

## Silicon–carbon unsaturated compounds. 73. Photolysis of *cis*- and *trans*-1,2-dimethyl-1,2-diphenyl-1,2-disilacyclohexane in the presence of *tert*-butyl alcohol and acetone

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### Abstract

Irradiation of *cis*-1,2-dimethyl-1,2-diphenyl-1,2-disilacyclohexane (**1a**) in the presence of *tert*-butyl alcohol in hexane with a low-pressure mercury lamp bearing a Vycor filter proceeded with high stereospecificity to give *cis*-2,3-benzo-1-*tert*-butoxy-1,4-dimethyl-4-phenyl-1,4-disilacyclooct-2-ene (**2a**), in 33% isolated yield, together with a 15% yield of 1-[(*tert*-butoxy)methylphenylsilyl]-4-(methylphenylsilyl)butane (**3**). The photolysis of *trans*-1,2-dimethyl-1,2-diphenyl-1,2-disilacyclohexane (**1b**) with *tert*-butyl alcohol under the same conditions gave stereospecifically *trans*-2,3-benzo-1-*tert*-butoxy-1,4-dimethyl-4-phenyl-1,4-disilacyclooct-2-ene (**2b**) in 41% isolated yield, along with a 12% yield of **3**. Similar photolysis of **1a** and **1b** with *tert*-butyl alcohol-*d*<sub>1</sub> produced **2a** and **2b**, respectively, in addition to 1-[(*tert*-butoxy)(monodeuteriomethyl)(phenyl)silyl]-4-(methylphenylsilyl)butane. When **1a** and **1b** were photolyzed with acetone in a hexane solution, *cis*- and *trans*-2,3-benzo-1-isopropoxy-1,4-dimethyl-4-phenyl-1,4-disilacyclooct-2-ene (**4a** and **4b**) were obtained in 25% and 23% isolated yield. In both photolyses, 1-(hydroxymethylphenylsilyl)-4-(methylphenylsilyl)butane (**5**) was also isolated in 4% and 5% yield, respectively. The photolysis of **1a** with acetone-*d*<sub>6</sub> under the same conditions gave **4a-d**<sub>6</sub> and **5-d**<sub>1</sub> in 18% and 4% yields. © 2006 Elsevier B.V. All rights reserved.

**Keywords:** Photochemical reaction; Stereochemistry; *cis*- and *trans*-Disilacyclohexane; Rearranged silenes

### 1. Introduction

Previously, we reported that the photolysis of arylsilylanes afforded rearranged silenes arising from migration of a terminal silyl group onto the *ortho* carbon atom in the aryl ring, and the silenes thus formed react with various substrates to give the ene-type adducts as the main products [1,2]. Subsequently, we investigated the photolysis of *meso*- and *rac*-1,2-diethyl-1,2-dimethyl-1,2-diphenyldisilane and found that the rearranged silenes react stereospecifically with olefins, such as isobutene, 1,1-diphenylethylene, and 2,3-dimethylbutadiene to give the respective ene-type adducts [3]. With carbonyl compounds, however, the rearranged silenes proceed with stereoselectivity, but not stereospecificity, to give the respective adducts [4]. Since that time,

many papers concerning the photochemistry and photophysics of the benzenoid arylsilylanes have been published to date [5,6]. In spite of these studies, no interest has been shown in the photolysis of aryl-substituted 1,2-disilacycloalkanes.

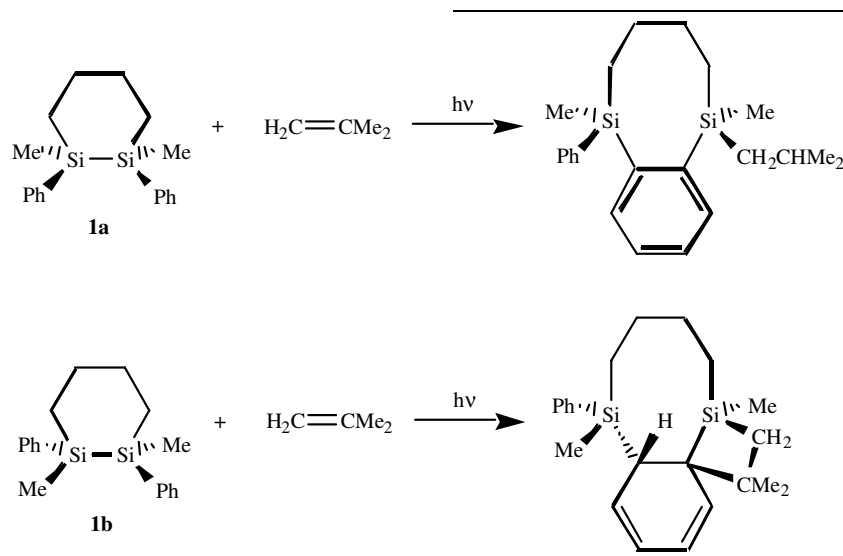
Recently, we have found that the photolysis of *cis*- and *trans*-1,2-dimethyl-1,2-diphenyl-1,2-disilacyclohexane (**1a** and **1b**) affords the rearranged silenes, which react stereospecifically with isobutene to give the adducts [7]. The structures of the adducts thus obtained, however, differ from each other. Thus, the photolysis of **1a** with isobutene produced the ene-type adduct, *cis*-2,3-benzo-1-isobutyl-1,4-dimethyl-4-phenyl-1,4-disilacyclooct-2-ene, as the main product, while **1b** under the same conditions gave formal [2 + 2] cycloadduct with *trans*-configuration.

In contrast to the disilacyclohexane system, the photolysis of *trans*-1,2-dimethyl-1,2-diphenyl-1,2-disilacyclopen-

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tane in the presence of isobutene proceeded to give the *cis*-ene-type adduct and *trans*-[2 + 2] adduct, while the photolysis of *cis*-isomer with isobutene under the same conditions afforded the *cis*-ene adduct with high stereospecificity, in addition to a small amount of the *cis*-[2 + 2] adduct [8]. The photolysis of the *cis*-disilacyclopentane derivative with *tert*-butyl alcohol, however, gave *cis*- and *trans*-2,3-benzo-1-*tert*-butoxy-1,4-dimethyl-4-phenyl-1,4-disilacyclohept-2-ene, which were produced by addition of *tert*-butyl alcohol to the resulting two types of the rearranged silenes, followed by elimination of a hydrogen molecule from the adducts, in a ratio of 4:1. Similar photolysis of the *trans*-disilacyclopentane derivative afforded the same mixture, *cis*- and *trans*-addition/elimination product in the ratio of 1:4.



In order to learn more about the stereochemistry in the reactions of the rearranged silenes with substrates, we have investigated the photolysis of *cis*- and *trans*-1,2-dimethyl-1,2-diphenyl-1,2-disilacycloalkanes with various substrates, such as alkenes, alcohols, and carbonyl compounds. In this paper, we report the photolysis of **1a** and **1b** with *tert*-butyl alcohol and acetone.

## 2. Results and discussion

### 2.1. Photolysis of *cis*- and *trans*-1,2-dimethyl-1,2-diphenyl-1,2-disilacyclohexane with *tert*-butyl alcohol

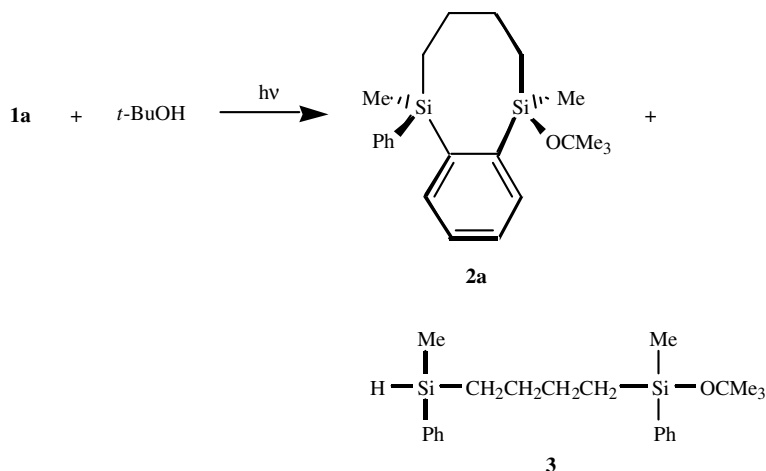
A mixture consisting of *cis*- and *trans*-1,2-dimethyl-1,2-diphenyl-1,2-disilacyclohexane **1a** and **1b** [9] was prepared by the condensation reaction of 1,4-bis(chloromethylphenylsilyl)butane with finely cut lithium metal in the presence of a catalytic amount of dimethylphenylsilyl lithium in THF [10]. Pure *cis*- and *trans*-1,2-disilacyclohexane **1a** and **1b** were isolated by fractional distillation of the mixture, using a spinning band column, as reported previously [7].

First, we carried out the photolysis of **1a** and **1b** in the presence of *tert*-butyl alcohol as a trapping agent in a hexane solution. Thus, irradiation of *cis*-isomer **1a** with a low-pressure mercury lamp bearing a Vycor filter at room temperature in the presence of ca. 10-fold excess of *tert*-butyl alcohol gave two products, *cis*-2,3-benzo-1-*tert*-butoxy-1,4-dimethyl-4-phenyl-1,4-disilacyclooct-2-ene (**2a**) and 1-[(*tert*-butoxy)(methyl)(phenyl)silyl]-4-(methylphenylsilyl)butane (**3**) in 33% and 15% isolated yields, respectively, in addition to 4% of the unchanged starting compound **1a** as shown in Scheme 1. In this photolysis, nonvolatile substances were produced in 15 wt% yield. The product **2a** was readily separated from **3** by recycling HPLC, after treatment of the photolysis mixture with a short silica-gel

column, using hexane as the eluent. Careful spectrometric analysis of the reaction mixture showed that no other stereoisomers for **2a** were detected.

The structures of **2a** and **3** were confirmed by mass and  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{29}\text{Si}$  NMR spectrometric analysis. The *cis*-configuration for **2a** was verified by NOE-FID difference experiments at 300 MHz. Thus, saturation of the *tert*-butoxy protons at 1.06 ppm reveals a strong enhancement of the resonance at 0.56 ppm, attributed to the methyl protons on the silicon atom bearing the *tert*-butoxy group, as well as the methylene protons at 2.00–2.11 ppm and the phenyl protons at 7.38–7.42 ppm. However, no enhancement of the resonance at 0.54 ppm, due to the methyl protons on the silicon atom at the 4-position in the 2,3-benzo-1,4-disilacyclooct-2-ene ring was observed. These results clearly indicate that two methyl groups on the different silicon atoms in **2a** are located *cis* each other and the photolysis of **1a** proceeds with high stereospecificity to give the *cis*-isomer **2a**.

We have reported that the photolysis of *cis*- and *trans*-1,2-dimethyl-1,2-diphenyl-1,2-disilacyclohexane gives two types of the rearranged silenes, which can be produced by



Scheme 1.

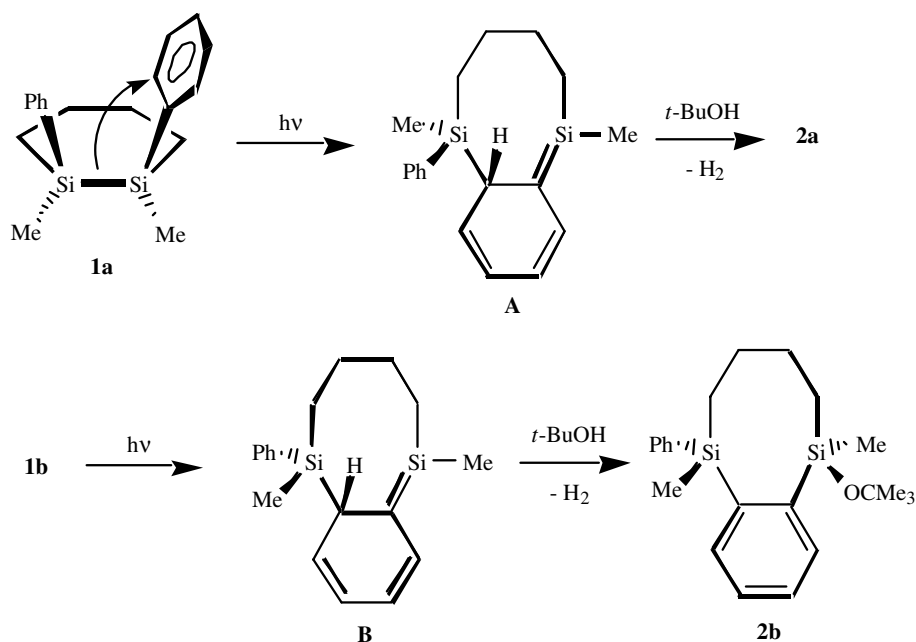
a 1,3-shift of one silyl group onto two *ortho* positions of the phenyl group in the other silyl moiety [8]. In the presence of *tert*-butyl alcohol, two-types of the rearranged silenes thus formed react stereospecifically with *tert*-butyl alcohol to give *cis*- and *trans*-2,3-benzo-1-(*tert*-butoxy)-1,4-dimethyl-4-phenyl-1,4-disilacyclohept-2-ene, respectively. In the photolysis of *cis*- and *trans*-disilacyclohexane **1a** and **1b**, however, a 1,3-silyl shift would occur exclusively at one of two *ortho* positions in the phenyl ring and produce a single silene, silene (A) from **1a** and silene (B) from **1b**, which reacts stereospecifically with a trapping agent to give the addition/elimination product.

The formation of **2a** may be best explained by *syn* addition of *tert*-butyl alcohol to a silicon-carbon double bond from the opposite side of the methylphenylsilyl group in the rearranged silene A formed photochemically from **1a**.

The *syn* elimination of a hydrogen molecule from the cyclohexadienyl ring in the resulting adduct, restoring the aromatic sextet, produces **2a** as a single geometrical isomer as shown in Scheme 2.

The *syn* additions of *tert*-butyl alcohol to the silenes are general reactions and well-known to date [8,11,12,14a].

It has been reported that the rearranged silenes generated photochemically from acyclic aryldisilanes react with alcohol in a different fashion from that of the 1,2-disilacycloalkanes [12–14]. Thus, the rearranged silenes formed from aryldisilanes react with methyl alcohol and *tert*-butyl alcohol to give 1-alkoxysilyl-2-silyl-substituted cyclohexadienes, arising from 1,4- and 1,6-addition of alcohol to the rearranged silenes [13], together with the addition/elimination products, 1-alkoxysilyl-2-silyl-substituted arenes. The reaction of the silene A with *tert*-butyl alcohol,



Scheme 2.

however, product **2a**, originating from 1,2-addition of **A** with alcohol, followed by elimination of the hydrogen molecule was obtained, as the sole product. No 1,4- and 1,6-adduct were detected by spectrometric analysis. These results are consistent with those observed in the photolysis of the *cis*- and *trans*-1,2-disilacyclopentane derivative with *tert*-butyl alcohol.

As mentioned above, in the photolysis of **1a**, only one silene, the silene **A**, is produced. The absence of the 1,3-silyl shift to the other *ortho* carbon in the phenyl ring, leading to the isomer of the silene **A** may be ascribed to the steric congestion between the migrating silyl group and the ring methylene groups. Such steric congestion for disilacyclohexane system may be expected to be much larger than that for the disilacyclopentane system.

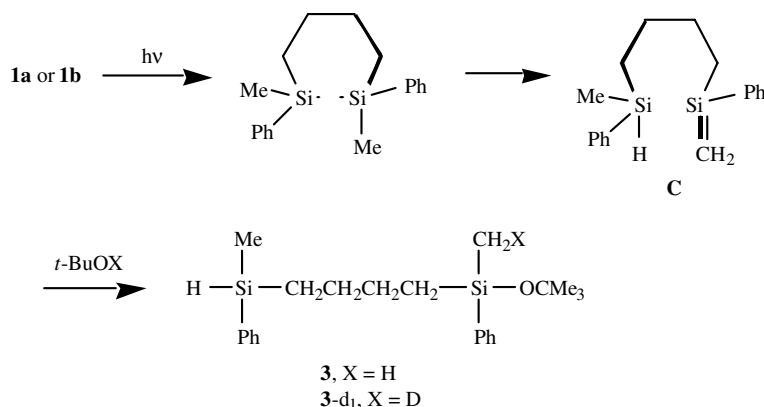
The production of **3** may be understood in terms of homolytic scission of a silicon–silicon bond in **1a**, followed by disproportionation of the resulting diradical species, leading to silene (**C**), different from the silene **A**. The addition of *tert*-butyl alcohol to the silene **C** would afford the product **3** (Scheme 3). To confirm this, we carried out the photolysis of **1a** with deuterated alcohol. Thus, irradiation of a hexane solution of **1a** in the presence of *tert*-butyl alcohol- $d_1$  again afforded two types of the products, the ene-adduct **2a** and 1-[(*tert*-butoxy)(monodeuteriomethyl)(phenyl)silyl]-4-(methylphenylsilyl)butane (**3-d<sub>1</sub>**), derived from homolytic scission of a silicon–silicon bond in **1a**, in 33% and 3% isolated yields, along with 4% of the unchanged starting compound **1a**. No deuterium atom was detected in **2a** by mass and spectrometric analysis, showing that an H–D molecule was eliminated from the *tert*-butyl alcohol- $d_1$ -adduct. However, for **3-d<sub>1</sub>**, the presence of the monodeuteriomethyl group was observed by mass and,  $^2\text{H}$  and  $^{13}\text{C}$  NMR spectrometric analysis. The  $^{13}\text{C}$  NMR spectrum for **3-d<sub>1</sub>** reveals a singlet at  $-5.69$  ppm and a triplet at  $-0.99$  ppm ( $J_{\text{C-D}} = 18.3$  Hz), due to MeSi and  $\text{DCH}_2\text{Si}$  carbons, respectively, in addition to resonances attributed to the other carbons, indicating that *tert*-butyl alcohol- $d_1$  adds across the silicon–carbon double bond. These results clearly indicate that the photolysis of **1a** produces two types of the silenes, **A** and **C**.

Irradiation of **1b** in the presence of *tert*-butyl alcohol in a hexane solution under the same conditions gave *trans*-2,3-benzo-1-*tert*-butoxy-1,4-dimethyl-4-phenyl-1,4-disilacyclooct-2-ene (**2b**) and **3** in 41% and 12% isolated yields, together with 11% of the unchanged starting compound **1b**. No other isomers for **2b** were detected in the reaction mixture by spectrometric analysis. The structure of **2b** was verified by spectrometric analysis, as well as by elemental analysis. The *trans* configuration of **2b** was confirmed by NOE-FID difference experiments at 300 MHz. Thus, saturation of a resonance at 1.29 ppm due to *tert*-butoxy protons led to enhancement of two resonances at 0.46 and 0.50 ppm, attributed to two different kinds of the methylsilyl protons, as well as the resonances due to the ring methylene protons and phenyl protons. Irradiation of the resonance at 0.46 ppm, attributable to one of the methylsilyl protons, however, resulted in no enhancement of the resonance at 0.50 ppm, due to the methylsilyl protons on the phenyl-substituted silicon atom. This result clearly indicates that **2b** must be a *trans* form. All spectral data for **3** obtained in this photolysis are identical with those of the product formed in the photolysis of **1a** with *tert*-butyl alcohol.

Similar photolysis of **1b** with *tert*-butyl alcohol- $d_1$  afforded **2b** and **3-d<sub>1</sub>** in 33% and 10% yields, in addition to 10% of the starting compound **1b**. Again, no deuterium atom in **2b** was detected, indicating that *syn*-elimination of an H–D molecule from the resulting *tert*-butyl alcohol- $d_1$ -adduct took place. On the other hand, all spectral data including  $^2\text{H}$  and  $^{13}\text{C}$  NMR spectra for **3-d<sub>1</sub>** are identical with those of the ring-opened product obtained from the photolysis of **1a** with *tert*-butyl alcohol- $d_1$ .

## 2.2. Photolysis of **1a** and **1b** with acetone

We carried out the photochemical reactions of **1a** and **1b** with acetone to confirm whether or not the reactions proceed stereospecifically to give the adducts. Thus, when a hexane solution of **1a** in the presence of a large excess of acetone was irradiated with a low-pressure mercury lamp, two products, *cis*-2,3-benzo-1-isopropoxy-1,4-dimethyl-4-



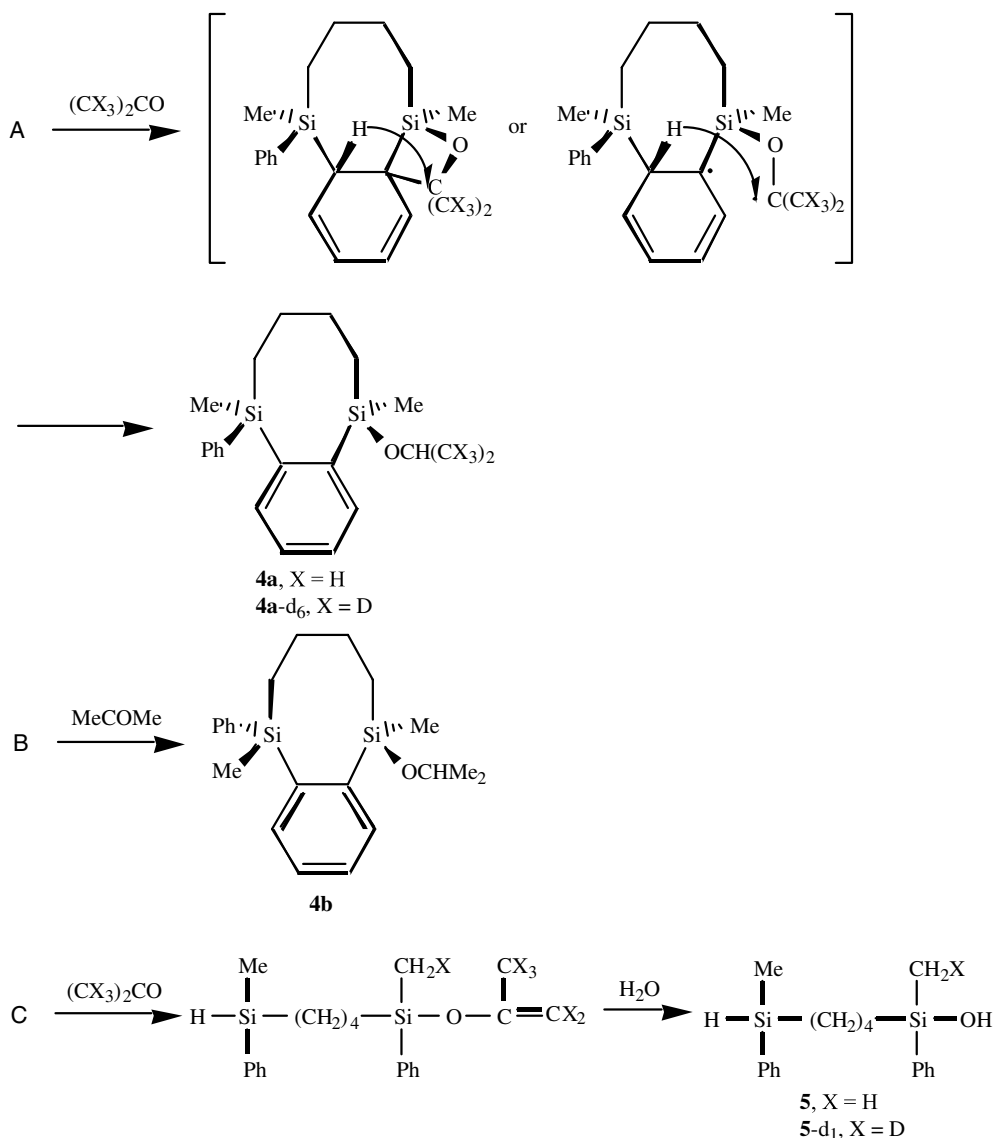
Scheme 3.

phenyl-1,4-disilacyclooct-2-ene (**4a**) and 1-(hydroxymethylphenylsilyl)-4-(methylphenylsilyl)butane (**5**) were obtained in 25% and 4% isolated yields, respectively, in addition to 29% of the unchanged starting compound **1a** as shown in Scheme 4.

The structures of **4a** and **5** were verified by mass and  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{29}\text{Si}$  NMR spectrometric analysis. The configuration of **4a** was confirmed by NOE-FID difference experiments at 300 MHz. Thus, saturation of a resonance at 3.88 ppm, due to a hydrogen atom on the secondary carbon of the isopropoxy group resulted in a strong enhancement of the resonances at 0.49 ppm, and 0.86 and 1.03 ppm, attributed to the methyl protons on the same silicon atom as the isopropoxy group and isopropoxy methyl groups, as well as the phenyl protons. No enhancement of the resonance at 0.54 ppm, due to the methyl protons on the silicon atom bearing a phenyl group was observed. These results clearly indicate that the product **4a** must have the *cis*-configuration.

The formation of **4a** may be explained by formal [2 + 2] cycloaddition of the silene **A** with acetone, followed by an H-shift from cyclohexadienyl ring to a dimethyl substituted carbon atom in the oxasilacyclobutane ring. Similar 1,3-hydrogen shifts in the [2 + 2] cycloadducts, arising from the photolysis of *trans*-1,2-dimethyl-1,2-diphenyl-1,2-disilacyclohexane and *cis*- and *trans*-1,2-dimethyl-1,2-diphenyl-1,2-disilacyclopentane with isobutene, leading to the 2,3-benzo-1,4-disilacycloalkene derivatives have already been reported [7,8]. In contrast, the production of **5** may be best understood by the ene-type reaction of the silene **C** with acetone, followed by decomposition of the resulting adduct to the observed product **5** during isolation of the adduct. Similar decomposition of the isopropenyloxysilane to the silanol derivative has also been observed in our previous study [8].

To confirm the mechanism proposed for the formation of **4a** and **5**, we carried out the photolysis of **1a** with acetone- $\text{d}_6$ . Thus, irradiation of **1a** in the presence of



Scheme 4.



acetone- $d_6$  in a hexane solution under the same conditions afforded **4a-d<sub>6</sub>** and **5-d<sub>1</sub>** in 18% and 4% yields, respectively, along with 30% of the unchanged starting compound **1a**. These results are wholly consistent with the proposed mechanism.

In the photolysis of acyclic aryldisilanes with acetone, the formation of the unstable [2 + 2] cycloadducts, siloxetane derivatives, has been reported by Leigh and co-workers [6f,14b]. However, all attempts to detect the siloxetane derivative in the present photolysis were unsuccessful, but the formation of **4a** and **5** were always observed.

Similar irradiation of **1b** in the presence of a large excess of acetone in hexane with a low-pressure mercury lamp again proceeded with high stereospecificity to give *trans*-1-isopropoxy-1,4-dimethyl-4-phenyl-1,4-disilacyclooct-2-ene (**4b**) and **5** in 23% and 5% yields, respectively, together with 10% of the unchanged starting compound **1b**. The structures of **4b** and **5** were verified by mass and,  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{29}\text{Si}$  NMR spectrometric analysis. The *trans*-configuration of **4b** was confirmed by NOE-FID difference experiments at 300 MHz. Thus, irradiation of a resonance at 4.07 ppm, due to a hydrogen on the secondary carbon atom in the isopropoxy group showed a strong enhancement of the resonances at 0.39 and 0.50 ppm, attributed to the methyl protons on two different silicon atoms, as well as two doublet resonances at 1.16 and 1.22 ppm, due to the isopropoxy methyl groups. The result indicates that the product **4b** must be a *trans* form.

In conclusion, the photolysis of **1a** and **1b** with a low-pressure mercury lamp in hexane produced the rearranged silene, **A** and **B**, respectively, in addition to silene **C**, arising from homolytic scission of a silicon–silicon bond in the starting disilacyclohexanes, followed by disproportionation of the resulting diradical species. The silene, **A** and **B** reacted stereospecifically with *tert*-butyl alcohol and acetone to give the *cis*- and *trans*-addition/elimination products, **2a** and **2b**, and the H-migration products, **4a** and **4b**, respectively. The reaction of the silene **C** with *tert*-butyl alcohol afforded the adduct **3**, while with acetone, the silene **C** gave the silanol derivative **5**, derived from decomposition of the resulting ene-adduct.

### 3. Experimental

#### 3.1. General procedure

All photolyses were carried out under an atmosphere of dry argon. NMR spectra were measured on a JNM-LA300 spectrometer and JNM-LA500 spectrometer. Infrared spectra were recorded on a JEOL Model JIR-DIAMOND 20 Infrared spectrophotometer. Mass spectra were measured on a JEOL Model JMS-700 instrument. Pure *cis*- and *trans*-1,2-dimethyl-1,2-diphenyl-1,2-disilacyclohexane were separated by a TSA-SB2 spinning band-type distillation column (Taika Kogyo). Column chromatography was performed by using Wakogel C-300 (WAKO). Gel permeation chromatographic separation was carried out with

the use of a Model LC-908 Recycling Preparative HPLC (Japan Analytical Industry Co. Ltd.). Hexane used as a solvent was dried over sodium metal, and distilled just before use. The starting compounds, **1a** and **1b** were prepared according to the method reported previously [10].

#### 3.2. Photolysis of **1a** in the presence of *tert*-butyl alcohol

A mixture of 0.3025 g (1.02 mmol) of **1a** and 0.8012 g (10.8 mmol) of *tert*-butyl alcohol in 65 mL of hexane was placed in a reaction vessel fitted internally with a low-pressure mercury lamp bearing a Vycor filter. The mixture was irradiated with 20 min at room temperature. After evaporation of the solvent, the residue was chromatographed on a short silica gel column to remove the nonvolatile products, with hexane as eluent. Pure **2a** (0.1240 g, 33% yield) and **3** (0.0546 g, 15% yield), along with 4% of the starting compound **1a** were isolated by recycling preparative HPLC. Data for **2a**: Anal. Calcd. for  $\text{C}_{22}\text{H}_{32}\text{OSi}_2$ : C, 71.67; H, 8.75. Found: C, 71.46; H, 8.61%. MS  $m/z$  368 ( $\text{M}^+$ ); IR 3066, 3045, 2973, 2923, 2904, 1427, 1363, 1253, 1191, 1110, 1041, 1020, 879, 794, 742  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR  $\delta(\text{CDCl}_3)$  0.54 (s, 3H, MeSi), 0.56 (s, 3H, MeSi), 0.81–0.85 (m, 2H,  $\text{CH}_2$ ), 1.06 (s, 9H, *t*-Bu), 1.16–2.11 (m, 6H,  $\text{CH}_2$ ), 7.21–7.42 (m, 7H, phenyl and phenylene ring protons), 7.63–7.66 (m, 1H, phenylene ring proton), 7.71–7.74 (m, 1H, phenylene ring proton);  $^{13}\text{C}$  NMR  $\delta(\text{CDCl}_3)$  –1.56, 2.85 (MeSi), 12.69, 17.97, 24.54, 25.17 ( $\text{CH}_2$ ), 31.84 ( $\text{Me}_3\text{C}$ ), 73.17 ( $\text{CMe}_3$ ), 127.36, 127.72, 128.10, 128.45, 134.58, 134.67, 136.03, 140.15, 144.63, 144.96 (phenyl and phenylene ring carbons);  $^{29}\text{Si}$  NMR  $\delta(\text{CDCl}_3)$  –5.0, 0.8. Data for **3**: Anal. Calcd. for  $\text{C}_{22}\text{H}_{34}\text{OSi}_2$ : C, 71.28; H, 9.25. Found: C, 71.21; H, 9.21%. MS  $m/z$  369 ( $\text{M}^+ - \text{H}$ ); IR 2974, 2920, 2114, 1429, 1365, 1252, 1196, 1115, 1049, 879, 850, 735  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR  $\delta(\text{CDCl}_3)$  0.31 (d, 3H, MeSi,  $J = 3.8$  Hz), 0.38 (s, 3H, MeSi), 0.75–0.90 (m, 4H,  $\text{CH}_2$ ), 1.23 (s, 9H, *t*-Bu), 1.30–1.42 (m, 4H,  $\text{CH}_2$ ), 4.32 (sext, 1H, SiH,  $J = 3.8$  Hz), 7.33–7.37 (m, 6H, phenyl ring protons), 7.50–7.59 (m, 4H, phenyl ring protons);  $^{13}\text{C}$  NMR  $\delta(\text{CDCl}_3)$  –5.69, –0.71 (MeSi), 13.08, 17.47, 26.89, 28.08 ( $\text{CH}_2$ ), 32.08 ( $\text{Me}_3\text{C}$ ), 72.60 ( $\text{CMe}_3$ ), 127.54, 127.79, 128.97, 129.10, 133.60, 134.29, 136.78, 139.85 (phenyl ring carbons);  $^{29}\text{Si}$  NMR  $\delta(\text{CDCl}_3)$  –13.6, –2.7.

#### 3.3. Photolysis of **1a** in the presence of *tert*-butyl alcohol- $d_1$

A mixture of 0.3000 g (1.01 mmol) of **1a** and 0.7512 g (10.0 mmol) of *tert*-butyl alcohol- $d_1$  in 65 mL hexane was irradiated with a low-pressure mercury lamp for 20 min. After evaporation of the solvent, the residue was chromatographed with a silica gel. Pure **2a** (0.1226 g, 33% yield) and **3-d<sub>1</sub>** (0.0114 g, 3% yield), together with 4% of the starting compound **1a** were isolated by recycling preparative HPLC. All spectral data for **2a** were identical with those of the authentic sample obtained from the photolysis of **1a** with *tert*-butyl alcohol. Data for **3-d<sub>1</sub>**: MS  $m/z$  314

( $M^+ - t\text{-Bu}$ ); IR 3068, 2973, 2919, 2113, 1427, 1363, 1251, 1195, 1114, 1049, 877, 732  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR  $\delta(\text{CDCl}_3)$  0.31 (d, 3H, MeSi,  $J = 3.8$  Hz), 0.38 (s, 2H,  $\text{CH}_2\text{DSi}$ ), 0.75–0.90 (m, 4H,  $\text{CH}_2$ ), 1.23 (s, 9H,  $t\text{-Bu}$ ), 1.30–1.42 (m, 4H,  $\text{CH}_2$ ), 4.32 (sext, 1H, SiH,  $J = 3.8$  Hz), 7.33–7.37 (m, 6H, phenyl ring protons), 7.50–7.59 (m, 4H, phenyl ring protons);  $^{13}\text{C}$  NMR  $\delta(\text{CDCl}_3)$  –5.69, (MeSi), –0.99 ( $\text{CH}_2\text{D}$ , t,  $J_{\text{C-D}} = 18.3$  Hz), 13.09, 17.48, 26.89, 28.08 ( $\text{CH}_2$ ), 32.08 ( $\text{Me}_3\text{C}$ ), 72.60 ( $\text{CMe}_3$ ), 127.54, 127.79, 128.97, 129.10, 133.60, 134.29, 136.80, 139.88 (phenyl ring carbons);  $^2\text{H}$  NMR  $\delta(\text{CDCl}_3)$  0.43.

### 3.4. Photolysis of **1b** in the presence of tert-butyl alcohol

A mixture of 0.3000 g (1.01 mmol) of **1b** and 0.7925 g (10.8 mmol) in 65 mL of hexane was irradiated with a low-pressure mercury lamp for 20 min. After evaporation of the solvent, the residue was chromatographed with a silica gel column, and then the products were isolated by recycling HPLC, to give 0.1512 g (41% yield) of **2b** and 0.0448 g (12% yield) of **3**, in addition to 11% of the starting compound **1b**. Data for **2b**: Anal. Calcd. for  $\text{C}_{22}\text{H}_{32}\text{OSi}_2$ : C, 71.67; H, 8.75. Found: C, 71.78; H, 8.77%. MS  $m/z$  368 ( $M^+$ ); IR 3066, 3045, 2973, 2925, 1427, 1363, 1249, 1193, 1108, 1041, 1020, 875, 821, 788, 738  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR  $\delta(\text{CDCl}_3)$  0.46 (s, 3H, MeSi), 0.50 (s, 3H, MeSi), 0.83–0.85 (m, 2H,  $\text{CH}_2$ ), 1.01–1.04 (m, 1H,  $\text{CH}_2$ ), 1.29 (s, 9H,  $t\text{-Bu}$ ), 1.57–1.59 (m, 1H,  $\text{CH}_2$ ), 1.66–1.68 (m, 2H,  $\text{CH}_2$ ), 1.89–1.92 (m, 2H,  $\text{CH}_2$ ), 7.26–7.46 (m, 7H, phenyl and phenylene ring protons), 7.52–7.53 (m, 1H, phenylene ring proton), 7.76–7.77 (m, 1H, phenylene ring proton);  $^{13}\text{C}$  NMR  $\delta(\text{CDCl}_3)$  –0.17, 3.24 (MeSi), 13.35, 17.86, 24.50, 25.01 ( $\text{CH}_2$ ), 32.14 ( $\text{Me}_3\text{C}$ ), 73.13 ( $\text{CMe}_3$ ), 127.55, 127.68, 128.06, 128.57, 134.67, 134.68, 136.26, 139.57, 144.47, 145.25 (phenyl and phenylene ring carbons);  $^{29}\text{Si}$  NMR  $\delta(\text{CDCl}_3)$  –3.6, 0.8. All spectral data for **3** were identical with those of the authentic sample.

### 3.5. Photolysis of **1b** in the presence of tert-butyl alcohol- $d_1$

A mixture of 0.2972 g (1.00 mmol) of **1b** and 0.8125 g (10.8 mmol) of tert-butyl alcohol- $d_1$  in 65 mL hexane was irradiated with a low-pressure mercury lamp for 20 min. After evaporation of the solvent, the residue was chromatographed with a silica gel. Pure **2b** (0.1428 g, 33% yield) and **3-d<sub>1</sub>** (0.0367 g, 10% yield), together with 10% of the starting compound **1b** were isolated by recycling preparative HPLC. All spectral data for **2b** and **3-d<sub>1</sub>** were identical with those of the authentic sample obtained from the reaction described above.

### 3.6. Photolysis of **1a** in the presence of acetone

A mixture of 0.3090 g (1.03 mmol) of **1a** and 0.615 g (10.6 mmol) of acetone in 65 mL of hexane was irradiated with a low-pressure mercury lamp for 20 min. After the solvent was evaporated, the residue was chromatographed on

a silica gel, and the products **4a** (0.0912 g, 25% yield) and **5** (0.0133 g, 4% yield), along with 28% of the starting compound **1a** were isolated by a recycling HPLC. Data for **4a**: Anal. Calcd. for  $\text{C}_{21}\text{H}_{30}\text{OSi}_2$ : C, 71.12; H, 8.53. Found: C, 71.23; H, 8.67%. MS  $m/z$  354 ( $M^+$ ); IR 3066, 3045, 2967, 2908, 1427, 1253, 1170, 1110, 1020, 877, 800, 744, 700  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR  $\delta(\text{CDCl}_3)$  0.49 (s, 3H, MeSi), 0.54 (s, 3H, MeSi), 0.83–1.11 (m, 4H,  $\text{CH}_2$ ), 0.86 (d, 3H, Me,  $J = 6.0$  Hz), 1.03 (d, 3H, Me,  $J = 6.0$  Hz), 1.69–1.74 (m, 2H,  $\text{CH}_2$ ), 1.86–1.94 (m, 2H,  $\text{CH}_2$ ), 3.88 (sep, 1H, CH,  $J = 6.0$  Hz), 7.24–7.44 (m, 7H, phenyl and phenylene ring protons), 7.66–7.74 (m, 2H, phenylene ring proton);  $^{13}\text{C}$  NMR  $\delta(\text{CDCl}_3)$  –1.25, –0.11 (MeSi), 12.54, 15.84, 24.35, 25.06 ( $\text{CH}_2$ ), 25.49, 25.59 (Me), 65.54 (CO), 127.45, 128.09, 128.13, 128.50, 134.41, 134.99, 136.05, 140.13, 143.59, 144.60 (phenyl and phenylene ring carbons);  $^{29}\text{Si}$  NMR  $\delta(\text{CDCl}_3)$  –5.2, 7.3. Data for **5**: Anal. Calcd. for  $\text{C}_{18}\text{H}_{26}\text{OSi}_2$ : C, 68.72; H, 8.33. Found: C, 68.91; H, 8.42%. MS  $m/z$  313 ( $M^+ - \text{H}$ ); IR 3389, 3068, 2956, 2919, 2111, 1427, 1251, 1116, 1062, 877, 848, 788, 732, 698  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR  $\delta(\text{CDCl}_3)$  0.31 (d, 3H, MeSi,  $J = 3.8$  Hz), 0.37 (s, 3H, MeSi), 0.78–0.86 (m, 4H,  $\text{CH}_2$ ), 1.40–1.46 (m, 4H,  $\text{CH}_2$ ), 1.63 (s, 1H, OH), 4.32 (sext, 1H, SiH,  $J = 3.8$  Hz), 7.31–7.40 (m, 6H, phenyl ring protons), 7.50–7.58 (m, 4H, phenyl ring protons);  $^{13}\text{C}$  NMR  $\delta(\text{CDCl}_3)$  –5.70, –1.66 (MeSi), 13.06, 16.23, 26.52, 28.00 ( $\text{CH}_2$ ), 127.82, 127.86, 129.15, 129.57, 133.21, 134.29, 136.70 (2C) (phenyl ring carbons);  $^{29}\text{Si}$  NMR  $\delta(\text{CDCl}_3)$  –13.6, 7.4.

### 3.7. Photolysis of **1a** in the presence of acetone- $d_6$

A mixture of 0.3178 g (1.07 mmol) of **1a** and 0.6959 g (10.9 mmol) of acetone- $d_6$  in 65 mL of hexane was irradiated with a low-pressure mercury lamp for 20 min. After the solvent was evaporated, the residue was chromatographed on a silica gel, and the products **4a-d<sub>6</sub>** (0.0704 g, 18% yield) and **5-d<sub>1</sub>** (0.0133 g, 4% yield), along with 30% of the starting compound **1a** were isolated by a recycling HPLC. Data for **4a-d<sub>6</sub>**:  $^1\text{H}$  NMR  $\delta(\text{CDCl}_3)$  0.48 (s, 3H, MeSi), 0.53 (s, 3H, MeSi), 0.80–1.10 (m, 4H,  $\text{CH}_2$ ), 1.67–1.72 (m, 2H,  $\text{CH}_2$ ), 1.84–1.94 (m, 2H,  $\text{CH}_2$ ), 3.88 (s, 1H, CH), 7.21–7.44 (m, 7H, phenyl and phenylene ring protons), 7.66–7.73 (m, 2H, phenylene ring proton);  $^{13}\text{C}$  NMR  $\delta(\text{CDCl}_3)$  –1.24, –0.11 (MeSi), 12.52, 15.82, 24.36, 25.06 ( $\text{CH}_2$ ), 24.50 (sep,  $\text{CD}_3$ ,  $J = 19.9$  Hz), 65.50 (CO), 127.45, 128.08, 128.10, 128.50, 134.41, 134.99, 136.04, 140.10, 143.58, 144.60 (phenyl and phenylene ring carbons);  $^2\text{H}$  NMR  $\delta(\text{CDCl}_3)$  0.85, 1.03. Data for **5-d<sub>1</sub>**:  $^1\text{H}$  NMR  $\delta(\text{CDCl}_3)$  0.31 (d, 3H, MeSi,  $J = 3.7$  Hz), 0.36 (br s, 2H,  $\text{CH}_2\text{D}$ ), 0.78–0.88 (m, 4H,  $\text{CH}_2$ ), 1.40–1.45 (m, 4H,  $\text{CH}_2$ ), 1.63 (s, 1H, OH), 4.31 (sext, 1H, SiH,  $J = 3.7$  Hz), 7.33–7.39 (m, 6H, phenyl ring protons), 7.49–7.54 (m, 4H, phenyl ring protons);  $^{13}\text{C}$  NMR  $\delta(\text{CDCl}_3)$  –5.70 (MeSi), –1.95 ( $\text{CDH}_2$ ,  $J = 18.3$  Hz), 13.06, 16.22, 26.52, 28.00 ( $\text{CH}_2$ ), 127.82, 127.86, 129.15, 129.57, 133.21, 134.29, 136.70 (2C) (phenyl ring carbons);  $^2\text{H}$  NMR  $\delta(\text{CDCl}_3)$  0.37.

### 3.8. Photolysis of **1b** in the presence of acetone

A mixture of 0.2990 g (1.01 mmol) of **1b** and 0.766 g (13.2 mmol) of acetone in 65 mL of hexane was irradiated with a low-pressure mercury lamp for 20 min. After evaporation of the solvent, the residue was chromatographed on a silica gel column, and the products **4b** (0.0821 g, 23% yield) and **5** (0.0170 g, 5% yield), together with 10% of the starting compound **1b** were isolated by a recycling HPLC. Data for **4b**: Anal. Calcd. for C<sub>21</sub>H<sub>30</sub>OSi<sub>2</sub>: C, 71.12; H, 8.53. Found: C, 71.17; H, 8.57%. MS *m/z* 354 (M<sup>+</sup>); IR 3066, 3047, 2967, 2921, 1427, 1251, 1110, 1020, 875, 808, 784, 736, 698 cm<sup>-1</sup>; <sup>1</sup>H NMR δ(CDCl<sub>3</sub>) 0.39 (s, 3H, MeSi), 0.50 (s, 3H, MeSi), 0.84–0.86 (m, 2H, CH<sub>2</sub>), 1.02–1.07 (m, 1H, CH<sub>2</sub>), 1.16 (d, 3H, Me, *J* = 6.0 Hz), 1.22 (d, 3H, Me, *J* = 6.0 Hz), 1.52–1.69 (m, 4H, CH<sub>2</sub>), 1.76–1.82 (m, 1H, CH<sub>2</sub>), 4.07 (sep, 1H, CH, *J* = 6.0 Hz), 7.29–7.46 (m, 7H, phenyl and phenylene ring protons), 7.54 (d, 1H, phenylene ring proton, *J* = 7.3 Hz), 7.77 (d, 1H, phenylene ring proton, *J* = 7.3 Hz); <sup>13</sup>C NMR δ(CDCl<sub>3</sub>) -0.25, 0.23 (MeSi), 13.12, 15.85, 24.25, 24.92 (CH<sub>2</sub>), 25.83, 25.86 (Me), 65.48 (CO), 127.59, 128.01, 128.09, 128.64, 134.66, 134.88, 136.34, 139.42, 143.76, 144.55 (phenyl and phenylene ring carbons); <sup>29</sup>Si NMR δ(CDCl<sub>3</sub>) -3.7, 7.0.

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