products **2a** and **2b** were obtained quantitatively. These results indicate that the formation of **2a–2d** in the co-thermolysis of **1a–1d** with benzil may be best explained by thermal isomerization of the dioxasilacyclohex-4-ene derivatives analogous to **3** once formed. A possible mechanism for the formation of **2a** and **2b** from **3a** and **3b** is shown in Scheme 3. At first, a 1,2-shift of a trimethylsilyloxy group on the sp³ ring carbon in **3** to the ring silicon occurs, accompanying a 1,2-trimethylsilyl shift from the ring silicon to the ring carbon to give 4,5-diphenyl-1-trimethylsilyloxy-1,2-bis(trimethylsilyl)-3,4-di-

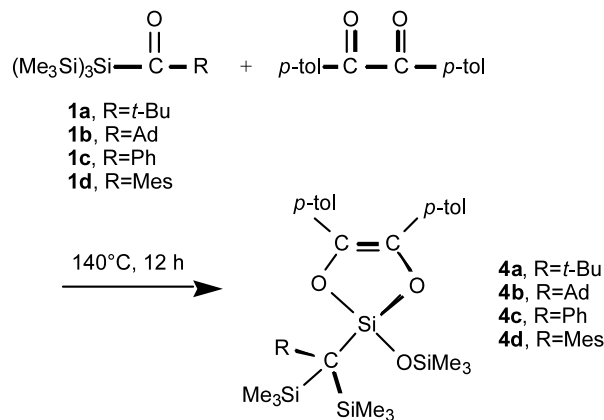


Scheme 3.

oxa-1-silacyclohex-4-ene (**A**). Unfortunately, evidence for the production of **A** in the thermolysis of **1** with benzil has not yet been obtained at present. However, such intramolecular exchange reaction between trimethylsilyloxy and trimethylsilyl group has been observed in the thermolysis of 2,3-di(*tert*-butyl)-2-(trimethylsilyloxy)-1,1-bis(trimethylsilyl)-1-silacyclobut-3-ene **3a** and 2-adamantyl-4,5-dimethyl-2-trimethylsilyloxy-1,1-bis(trimethylsilyl)-1-silacyclohex-4-ene **3b**. Finally, ring contraction of **A** would afford the observed product, 2,5-dioxo-1-silacyclopent-3-ene **2**.

Next, we carried out the reaction of **1a–1d** with 4,4'-dimethylbenzil in a sealed glass tube under the same conditions. The co-thermolysis of **1a** with 4,4'-dimethylbenzil at 140 °C for 24 h again gave 1-[(*tert*-butyl)bis(trimethylsilyl)methyl]-3,4-di(*p*-tolyl)-1-trimethylsilyloxy-2,5-dioxo-1-silacyclopent-3-ene (**4a**) in 63% yield, along with a 27% recovery of the starting acylpolysilane **1a**. Similarly, the reaction of **1b** with 4,4'-dimethylbenzil produced 2-[(adamantyl)bis(trimethylsilyl)methyl]-4,5-(*p*-tolyl)-2-trimethylsilyloxy-1,3-dioxo-2-silacyclopent-4-ene (**4b**) in 90% yield (Scheme 4). Compound **1c** and **1d** also reacted with 4,4'-dimethylbenzil under the same conditions to give 2-[(phenyl)bis(trimethylsilyl)methyl]-4,5-(*p*-tolyl)-2-trimethylsilyloxy-1,3-dioxo-2-silacyclopent-4-ene (**4c**) and 2-[(mesityl)bis(trimethylsilyl)methyl]-2-trimethylsilyloxy-4,5-(*p*-tolyl)-1,3-dioxo-2-silacyclopent-4-ene (**4d**) in 77 and 23% yields, respectively. The structures of **4a–4d** were verified by spectrometric analysis, as well as by elemental analysis (see Section 3).

The reactions of the present silenes with aliphatic diketones such as diacetyl, 3,4-hexanedione, and bipivaloyl gave complex mixtures. The reactions of **1a–1d** with diacetyl and 3,4-hexanedione in a sealed glass tube at 140 °C for 12 h afforded many volatile products. Presumably, enolization of the ketones is involved, and enols would also act as the reagents. The reactions of **1a–1d** with bipivaloyl, however, gave nonvolatile products. GLC analysis of the reaction mixture showed no



Scheme 4.

appreciable amount of volatile products except for a small amount of unchanged bipivaloyl.

In conclusion, the co-thermolysis of acylpolysilanes **1a–1d** with benzil and 4,4'-dimethylbenzil at 140 °C afforded the respective dioxasilacyclopentene derivatives **2a–2d** and **4a–4d**. The photolysis of **1a** and **1b** in the presence of benzil gave the 3,6-dioxa-1-silacyclohex-4-ene derivatives whose thermolysis produced **2a** and **2b** quantitatively.

3. Experimental

3.1. General procedure

All thermal reactions of acylpolysilanes **1a–1d** with diketones were carried out in a degassed sealed tube (1.0 cm × 15 cm). A 100-W mercury lamp was used for the photolysis experiment. Yields of the products were calculated on the basis of the isolated products. NMR spectra were recorded on JNM-LA300 spectrometer and JNM-LA500 spectrometer. Infrared spectra were recorded on a JEOL Model JIR-DIAMOND 20 infrared spectrophotometer. Low-resolution mass spectra were measured on a JEOL Model JMS-700 instrument. Column chromatography was performed by using Wakogel C-300 (WAKO).

3.2. Materials

Acylpolysilanes **1a** [4], **1b** [5], **1c** [4], **1d** [6] were prepared according to the method reported by Brook et al.

3.3. Thermolysis of **1a** with benzil

A mixture of 0.0820 g (0.246 mmol) of **1a** and 0.0630 g (0.300 mmol) of benzil was heated in a sealed glass tube at 140 °C for 12 h. Product **2a** (0.0899 g, 67% isolated yield) and the starting compound **1a** (0.0151 g, 18%) were isolated by column chromatography: MS *m/z* 542 [M^+]; IR 2956, 2900, 1600, 1498, 1446, 1259, 1062, 1041, 1022, 935, 902, 863, 840, 755 cm^{-1} ; $^1\text{H-NMR}$ $\delta(\text{CDCl}_3)$ 0.12 (s, 9H, Me_3Si), 0.34 (s, 18H, Me_3Si), 1.34 (s, 9H, *t*-Bu), 7.18–7.26 (m, 6H, phenyl ring protons), 7.42–7.44 (m, 4H, phenyl ring protons); $^{13}\text{C-NMR}$ $\delta(\text{CDCl}_3)$ 1.49, 5.22 (Me_3Si), 22.64 ($\text{C}(\text{SiMe}_3)_2$), 33.50 (Me_3C), 37.10 (CMe_3), 127.05, 127.32, 128.09, 133.47 (phenyl ring carbons), 136.69 (olefinic carbons); $^{29}\text{Si-NMR}$ $\delta(\text{CDCl}_3)$ –31.5, –0.6, 12.7. Anal. Calc. for $\text{C}_{28}\text{H}_{46}\text{O}_3\text{Si}_4$: C, 61.93; H, 8.54%. Found: C, 61.88; H, 8.24%.

3.4. Thermolysis of **1b** with benzil

A mixture of 0.0792 g (0.193 mmol) of **1b** and 0.0415 g (0.197 mmol) of benzil was heated at 140 °C for 12 h. Product **2b** (0.1077 g, 90% isolated yield) was isolated by column chromatography: MS *m/z* 620 [M^+]; IR 3054, 2956, 2906, 2848, 1600, 1498, 1446, 1261, 1064, 1041, 1022, 937, 906, 844, 755, 734 cm^{-1} ; $^1\text{H-NMR}$ $\delta(\text{CDCl}_3)$ 0.19 (s, 9H, Me_3Si), 0.42 (s, 18H, Me_3Si), 1.67–2.20 (m, 15H, Ad), 7.24–7.32 (m, 6H, phenyl ring protons), 7.48–7.50 (m, 4H, phenyl ring protons); $^{13}\text{C-NMR}$ $\delta(\text{CDCl}_3)$ 1.52, 5.79 (Me_3Si), 26.13 ($\text{C}(\text{SiMe}_3)_2$), 29.84, 36.57, 40.30, 43.42 (Ad), 127.08, 127.28, 128.09, 133.54 (phenyl ring carbons), 136.74 (olefinic carbons); $^{29}\text{Si-NMR}$ $\delta(\text{CDCl}_3)$ –31.3, –1.4, 12.3. Anal. Calc. for $\text{C}_{34}\text{H}_{52}\text{O}_3\text{Si}_4$: C, 65.75; H, 8.44%. Found: C, 65.77; H, 8.22%.

3.5. Thermolysis of **1c** with benzil

A mixture of 0.0452 g (0.128 mmol) of **1c** and 0.0288 g (0.137 mmol) of benzil was heated at 140 °C for 12 h. Product **2c** (0.0473 g, 66% isolated yield) was isolated by column chromatography: MS *m/z* 562 [M^+]; IR 3054, 2956, 2898, 1596, 1498, 1444, 1257, 1157, 1064, 1049, 1024, 935, 902, 838, 755 cm^{-1} ; $^1\text{H-NMR}$ $\delta(\text{CDCl}_3)$ 0.14 (s, 9H, Me_3Si), 0.27 (s, 18H, Me_3Si), 7.15 (t, 1H, phenyl ring proton, $J = 7.3$ Hz), 7.27–7.34 (m, 8H, phenyl ring protons), 7.52–7.57 (m, 6H, phenyl ring protons); $^{13}\text{C-NMR}$ $\delta(\text{CDCl}_3)$ 1.33, 1.96 (Me_2Si), 24.40 ($\text{C}(\text{SiMe}_3)_2$), 124.15, 127.13, 127.47, 127.87, 128.15, 131.33, 133.24, 136.99, 139.74 (phenyl ring and olefinic carbons); $^{29}\text{Si-NMR}$ $\delta(\text{CDCl}_3)$ –34.2, 2.0, 13.8. Anal. Calc. for $\text{C}_{30}\text{H}_{42}\text{O}_3\text{Si}_4$: C, 64.00; H, 7.52%. Found: C, 64.30; H, 7.50%.

3.6. Thermolysis of **1d** with benzil

A mixture of 0.0770 g (0.195 mmol) of **1d** and 0.0430 g (0.205 mmol) of benzil was heated at 140 °C for 12 h. Product **2d** (0.0520 g, 44% isolated yield) and the starting compound **1d** (0.0326 g, 42%) were isolated by column chromatography: MS *m/z* 604 [M^+]; IR 3027, 2956, 2919, 2890, 1600, 1448, 1263, 1064, 1024, 939, 885, 844, 754 cm^{-1} ; $^1\text{H-NMR}$ $\delta(\text{CDCl}_3)$ 0.11 (s, 9H, Me_3Si), 0.31 (s, 18H, Me_3Si), 2.23 (s, 3H, Me–Ar), 2.66 (s, 6H, Me–Ar), 6.82 (s, 2H, H–Ar), 7.21–7.29 (m, 6H, phenyl ring protons), 7.47–7.49 (m, 4H, phenyl ring protons); $^{13}\text{C-NMR}$ $\delta(\text{CDCl}_3)$ 1.39, 5.82 (Me_2Si), 20.03 (Me–Ar), 25.07 ($\text{C}(\text{SiMe}_3)_2$), 26.59 (Me–Ar), 126.93, 127.23, 128.06, 131.17, 133.33, 133.39, 136.87, 136.91, 139.48 (phenyl and mesityl ring and olefinic carbons); $^{29}\text{Si-NMR}$ $\delta(\text{CDCl}_3)$ –36.2, 4.1, 12.6. Anal. Calc. for $\text{C}_{33}\text{H}_{48}\text{O}_3\text{Si}_4$: C, 65.51; H, 8.00%. Found: C, 65.31; H, 8.16%.

3.7. Photolysis of **1a** with benzil

A solution of 0.0646 g (0.194 mmol) of **1a** and 0.0424 g (0.202 mmol) of benzil in 0.3 ml of benzene-*d*₆ was placed in an NMR tube with a rubber septum cap. This tube was irradiated over 12 h, by which time NMR spectra indicated the absence of starting material. The mixture was analyzed by NMR spectra as being **3a**. Product **3a** (0.0963 g, 91%) were isolated by column chromatography. For **3a**: MS *m/z* 542 [M^+]; IR 3054, 2954, 2898, 1612, 1494, 1444, 1263, 1133, 1056, 1025, 923, 844, 754, 696 cm^{-1} ; ¹H-NMR $\delta(\text{CDCl}_3)$ 0.23 (s, 9H, Me₃Si), 0.28 (s, 9H, Me₃Si), 0.29 (s, 9H, Me₃Si), 1.22 (s, 9H, *t*-Bu), 7.11–7.31 (m, 10H, phenyl ring protons); ¹³C-NMR $\delta(\text{CDCl}_3)$ –1.23, 2.47, 2.97 (Me₃Si), 28.36 (Me₃C), 38.04 (CMe₃), 82.58 (CO), 126.27, 126.91, 127.47, 127.58, 128.65, 129.64, 131.75, 137.48, 137.60, 138.14 (phenyl and olefinic carbons); ²⁹Si-NMR $\delta(\text{CDCl}_3)$ –24.9, –21.0, 3.2, 10.4. Anal. Calc. for C₂₈H₄₆O₃Si₄: C, 61.93; H, 8.54%. Found: C, 61.67; H, 8.24%.

3.8. Thermolysis of **3a** at 140 °C

Compound **3a** (0.0453 g, 0.0834 mmol) was heated in a sealed glass tube at 140 °C for 12 h. The mixture was analyzed by NMR spectra as being **2a**. Product **2a** (0.0450 g, 99%) were isolated by column chromatography. All spectral data obtained for **2a** were identical with those of an authentic sample obtained from the above reaction.

3.9. Photolysis of **1b** with benzil

A solution of 0.0565 g (0.138 mmol) of **1b** and 0.0286 g (0.136 mmol) of benzil in 0.3 ml of benzene-*d*₆ was placed in an NMR tube with a rubber septum cap. This tube was irradiated over 12 h, by which time NMR spectra indicated the absence of starting material. The mixture was analyzed by NMR spectra as being **3**. Product **3** (0.0799 g, 93%) were isolated by column chromatography. For **3**: MS *m/z* 620 [M^+]; IR 2948, 2904, 2848, 1612, 1444, 1261, 1054, 1024, 842, 755, 694 cm^{-1} ; ¹H-NMR $\delta(\text{CDCl}_3)$ 0.24 (s, 9H, Me₃Si), 0.30 (s, 9H, Me₃Si), 0.32 (s, 9H, Me₃Si), 1.71–2.04 (m, 15H, Ad), 7.10–7.32 (m, 10H, phenyl ring protons); ¹³C-NMR $\delta(\text{CDCl}_3)$ –1.09, 2.47, 3.58 (Me₃Si), 28.92, 36.99, 40.35, 40.54 (Ad), 84.58 (CO), 126.26, 126.85, 127.48, 127.55, 128.70, 129.66, 131.97, 137.41 (2C), 138.20 (phenyl and olefinic carbons); ²⁹Si-NMR $\delta(\text{CDCl}_3)$ –25.7, –20.8, 2.8, 10.2. Anal. Calc. for C₃₄H₅₂O₃Si₄: C, 65.75; H, 8.44%. Found: C, 65.55; H, 8.14%.

3.10. Thermolysis of **3b** at 140 °C

Compound **3** (0.0510 g, 0.0822 mmol) was heated in a sealed glass tube at 140 °C for 12 h. The mixture was analyzed by NMR spectra as being **2b**. Product **2b** (0.0501 g, 98%) were isolated by column chromatography. All spectral data obtained for **2b** were identical with those of an authentic sample obtained from the above reaction.

3.11. Thermolysis of **1a** with 4,4'-dimethylbenzil

A mixture of 0.0442 g (0.133 mmol) of **1a** and 0.0332 g (0.139 mmol) of 4,4'-dimethylbenzil was heated in a sealed glass tube at 140 °C for 12 h. Product **4a** (0.0482 g, 63% isolated yield) and the starting compound **1a** (0.0121 g, 27%) were isolated by column chromatography: MS *m/z* 570 [M^+]; IR 2956, 2919, 1610, 1515, 1255, 1058, 1039, 1018, 935, 904, 863, 842, 755 cm^{-1} ; ¹H-NMR $\delta(\text{CDCl}_3)$ 0.15 (s, 9H, Me₃Si), 0.36 (s, 18H, Me₃Si), 1.36 (s, 9H, *t*-Bu), 2.35 (s, 6H, Me–Ar), 7.09 (d, 4H, phenylene ring protons, *J* = 8.3 Hz), 7.36 (d, 4H, phenylene ring protons, *J* = 8.3 Hz); ¹³C-NMR $\delta(\text{CDCl}_3)$ 1.47, 5.21 (Me₃Si), 21.27 (Me–Ar), 22.64 (C(SiMe₃)₂), 33.50 (Me₃C), 37.09 (CMe₃), 126.93, 128.78, 130.77, 136.26, 136.94 (phenylene ring and olefinic carbons); ²⁹Si-NMR $\delta(\text{CDCl}_3)$ –31.6, –0.7, 12.5. Anal. Calc. for C₃₀H₅₀O₃Si₄: C, 63.10; H, 8.83%. Found: C, 63.00; H, 8.50%.

3.12. Thermolysis of **1b** with 4,4'-dimethylbenzil

A mixture of 0.0691 g (0.168 mmol) of **1b** and 0.0465 g (0.195 mmol) of 4,4'-dimethylbenzil was heated at 140 °C for 12 h. Product **4b** (0.0983 g, 90% isolated yield) was isolated by column chromatography: MS *m/z* 648 [M^+]; IR 2956, 2906, 2848, 1608, 1515, 1448, 1253, 1060, 1037, 1018, 935, 906, 842, 734 cm^{-1} ; ¹H-NMR $\delta(\text{CDCl}_3)$ 0.18 (s, 9H, Me₃Si), 0.41 (s, 18H, Me₃Si), 1.66–1.74 (m, 6H, Ad), 2.03 (br s, 3H, Ad), 2.19 (br s, 6H, Ad), 2.37 (s, 6H, Me–Ar), 7.11 (d, 4H, phenylene ring protons, *J* = 8.2 Hz), 7.39 (d, 4H, phenylene ring protons, *J* = 8.2 Hz); ¹³C-NMR $\delta(\text{CDCl}_3)$ 1.51, 5.78 (Me₃Si), 21.28 (Me–Ar), 26.06 (C(SiMe₃)₂), 29.84, 36.58, 40.27, 43.40 (Ad), 126.94, 128.78, 130.84, 136.31, 136.89 (phenylene ring and olefinic carbons); ²⁹Si-NMR $\delta(\text{CDCl}_3)$ –31.3, –1.4, 2.1. Anal. Calc. for C₃₆H₅₆O₃Si₄: C, 66.61; H, 8.69%. Found: C, 66.23; H, 8.68%.

3.13. Thermolysis of **1c** with 4,4'-dimethylbenzil

A mixture of 0.0459 g (0.130 mmol) of **1c** and 0.0311 g (0.131 mmol) of 4,4'-dimethylbenzil was heated at 140 °C for 12 h. Product **4c** (0.0595 g, 77% isolated yield) was isolated by column chromatography: MS *m/z*

590 [M⁺]; IR 3054, 3029, 2956, 2898, 1608, 1515, 1498, 1253, 1058, 1045, 935, 904, 840, 755 cm⁻¹; ¹H-NMR δ(CDCl₃) 0.12 (s, 9H, Me₃Si), 0.26 (s, 18H, Me₃Si), 2.38 (s, 6H, Me–Ar), 7.13–7.16 (m, 5H, phenyl and phenylene ring protons), 7.28 (m, 2H, phenyl ring protons), 7.42 (d, 4H, phenyl ring protons, *J* = 8.2 Hz), 7.55 (d, 2H, phenyl ring protons, *J* = 8.2 Hz); ¹³C-NMR δ(CDCl₃) 1.32, 1.92 (Me₂Si), 21.13 (Me–Ar), 24.32 (C(SiMe₃)₂), 124.06, 126.98, 127.83, 128.85, 130.51, 131.34, 136.53, 137.12, 139.82 (phenyl and phenylene ring and olefinic carbons); ²⁹Si-NMR δ(CDCl₃) –34.3, 2.0, 13.6. Anal. Calc. for C₃₂H₄₆O₃Si₄: C, 65.03; H, 7.84%. Found: C, 65.00; H, 7.77%.

3.14. Thermolysis of **1d** with benzil

A mixture of 0.0788 g (0.200 mmol) of **1d** and 0.0580 g (0.243 mmol) of benzil was heated at 140 °C for 12 h. Product **4d** (0.0286 g, 23% isolated yield) and the starting compound **1d** (0.0492 g, 62%) were isolated by column chromatography: MS *m/z* 632 [M⁺]; IR 2958, 2919, 1610, 1515, 1263, 1091, 1058, 1018, 937, 887, 846, 798, 755 cm⁻¹; ¹H-NMR δ(CDCl₃) 0.10 (s, 9H, Me₃Si), 0.30 (s, 18H, Me₃Si), 2.19 (s, 3H, Me–Ar), 2.34 (s, 6H, Me–Ar), 2.65 (s, 6H Me–Ar), 6.81 (s, 2H, H–Ar), 7.08 (d, 4H, phenylene ring protons, *J* = 8.2 Hz), 7.36 (d, 4H, phenylene ring protons, *J* = 8.2 Hz); ¹³C-NMR δ(CDCl₃) 1.38, 5.80 (Me₂Si), 20.03 (Me–Ar), 21.29 (Me–Ar), 25.04 (C(SiMe₃)₂), 26.59 (Me–Ar), 126.80, 128.76, 130.68, 131.15, 133.27, 136.48, 136.87, 136.94, 139.51 (phenylene and mesityl ring and olefinic carbons); ²⁹Si-NMR δ(CDCl₃) –36.2, 4.1, 12.5. Anal.

Calc. for C₃₅H₅₂O₃Si₄: C, 66.40; H, 8.28%. Found: C, 66.44; H, 8.16%.

Acknowledgements

This work was supported by a Grant-in Aid for Scientific Research (No. 14750687) from the Ministry of Education, Science, Sports, and Culture of Japan to which our thanks are due.

References

- [1] (a) A.G. Brook, *J. Organomet. Chem.* 300 (1986) 21; (b) A.G. Brook, in: S. Patai, Z. Rappoport (Eds.), *The Chemistry of Organic Silicon Compounds; Part 2* (Chapter 15), Wiley, New York, 1989 (Chapter 15).
- [2] (a) M. Ishikawa, S. Matsui, A. Naka, J. Ohshita, *Main Group Chem.* 1 (1996) 219; (b) M. Ishikawa, S. Matsui, A. Naka, J. Ohshita, *Organometallics* 15 (1996) 3836; (c) A. Naka, M. Ishikawa, S. Matsui, J. Ohshita, A. Kunai, *Organometallics* 15 (1996) 5759; (d) A. Naka, M. Ishikawa, *J. Organomet. Chem.* 611 (2000) 248; (e) A. Naka, M. Ishikawa, *Organometallics* 19 (2000) 4921; (f) A. Naka, M. Ishikawa, *Chem. Lett.* (2002) 364.
- [3] (a) A. Naka, J. Ikadai, S. Motoike, K. Yoshizawa, Y. Kondo, S.-Y. Kang, M. Ishikawa, *Organometallics* 21 (2002) 2033; (b) A. Naka, M. Ishikawa, manuscript in preparation.
- [4] A.G. Brook, J.W. Harris, J. Lennon, M. Elsheikh, *J. Am. Chem. Soc.* 101 (1979) 83.
- [5] A.G. Brook, S.C. Nyburg, F. Abdesaken, B. Gutekunst, G. Gutekunst, R. Krishna, M.R. Kallury, Y.C. Poon, Y.-M. Chan, W. Wong-Ng, *J. Am. Chem. Soc.* 104 (1982) 5667.
- [6] A.G. Brook, H.-J. Wessely, *Organometallics* 4 (1985) 1487.