

Silicon–Carbon Unsaturated Compounds. 67. Photolysis of *cis*- and *trans*-1,2-Dimethyl-1,2-diphenyl-1,2-disilacyclopentane

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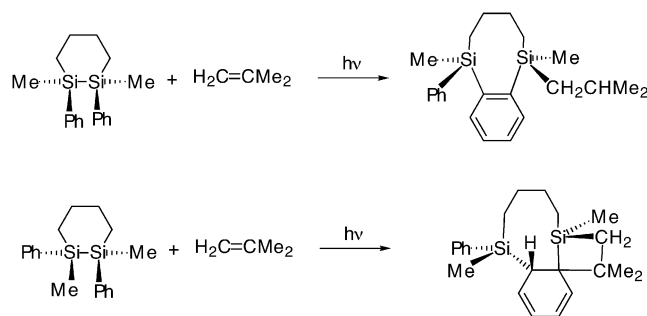
The photolysis of *cis*- and *trans*-1,2-dimethyl-1,2-diphenyl-1,2-disilacyclopentane (**1a,b**) was carried out in the presence of isobutene, acetone, and *tert*-butyl alcohol. Irradiation of **1a** with a low-pressure mercury lamp in the presence of isobutene in hexane proceeded stereospecifically to give a *cis* ene-type adduct (**2a**) and a *cis* [2 + 2] cycloadduct (**3a**) in 34% and 8% yields, respectively. Similar irradiation of **1a** with acetone afforded a *cis*-ene-type adduct (**4a**) with high stereospecificity and 1-[hydroxymethylphenylsilyl]-3-(methylphenylsilyl)propane (**5**) in 28% and 15% yields. The photolysis of **1b** with isobutene gave a *trans* [2 + 2] cycloadduct (**3b**) and the *cis* ene-type adduct **2a** in 20% and 6% yields, respectively. With acetone, **1b** afforded compound **5** as the major product. The photolysis of **1a** in the presence of *tert*-butyl alcohol produced a mixture of *cis*- and *trans*-2,3-benzo-1-*tert*-butoxy-1,4-dimethyl-4-phenyl-1,4-disilacyclohept-2-ene (**6a,b**) in a 4:1 ratio in 30% combined yield, in addition to a 14% yield of 1-[*tert*-butoxymethylphenylsilyl]-3-(methylphenylsilyl)propane (**7**). Similar photolysis of **1b** with *tert*-butyl alcohol gave again a mixture of **6a** and **6b** in 22% yield, in a 1:4 ratio, along with **7** in 15% yield. The thermolysis of **3a** and **3b** proceeded stereospecifically to give the respective ene-type products **2a** and **2b** in quantitative yields. Computational analyses for the formation of the rearranged silenes have also been reported.

Introduction

In 1975, we found that the photolysis of aryldisilanes readily 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 stereochemistry in this photolysis using *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

Recently, we have found that the photolysis of *cis*- and *trans*-1,2-dimethyl-1,2-diphenyl-1,2-disilacyclohexane

gives the rearranged silenes, which can be trapped by isobutene with high stereospecificity. Thus, the cophotolysis of *cis*-1,2-dimethyl-1,2-diphenyl-1,2-disilacyclohexane with isobutene afforded the ene-type product *cis*-2,3-benzo-1-isobutyl-1,4-dimethyl-4-phenyl-1,4-disilacyclooct-2-ene, along with a trace amount of a *cis* [2 + 2] cycloadduct, while the *trans* isomer gave the adduct with a *trans* configuration, arising from formal [2 + 2] cycloaddition of the rearranged silene with isobutene as the main product.⁴



It was of interest to us to investigate the stereochemistry in the photolysis of disilanyl-ene-containing cyclic systems involving geometrical isomers other than 1,2-disilacyclohexane system. In this paper we report the

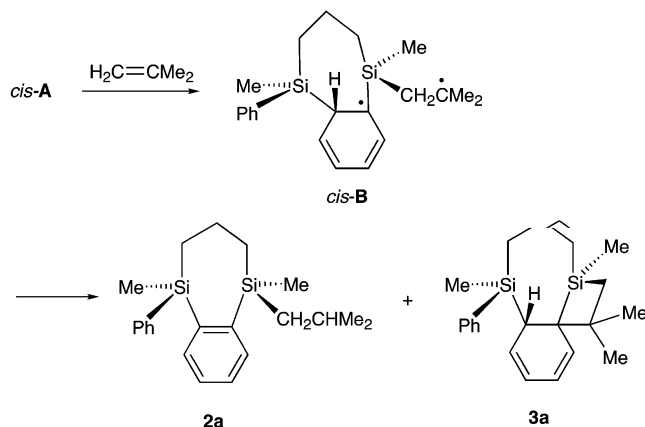
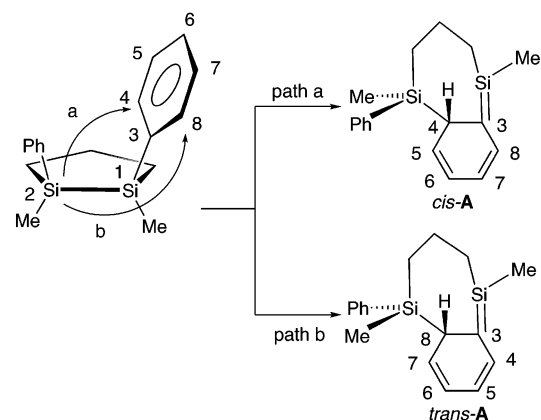
(1) (a) Ishikawa, M.; Fuchikami, T.; Sugaya, T.; Kumada, M. *J. Am. Chem. Soc.* **1975**, *97*, 5923. (b) Ishikawa, M. *Pure Appl. Chem.* **1978**, *50*, 11. (c) Ishikawa, M.; Kumada, M. *Adv. Organomet. Chem.* **1981**, *19*, 51.

(2) For photolysis of aryldisilanes, see for example: (a) Shizuka, H.; Obuchi, H.; Ishikawa, M.; Kumada, M. *J. Chem. Soc., Faraday Trans. 1* **1984**, *80*, 383. (b) Sakurai, H.; Sugiyama, H.; Kira, M. *J. Phys. Chem.* **1990**, *94*, 1837. (c) Shizuka, H. *Pure Appl. Chem.* **1993**, *65*, 1635. (d) Kira, M.; Miyazawa, T.; Sugiyama, H.; Yamaguchi, M.; Sakurai, H. *J. Am. Chem. Soc.* **1993**, *115*, 3116. (e) Leigh, W. J.; Sluggett, G. W. *J. Am. Chem. Soc.* **1993**, *115*, 7531. (f) Leigh, W. J.; Sluggett, G. W. *Organometallics* **1994**, *13*, 269. (g) Toltl, N. P.; Leigh, W. J. *Organometallics* **1996**, *15*, 2554. (h) Tajima, Y.; Ishikawa, H.; Miyazawa, T.; Kira, M.; Mikami, N. *J. Am. Chem. Soc.* **1997**, *119*, 7400. (i) Yamamoto, M.; Kudo, T.; Ishikawa, M.; Tobita, S.; Shizuka, H. *J. Phys. Chem. A* **1999**, *103*, 3144.

(3) (a) Ohshita, J.; Niwa, H.; Ishikawa, M.; Yamabe, T.; Nakamura, K. *J. Am. Chem. Soc.* **1996**, *118*, 6853. (b) Ohshita, J.; Niwa, H.; Ishikawa, M. *Organometallics* **1996**, *15*, 4632.

(4) Ishikawa, M.; Shirai, S.; Naka, A.; Kobayashi, H.; Ohshita, J.; Kunai, A.; Yamamoto, Y.; Cha, S.-H.; Lee, K.-K.; Kwak, Y.-W. *Organometallics* **2002**, *21*, 4206.

Scheme 1



photolysis of *cis*- and *trans*-1,2-dimethyl-1,2-diphenyl-1,2-disilacyclopentane, which shows behavior different from that of 1,2-disilacyclohexane systems.

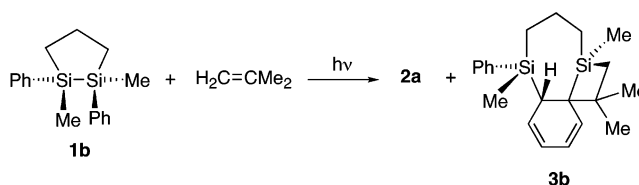
Results and Discussion

Pure *cis*- and *trans*-1,2-dimethyl-1,2-diphenyl-1,2-disilacyclopentane (**1a,b**) were prepared by Wurtz coupling of 1,3-bis(chloromethylphenylsilyl)propane with sodium metal, according to the method reported recently.⁵

When the *cis* isomer **1a** was photolyzed by irradiating with a low-pressure mercury lamp bearing a Vycor filter in the presence of isobutene in a hexane solution, two adducts, *cis*-2,3-benzo-1-isobutyl-1,4-dimethyl-4-phenyl-1,4-disilacyclohept-2-ene (**2a**) and *cis*-7-phenyl-7,11,13,13-tetramethyl-7,11-disilatricyclo[7.4.0.0^{1,11}]trideca-2,4-diene (**3a**), were obtained stereospecifically in 34% and 8% yields, respectively, in addition to 29% of the unchanged starting compound **1a** (Scheme 1). No stereoisomers of the adducts were detected in the reaction mixture by mass and NMR spectrometric analysis.

The configuration of **2a** was confirmed by NOE-FID difference experiments at 300 MHz. Thus, saturation of the signal at δ 0.50 ppm due to methyl protons on silicon bearing a phenyl group resulted in strong enhancement of the signal at 0.31 ppm, attributed to the methyl protons on the silicon atom attached to an isobutyl group, as well as methylene protons and phenyl protons. These results clearly indicate that the configuration of compound **2a** must be a *cis* form.

Scheme 2

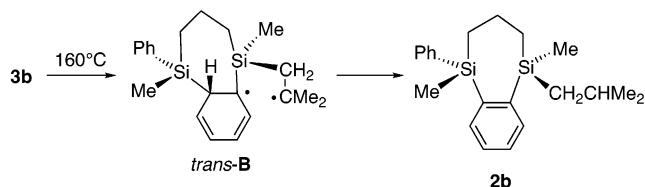


The photolysis of **1a** produces two types of silenes, *cis*-A and *trans*-A, which can be formed by a 1,3-shift of one silyl group onto two ortho positions of the phenyl group in the other silyl moiety (path a and b), as shown in Scheme 1. The formation of **2a** and **3a** may be explained in terms of the stereospecific addition of isobutene to the silene intermediate *cis*-A but not to *trans*-A. Thus, isobutene approaches the silicon-carbon double bond of *cis*-A from the side opposite to the methylphenylsilyl group in the 1,4-disilacycloheptyl ring to avoid a significant steric interaction. The reaction probably proceeds in a stepwise manner, as in the similar photolysis of the disilacyclohexane system.⁴ In the initial step, a silicon-methylene bond may be formed to give a diradical species (*cis*-B), and then a hydrogen on the sp^3 carbon in the cyclohexadienyl ring migrates to the resulting isobutyl radical center, reproducing the aromatic sextet. On the other hand, a radical coupling in *cis*-B produces **3a** with a *cis* configuration. In marked contrast to the cophotolysis of **1a** with isobutene, the photolysis of *trans* isomer **1b** under the same conditions gave the *cis* adduct **2a** and *trans* [2 + 2] adduct **3b** in 6% and 20% yields, respectively, as shown in Scheme 2. In this photolysis, a large amount of nonvolatile products was produced (48 wt %). All spectral data for **2a** were identical with those of the enantiomeric adduct obtained from the photolysis of **1a** with isobutene. The structure for **3b** was confirmed by mass and ^1H , ^{13}C , and ^{29}Si NMR spectrometric analysis. Its configuration was verified by NOE-FID difference experiments at 300 MHz. Irradiation of the methyl protons on the silicon atom bearing a phenyl group at 0.30 ppm resulted in a positive NOE of the signals at 0.71 and 1.19 ppm, due to one proton of the methylene group and one methyl proton from each of two methyl substituents on the carbon atom in the silacyclobutanyl ring. However, no enhancement was observed for the signal at 0.05 ppm attributed to the methyl protons on the silicon atom in the four-membered ring. These results indicate that the methyl group at 0.30 ppm must be located in a *trans* fashion to the methyl group on the different silicon atom.

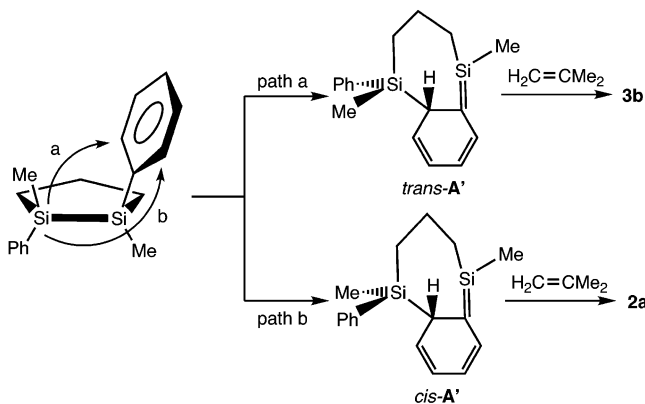
Interestingly, when the tricyclic compound **3b** was heated in a degassed, sealed tube at 160 °C for 24 h, *trans*-2,3-benzo-1-isobutyl-1,4-dimethyl-4-phenyl-1,4-disilacyclohept-2-ene (**2b**) was obtained in quantitative yield. No *cis* isomer **2a** was detected in the thermal product by ^1H , ^{13}C , and ^{29}Si NMR spectrometric analysis, indicating that isomerization of **3b** to **2b** proceeded with high stereospecificity. Scheme 3 illustrates a possible mechanistic interpretation of thermal isomerization of **3b** to **2b**. Radical scission of a C(1)–C(13) bond in the silacyclobutanyl ring of **3b** would occur to afford diradical species (*trans*-B), which is the same intermediate arising from addition of isobutene to the rearranged silene, *trans*-A. Migration of the hydrogen atom

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Scheme 3



Scheme 4



on an sp^3 carbon in the cyclohexadienyl ring of *trans-B* to an isobutyl radical center produces **2b** stereospecifically. As expected, the thermolysis of **3a** under the same conditions also proceeded stereospecifically to give **2a** quantitatively. Thus, when a mixture involving **2a** and **3a** in a ratio of 3:1 was heated in a sealed glass tube at 160 °C for 24 h, compound **3a** was completely transformed into **2a**. The ^1H NMR spectrometric analysis of the product indicated the presence of **2a**, but no other products were detected. A similar stereospecific isomerization of the [2 + 2] cycloadduct to the ene-type product has been observed in the 1,2-disilacyclohexane system.⁴

In the photolysis of **1b**, two types of rearranged silenes (*cis-A'* and *trans-A'*), different conformers from *cis-A* and *trans-A*, formed from the photolysis of **1a** may be produced. The silenes *cis-A'* and *trans-A'* thus formed react stereospecifically with isobutene to give the *cis*-ene-adduct **2a** and *trans* [2 + 2] cycloadduct **3b**, respectively (Scheme 4). The absence of the *trans* adduct in the photolysis of **1a** may be ascribed to the steric congestion in the reaction of *trans-A* with isobutene, as well as the instability of the intermediate *trans-A*.

Next, we investigated the photolysis of **1a** and **1b** in the presence of acetone. Thus, the cophotolysis of **1a** with acetone under the same conditions produced two products, *cis*-2,3-benzo-1-isopropoxy-1,4-dimethyl-4-phenyl-1,4-disilacyclohept-2-ene (**4a**) and 1-[hydroxymethylphenylsilyl]-4-(methylphenylsilyl)propane (**5**), in 28% and 15% yields, respectively, in addition to a 15% yield of the starting compound **1a** (Scheme 5). In this photolysis, nonvolatile products were also obtained (19 wt %).

Product **4a** was readily separated from **5** by column chromatography. Again, the configuration of **4a** was verified by NOE-FID difference experiments at 300 MHz to be a *cis* form, indicating that the reaction proceeded stereospecifically. No adduct arising from the reaction of *trans-A* with acetone was detected in the reaction mixture.

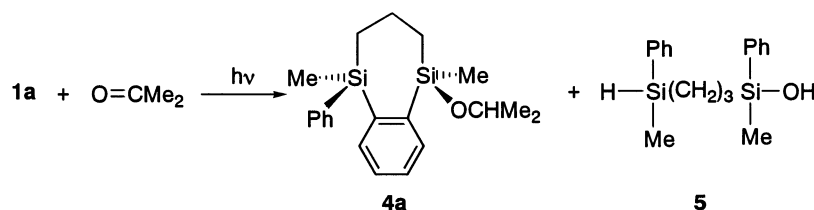
To learn more about the production of **5** in this photolysis, we carried out the photolysis of **1a** in the presence of acetone- d_6 in hexane. The deuterium-containing compounds *cis*-2,3-benzo-1-(deuterioisopropoxy)-1,4-dimethyl-4-phenyl-1,4-disilacyclohept-2-ene (**4a-d₆**) and 1-[(deuteriomethyl)hydroxyphenylsilyl]-3-(methylphenylsilyl)propane (**5-d**) were obtained in 33% and 7% yields, respectively, together with a 12% yield of the starting compound **1a**. The production of **5** may be best explained by the ene-type reaction of the silene, originating from homolytic scission of a silicon–silicon bond of **1a**, followed by disproportionation of the resulting diradical species with acetone and decomposition of the resulting product to the observed adduct **5** during isolation (Scheme 6). In fact, the GC-mass spectrometric analysis of the photolysis mixture showed the presence of a compound that has a molecular ion at m/z 340, corresponding to the calculated molecular weight of $\text{C}_{20}\text{H}_{28}\text{OSi}_2$. However, after treatment of the photolysis mixture by column chromatography, this compound was completely transformed into **5**.

The cophotolysis of **1b** with acetone under the same conditions gave **5** in 26% yield, along with a trace amount of **4a** (less than 3% yield) and a 23% yield of the starting compound **1b**, after treatment of the reaction mixture with a short silica gel column. Although **4a** isolated in this photolysis also contained a small amount of impurity, all spectral data were identical with those of the authentic sample obtained from the photolysis of **1a** with acetone. A similar photolysis of **1b** with acetone- d_6 gave the deuterium-containing compound **5-d** in 15% yield, in addition to a 18% yield of the starting compound **1b**. Unfortunately, the compound **4a-d₆**, which might be produced in this photolysis, could not be detected, due to very low yield.

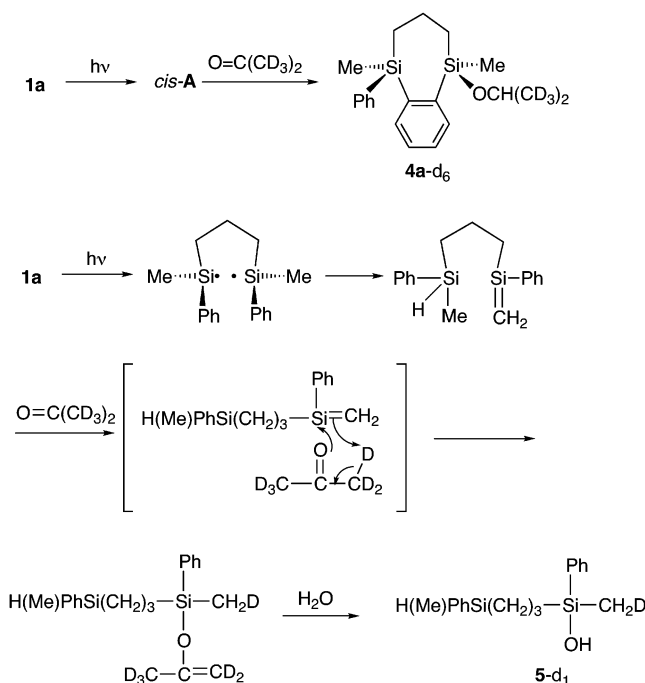
Leigh and co-workers have reported that the unstable siloxetane formed in the photolysis of arylsilylanes with acetone are observable only in the crude photoproducts by NMR spectroscopy,^{2f,g} but the photoproducts are decomposed by treatment with column chromatography. To examine the presence of such a siloxetane in the present photolysis, we analyzed the crude photolysis mixture by ^1H NMR spectroscopy. However, no evidence for the formation of the siloxetane was obtained.

The photolysis of **1a** with isobutene and acetone proceeds with high stereospecificity to give the ene-type adducts derived from the rearranged silene *cis-A*. However, the cophotolysis of **1a** with *tert*-butyl alcohol gave a mixture of *cis*- and *trans*-2,3-benzo-1-*tert*-butoxy-

Scheme 5



Scheme 6



1,4-dimethyl-4-phenyl-1,4-disilacyclohept-2-ene (**6a,b**) in 30% combined yield (Scheme 7). The ratio of **6a** to **6b** was determined to be 4:1 by ^1H NMR spectrometric analysis of the mixture, indicating that the *cis* isomer **6a** was produced as the major product. In this photolysis, 1-(*tert*-butoxymethylphenylsilyl)-3-(methylphenylsilyl)propane (**7**) was obtained in 14% yield, together with the recovered starting compound **1a** (24%). Products **6a**, **6b** and **7** were isolated by recycling HPLC.

The production of **6a** can be understood in terms of syn addition of *tert*-butyl alcohol to the silicon–carbon double bond from the opposite side of the methylphenylsilyl group of *cis*-**A**, followed by syn elimination of a hydrogen molecule from the resulting adduct. The formation of **6b** may be explained by syn addition of *tert*-butyl alcohol to *trans*-**A** and syn elimination of hydrogen. Presumably, the more reactive *tert*-butyl alcohol, as compared to isobutene and acetone, can react with *trans*-**A** in this photolysis. One might consider that the adduct **6b** is the result of anti addition of *tert*-butyl alcohol to the silene *cis*-**A**. In general, the degree of syn stereoselectivity for addition of alcohols to the silenes decreases with increasing alcohol concentration.^{2f,7} To examine this, we carried out the photolysis of **1a** with different concentrations of *tert*-butyl alcohol in hexane. Thus, irradiation of a hexane solution of **1a** (0.01 M) containing *tert*-butyl alcohol (0.04 M) for 20 min led to the formation of **6a** and **6b** in 22% combined yield, along

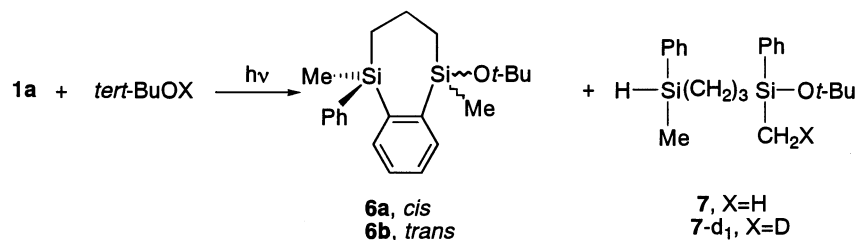
with a 22% yield of the ring-opened product **7** and 20% of the unchanged starting compound **1a**. The ratio of **6a** to **6b** was calculated to be 4:1. Similar irradiation of a hexane solution of **1a** (0.17 M) and *tert*-butyl alcohol (0.34 M) afforded a mixture of **6a** and **6b** in 22% combined yield, in addition to a 30% yield of **7** and 22% of **1a**. Again, the ratio of **6a** and **6b** was calculated to be 4:1. No change in the ratio of **6a** and **6b** was observed in the different alcohol concentrations. Therefore, we concluded that no anti addition occurs in the present photolysis. The syn additions of *tert*-butyl alcohol to the silenes are general reactions and well-known to date.^{6,7} We have recently found that the cophotolysis of *cis*- and *trans*-1,2-dimethyl-1,2-diphenyl-1,2-disilacyclohexane with *tert*-butyl alcohol proceeds stereospecifically to give the respective *cis* and *trans* products derived from syn addition of the alcohol to silenes and syn elimination of the resulting adducts.⁸ The formation of **7** may be explained by addition of *tert*-butyl alcohol to the silene formed by homolytic scission of a silicon–silicon bond in **1a**, followed by disproportionation of the resulting diradical.

The photolysis of **1a** in the presence of *tert*-butyl alcohol-*d* again afforded a mixture of **6a** and **6b** in the ratio of 4:1 as expected, in 24% combined yield, and deuterium-containing compound **7-d** in 19% yield, together with a 19% yield of the unchanged starting compound **1a**. No deuterium atom was detected in **6a** and **6b**, showing that the H–D molecule was eliminated from the *tert*-butyl alcohol adducts. For **7-d**, however, a deuterium atom was determined to be incorporated in a methyl group on a *tert*-butoxy-substituted silicon atom.

Similar photolysis of the *trans* isomer **1b** with *tert*-butyl alcohol again gave a mixture of **6a** and **6b** in a ratio of 1:4 in 22% combined yield and compound **7** in 15% yield, in addition to 26% of the unchanged starting compound **1b**, indicating that both *cis*-**A'** and *trans*-**A'** reacted with *tert*-butyl alcohol. In contrast to the photolysis of **1a**, which afforded **6a** as the major product, the *trans* isomer **1b** gave **6b** as the major product, indicating that the cophotolysis of **1a** and **1b** with *tert*-butyl alcohol proceeded stereoselectively to give the addition–elimination products **6a** and **6b**. With *tert*-butyl alcohol-*d* under the same conditions, **1b** afforded again a mixture of **6a** and **6b** in a ratio of 1:4 in 22% combined yield. In analogy with the photolysis of **1a**, no deuterium atom was incorporated in the products **6a** and **6b**, obtained from the photolysis with *tert*-butyl alcohol-*d*. The product **7-d** was also obtained in 28% yield, along with 11% of the unchanged starting compound **1b**.

Theoretical Calculations. To obtain a better understanding of the results obtained in the present

Scheme 7



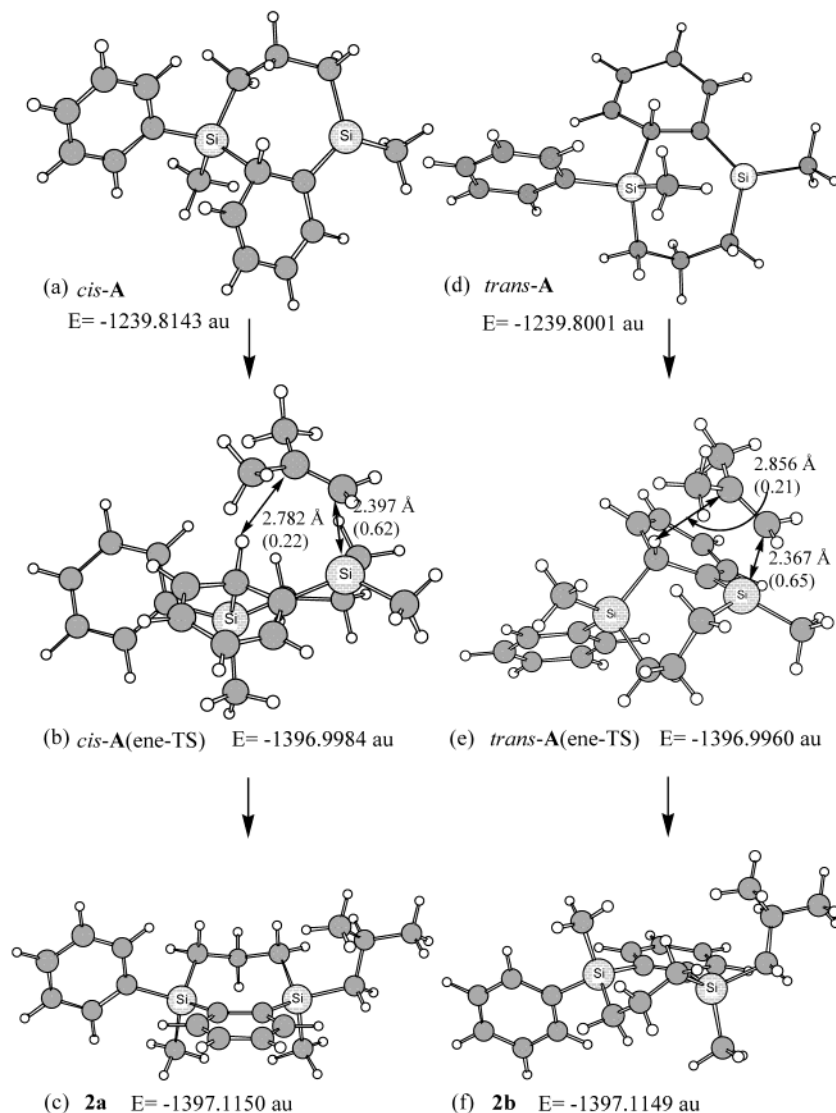


Figure 1. Optimized structures of the local minimum and transition states from silene to ene-type adduct for the *cis* isomer: (a) *cis-A*; (b) *cis-A(ene-TS)*; (c) **2a**; (d) *trans-A*; (e) *trans-A(ene-TS)*; (f) **2b**. In (b) and (e), the Si–C and C–H distances are indicated. Their weights in the reaction coordinate are given in parentheses.

reactions, computational analyses for the formation of the *cis* and *trans* ene-type adducts and *trans* [2 + 2] cycloadduct were carried out using the Gaussian 98 program package.⁹ The hybrid DFT calculation with the Becke three-parameter Lee–Yang–Parr (B3LYP) functional was employed,^{10,11} together with the 6-31G basis set. The calculation was restricted to the formation of the ene-type adduct in the reaction of the silene, *cis-A* and *trans-A*, with isobutene arising from **1a** and the formation of the ene-type adduct and [2 + 2] cycloadduct for the reaction of *cis-A'* and *trans-A'* arising from **1b**.

Figure 1 shows the structural changes from *cis-A* to the ene-type adduct through TS for two conformers. One is labeled as *cis-A*, *cis-A(ene-TS)*, **2a**, and the other is *trans-A*, *trans-A(ene-TS)*, **2b**. At the TS structures, the Si–C bond formation has a much larger contribution to the reaction coordinate than the H–C bond formation.

The continuity of the reaction coordinate is confirmed by the intrinsic reaction coordinate analysis¹² and followed full optimization. The total energies calculated for the local minima and TS's examined in this study are shown in Figure 1 and Table 1. All the energies of the *cis-A*, *cis-A(ene-TS)*, and **2a** route are lower than those of the *trans-A*, *trans-A(ene-TS)*, and **2b** route, respectively. This result is consistent with the experimental findings that **2a** is the major product. Furthermore, we can expect that the selectivity is determined by the relative stability of silene or before the TS, since

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Table 1. Total Energies for Calculated Local Minima and Transition States

Cis Isomer				
isomer	E (au)	isomer	E (au)	$\Delta E(\text{trans-A} - \text{cis-A})$ (kcal/mol) ^a
Ene Reaction				
<i>cis-A</i>	-1239.8143	<i>trans-A</i>	-1239.8001	8.9
<i>cis-A</i> (ene-TS)	-1396.9984	<i>trans-A</i> (ene-TS)	-1396.9960	1.5
2a	-1397.1150	2b	-1397.1149	0.1
Trans Isomer				
isomer	E (au)	isomer	E (au)	$\Delta E(\text{trans-A}' - \text{cis-A}')$ (kcal/mol) ^a
Ene Reaction				
<i>cis-A'</i>	-1239.8143	<i>trans-A'</i>	-1239.8129	0.9
<i>cis-A'</i> (ene-TS)	-1396.9978	<i>trans-A'</i> (ene-TS)	-1396.9961	1.1
2a	-1397.1130	2b	-1397.1088	2.6
[2 + 2] Reaction				
<i>cis-A'</i> ([2 + 2]-TS1)	-1396.9721	<i>trans-A'</i> ([2 + 2]-TS1)	-1396.9965	-15.3
<i>cis-A'</i> ([2 + 2]-LM)	-1397.0115	<i>trans-A'</i> ([2 + 2]-LM)	-1397.0093	1.4
<i>cis-A'</i> ([2 + 2]-TS2)	-1397.0008	<i>trans-A'</i> ([2 + 2]-TS2)	-1396.9989	1.2
3a	-1397.0396	3b	-1397.0372	1.5

^a The relative energy is obtained by subtracting the value in the second column from the value in the fourth column and multiplying the resulting value by 627.5.

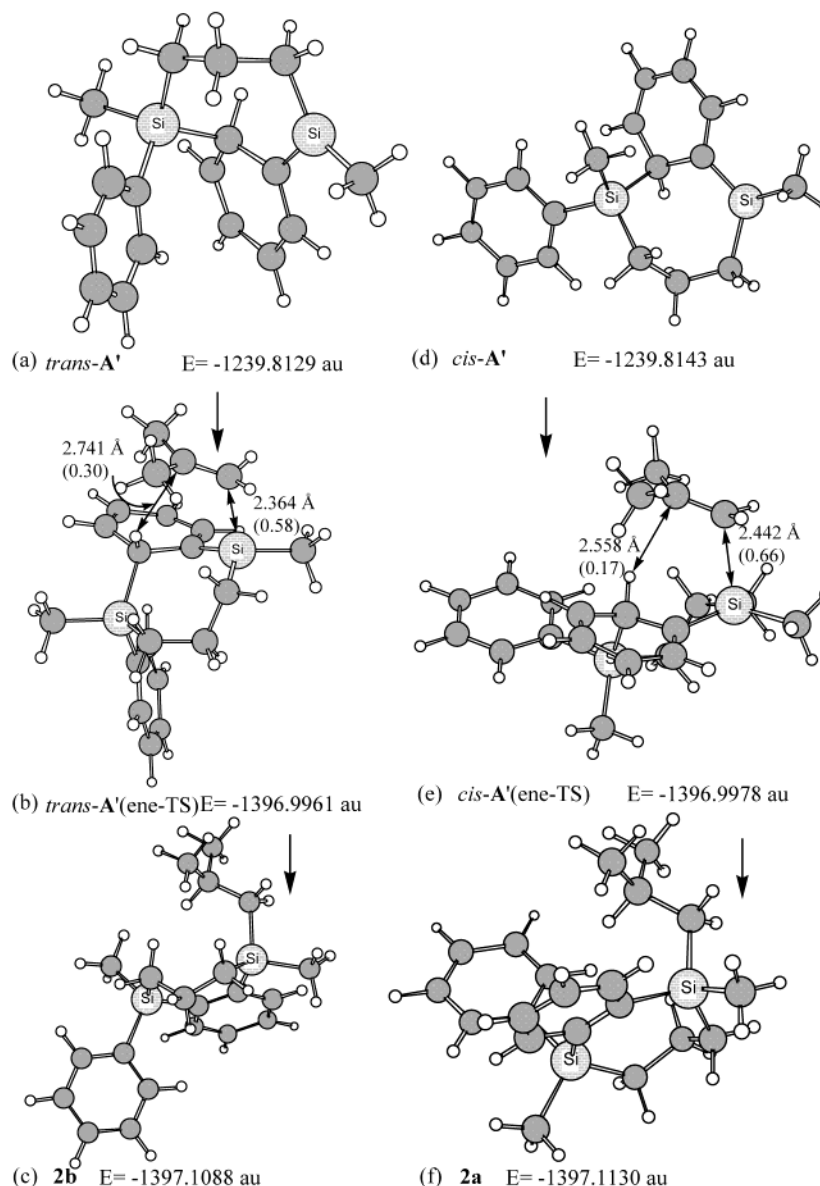


Figure 2. Optimized structures of the local minimum and transition states from silene to ene-type adduct for the trans isomer: (a) *trans-A'*; (b) *trans-A'*(ene-TS); (c) **2b**; (d) *cis-A'*; (e) *cis-A'*(ene-TS); (f) **2a**. See the caption of Figure 1 for an explanation of the values given with the TS structures.

the energy difference is the largest between *cis-A* and *trans-A*. For **1b**, the structures for *trans-A'*, TS, and the ene-type adduct **2b** are shown in Figure 2 a–c and those

for *cis-A'*, TS, and the ene-type adduct **2a** in Figure 2d–f. The total energies are shown in Figure 2 and Table 1. Although the ene-type adduct **2a** is not the major

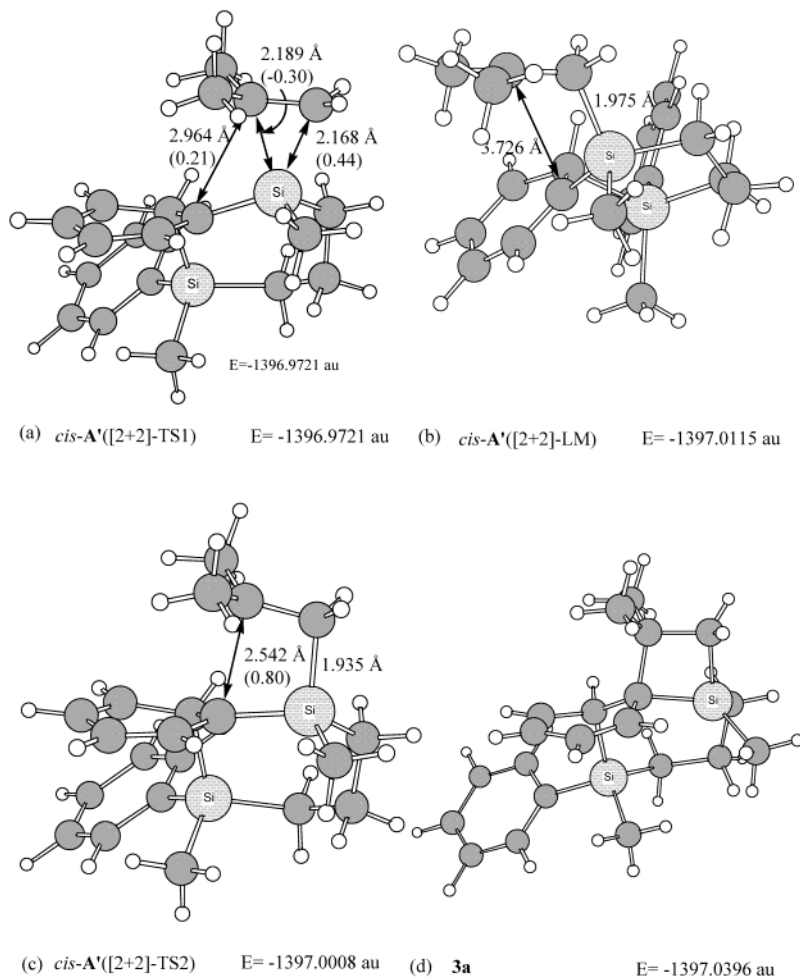


Figure 3. Optimized structures of the local minimum and transition states from *cis-A'* to the [2 + 2] cycloadduct for the trans isomer: (a) *cis-A'*([2 + 2]-TS1); (b) *cis-A'*([2 + 2]-LM); (c) *cis-A'*([2 + 2]-TS2); (d) **3a**. See the caption of Figure 1 for an explanation of the values given with the structures.

product, the route to **2a** is slightly more stable than that to **2b**, which is again consistent with the experiment.

The major product for the reaction of *trans-A'* with isobutene is the [2 + 2] cycloadduct **3a**. The mechanism for the formation of the cycloadduct was examined in detail only for the reaction of **1b**. The structural changes along the reaction coordinate are shown in Figures 3 and 4 for *cis-A'* and *trans-A'*, respectively. It is found that the four-membered-ring formation proceeds with two steps. Upon approach of an isobutene molecule, the first TS (labeled TS1) is located before the formation of a Si–C bond. The structures of TS1 are shown in Figures 3a and 4a. Both of the contributions from the Si–C and C–C distances have significant values in the reaction coordinate, whereas the former is much larger. After the formation of the Si–C bond, the isobutene moiety bends back against the silene moiety, and the local minimum is obtained, as shown in Figures 3b and 4b. The second TS (labeled TS2) is located before closing the four-membered ring. The structures for TS2 are shown in Figures 3c and 4c. The energies for TS2 are lower than those of TS1. Figures 3d and 4d show the

final structures of the [2 + 2] cycloadduct. In the calculation of this part, the electron density corresponding to the symmetry-broken singlet wave functions is employed to represent the spin polarization even approximately. With regard to the energy in Table 1, a dominant energy difference is found for *cis-A'*([2 + 2]-TS1) and *trans-A'*([2 + 2]-TS1), and the latter is more stable. We expect that this energy difference is important to determine the formation of the trans cycloadduct (**3b**) as the major product, although the energies between **3b** and **3a** are not significant.

Conclusion

The photolysis of **1a** and **1b** produced two types of rearranged silenes, *cis-A* and *trans-A*, and *cis-A'* and *trans-A'*, respectively. The photochemical reaction of **1a** with isobutene and acetone proceeded with high stereospecificity to give the respective adducts arising from the reaction of the silene, with the substrates as the major products. Similar photolysis of the trans isomer **1b** with isobutene proceeded nonstereospecifically to give both the cis ene-adduct and trans [2 + 2] adduct. With acetone, however, **1b** afforded the product originating from the reaction of the silene arising from scission of the silicon–silicon bond in **1b**, followed by disproportionation of the resulting diradical species as

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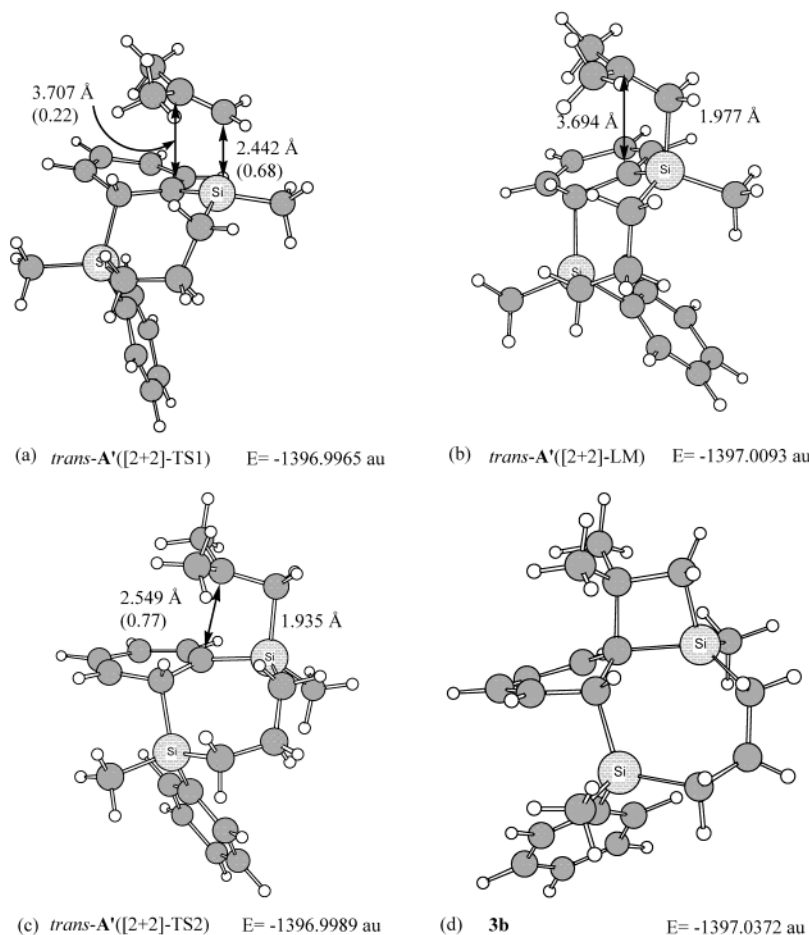


Figure 4. Optimized structures of the local minimum and transition states from *trans-A'* to the [2 + 2] cycloadduct for the trans isomer: (a) *trans-A'*([2 + 2]-TS1); (b) *trans-A'*([2 + 2]-LM); (c) *trans-A'*([2 + 2]-TS2); (d) **3b**. See the caption of Figure 1 for an explanation of the values given with the structures.

the main product. The photolysis of **1a** and **1b** in the presence of *tert*-butyl alcohol proceeded stereoselectively to give the addition–elimination products. Theoretical calculations for the reactions of the silenes with isobutene are consistent with the results obtained from experiments.

Experimental Section

General Procedure. All photolyses were carried out under an atmosphere of dry argon. NMR spectra were recorded on a JNM-LA300 spectrometer and a JNM-LA500 spectrometer. Infrared spectra were recorded on a JEOL Model JIR-DIAMOND 20 infrared spectrophotometer. Low- and high-resolution mass spectra were measured on a JEOL Model JMS-700 instrument. The melting point was measured with a Yanaco-MP-S3 apparatus. 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 under a nitrogen atmosphere and distilled just before use.

Materials. Pure *cis*- and *trans*-1,2-dimethyl-1,2-diphenyl-1,2-disilacyclopentane were separated by a TSA-SB2 spinning band type distillation column (Taika Kogyo).

Photolysis of 1a in the Presence of Isobutene. A mixture of 0.2805 g (0.993 mmol) of **1a** and 1.256 g (22.385 mmol) of isobutene 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 for 10 min

at room temperature. After evaporation of the solvent, the residue was chromatographed on a silica gel column, with hexane as eluent, to give 0.1145 g (0.338 mmol) of **2a** (34%), 0.0255 g (0.075 mmol) of **3a** (8%), and 0.0804 g (0.285 mmol) of the starting compound **1a** (29%). Pure **2a** and **3a** were separated by recycling preparative HPLC. Data for **2a**: MS *m/z* 338 (M^+); IR 3066, 2950, 2865, 1463, 1427, 1249, 1116, 910, 792, 736, 709 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.31 (s, 3H, MeSi), 0.50 (s, 3H, MeSi), 0.69 (d, 3H, CH_3 , $J = 6.6$ Hz), 0.75 (d, 3H, CH_3 , $J = 6.6$ Hz), 0.85–1.04 (m, 2H, CH_2), 1.09–1.19 (m, 1H, CH_2), 1.26–1.34 (m, 1H, CH_2), 1.44–1.65 (m, 3H, CH_2 , CH), 1.87–2.06 (m, 2H, CH_2), 7.27–7.41 (m, 7H, phenyl and phenylene ring protons), 7.62–7.67 (m, 2H, phenyl ring protons); ^{13}C NMR (CDCl_3) δ -1.30, -0.52 (MeSi), 16.85, 17.06, 18.04 (CH_2Si), 24.73, 26.10, 26.14, 26.24 (Me, CH_2 , CH), 127.50, 127.72, 127.94, 128.79, 134.40, 134.93, 135.91, 139.25, 143.85, 147.75 (phenyl and phenylene ring carbons); ^{29}Si NMR (CDCl_3) δ -4.3, -0.4. Anal. Calcd for $\text{C}_{21}\text{H}_{30}\text{Si}_2$: C, 74.48; H, 8.93. Found: C, 74.37; H, 8.88. Data for **3a**: MS *m/z* 338 (M^+); IR 3068, 3020, 2952, 2900, 2861, 1427, 1251, 1112, 941, 821, 808, 771, 734, 698 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.26 (s, 3H, MeSi), 0.39 (s, 3H, MeSi), 0.85 (d, 2H, CH_2 , $J = 6$ Hz), 0.89–1.07 (m, 4H, CH_2), 1.15 (s, 3H, CH_3), 1.23 (s, 3H, CH_3), 1.57–1.69 (m, 1H, CH_2), 2.01–2.11 (m, 1H, CH_2), 1.86–1.99 (m, 1H, CH_2), 2.12–2.23 (m, 1H, CH_2), 2.64 (d, 1H, CH, $J = 6.4$ Hz), 5.15–5.21 (m, 1H, cyclohexadienyl ring proton), 5.56 (dd, 1H, cyclohexadienyl ring proton, $J = 9.4$ Hz, 4.9 Hz), 5.72 (dd, 1H, cyclohexadienyl ring proton, $J = 9.4$ Hz, 0.9 Hz), 5.87 (ddd, 1H, cyclohexadienyl ring proton, $J = 9.4$ Hz, 4.9 Hz, 0.9 Hz), 7.31–7.36 (m, 3H, phenyl ring protons), 7.49–7.53 (m, 2H, phenyl ring protons); ^{13}C NMR (CDCl_3) δ -5.79, -2.83 (MeSi),

18.06, 19.90, 20.54, 24.94, 28.73, 30.68, 32.17, 36.30, 44.04 (sp³ carbons), 120.57, 123.22, 127.60, 127.94, 128.60, 130.15, 133.72, 138.95 (phenyl ring and olefinic carbons); ²⁹Si NMR (CDCl₃) δ -1.2, 17.1; exact mass calcd for C₂₁H₃₀Si₂ (M⁺) 338.1886, found 338.1883.

Photolysis of 1b in the Presence of Isobutene. A mixture of 0.3098 g (1.097 mmol) of **1b** and 2.550 g (45.446 mmol) of isobutene in 65 mL of hexane was placed in a reaction vessel. The mixture was irradiated for 17 min at room temperature. After evaporation of the solvent, the residue was chromatographed on a silica gel column, with hexane as eluent, to give 0.0213 g (6% yield) of **2a**, 0.0732 g (20% yield) of **3b**, and 0.0696 g (23%) of the starting compound **1b**. Data for **3b**: MS *m/z* 338 (M⁺); IR 3066, 3043, 3021, 2950, 2906, 2861, 1459, 1427, 1249, 1110, 923, 802, 782, 730, 698 cm⁻¹; ¹H NMR (CDCl₃) δ 0.06 (s, 3H, MeSi), 0.30 (s, 3H, MeSi), 0.71 (d, 1H, CH, *J* = 14 Hz), 0.76–0.82 (m, 1H, CH₂), 0.97–1.00 (m, 1H, CH₂), 1.03 (d, 1H, CH₂, *J* = 14 Hz), 1.14 (s, 3H, Me), 1.19 (s, 3H, Me), 1.16–1.27 (m, 2H, CH₂), 1.92–1.97 (m, 2H, CH₂), 2.71 (d, 1H, CH, *J* = 6.7 Hz), 5.77 (dd, 1H, cyclohexadienyl ring proton, *J* = 9.2 Hz, 6.7 Hz), 5.87 (dd, 1H, cyclohexadienyl ring proton, *J* = 9.2 Hz, 4.9 Hz), 6.00 (d, 1H, cyclohexadienyl ring proton, *J* = 9.2 Hz), 6.10 (dd, 1H, cyclohexadienyl ring proton, *J* = 9.2 Hz, 4.9 Hz), 7.33–7.39 (m, 3H, phenyl ring protons), 7.53–7.55 (m, 2H, phenyl ring protons); ¹³C NMR (CDCl₃) δ -0.62, 1.93 (MeSi), 15.88, 17.50, 18.04, 26.25, 28.00, 30.15, 31.97, 37.68, 42.98 (sp³ carbons), 123.06, 125.14, 127.60, 127.83, 128.59, 131.89, 133.45, 140.76 (cyclohexadienyl and phenyl ring carbons); ²⁹Si NMR (CDCl₃) δ 5.8, 12.9; exact mass calcd for C₂₁H₃₀Si₂ (M⁺) 338.1886, found 338.1908. All spectral data for **2a** were identical with those of an authentic sample obtained from the above reaction.

Thermolysis of 3b. In a sealed glass tube was placed 0.0620 g (0.185 mmol) of **3b**. The glass tube was heated to 160 °C for 24 h. The ¹H NMR spectrometric analysis of the thermolysis product indicated the presence of the resonances due to **2a**, but no other resonances were obtained. The product was chromatographed on a short silica gel column, with hexane as eluent, to give 0.0547 g (87% yield) of **2b**. For **2b**: MS *m/z* 338 (M⁺); IR 3068, 3045, 2952, 2896, 2865, 1461, 1427, 1249, 1116, 908, 815, 794, 738, 700 cm⁻¹; ¹H NMR (CDCl₃) δ 0.19 (s, 3H, MeSi), 0.53 (s, 3H, MeSi), 0.83–0.86 (m, 2H, CH₂), 0.91 (d, 3H, CH₃, *J* = 6.4 Hz), 0.95 (d, 3H, CH₃, *J* = 6.4 Hz), 0.97–0.99 (m, 2H, CH₂), 1.18–1.24 (m, 1H, CH₂), 1.35–1.40 (m, 1H, CH₂), 1.79–1.98 (m, 3H, CH₂, CH), 7.27–7.38 (m, 5H, phenyl and phenylene ring protons), 7.42–7.44 (m, 2H, phenyl ring protons), 7.50 (d, 1H, phenyl ring proton, *J* = 7.3 Hz), 7.65 (d, 1H, phenyl ring proton, *J* = 7.3 Hz); ¹³C NMR (CDCl₃) δ -1.14, -0.97 (MeSi), 16.87, 17.20, 18.00 (CH₂Si), 24.97, 26.40, 26.51, 26.72 (Me, CH₂, CH), 127.45, 127.72, 127.83, 128.81, 134.41, 134.85, 136.04, 139.24, 144.15, 147.77 (phenyl and phenylene ring carbons); ²⁹Si NMR (CDCl₃) δ -4.1, 0.6. Anal. Calcd for C₂₁H₃₀Si₂: C, 74.48; H, 8.93. Found: C, 74.26; H, 8.83.

Thermolysis of a Mixture of 2a and 3a. A mixture of 0.0682 g of **2a** and **3a** in a ratio of 3:1 was heated in a sealed glass tube at 160 °C for 24 h. The ¹H NMR spectrometric analysis of the product indicated that **3a** was transformed completely into **2a**. The proton chemical shifts for **2a** were identical with those of the authentic sample.

Photolysis of 1a in the Presence of Acetone. A mixture of 0.3042 g (1.077 mmol) of **1a** and 1.4460 g (24.897 mmol) of acetone 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 for 15 min at room temperature. After evaporation of the solvent, the residue was chromatographed on a silica gel column, with hexane as eluent, to give 0.1042 g (0.306 mmol) of **4a** (28%), 0.0486 g (0.162 mmol) of **5** (15%), and 0.0449 g (0.159 mmol) of the starting compound **1a** (15%). Pure **4a** and **5** were separated by recycling preparative HPLC. Data for **4a**: MS *m/z* 325 (M⁺ - Me); IR 3066, 2969, 2919, 2867, 1427, 1251, 1118, 1024, 813, 788, 744,

700 cm⁻¹; ¹H NMR (CDCl₃) δ 0.42 (s, 3H, MeSi), 0.53 (s, 3H, MeSi), 1.01 (d, 3H, CH₃, *J* = 6.2 Hz), 1.08 (d, 3H, CH₃, *J* = 6.2 Hz), 1.00–1.21 (m, 2H, CH₂), 1.49–1.59 (m, 2H, CH₂), 1.86–2.00 (m, 2H, CH₂), 3.90 (sep, 1H, OCH, *J* = 6.2 Hz), 7.32–7.49 (m, 5H, phenyl ring protons), 7.60 (d, 2H, phenylene ring protons, *J* = 7.3 Hz), 7.85 (d, 2H, phenylene ring protons, *J* = 7.3 Hz); ¹³C NMR (CDCl₃) δ -1.19, -0.44 (MeSi), 16.67, 16.92, 17.58 (CH₂Si), 25.60, 25.63 (Me), 65.23 (CO), 127.67, 127.96, 128.23, 128.78, 134.35, 134.87, 135.95, 139.07, 143.91, 145.97 (phenyl and phenylene ring carbons); ²⁹Si NMR (CDCl₃) δ -4.2, 6.3. Anal. Calcd for C₂₀H₂₈Si₂O: C, 70.53; H, 8.29. Found: C, 70.92; H, 8.28. Data for **5**: MS *m/z* 299 (M⁺ - H); IR 3305, 3068, 3048, 2956, 2915, 2111, 1427, 1253, 1116, 1066, 908, 877, 935, 792, 732, 700 cm⁻¹; ¹H NMR (CDCl₃) δ 0.32 (d, 3H, MeSi, *J* = 3.7 Hz), 0.37 (s, 3H, MeSi), 0.93–0.99 (m, 4H, CH₂), 1.56 (quint, 2H, CH₂, *J* = 8.0 Hz), 1.72 (br s, 1H, OH), 4.35 (sext, 1H, SiH, *J* = 3.7 Hz), 7.34–7.40 (m, 6H, phenyl ring protons), 7.50–7.57 (m, 4H, phenyl ring protons); ¹³C NMR (CDCl₃) δ -5.67, -1.58 (MeSi), 17.55, 18.20, 20.48 (CH₂), 127.84, 127.87, 129.16, 129.57, 133.20, 134.29, 136.57, 138.42 (phenyl ring carbons); ²⁹Si NMR (CDCl₃) δ -14.5, 6.9. Anal. Calcd for C₁₇H₂₄Si₂O: C, 67.94; H, 8.05. Found: C, 67.71; H, 8.08.

Photolysis of 1b in the Presence of Acetone. A mixture of 0.3019 g (1.069 mmol) of **1b** and 1.5335 g (26.323 mmol) of acetone in 65 mL of hexane was placed in a reaction vessel. The mixture was irradiated for 15 min at room temperature. After evaporation of the solvent, the residue was chromatographed on a silica gel column, with hexane as eluent, to give a trace amount of **4a** (less than 3%), 0.0825 g (26% yield) of **5**, and 0.0690 g (23%) of the starting compound **1b**. All spectral data for **4a** and **5** were identical with those of authentic samples obtained from the above reaction.

Photolysis of 1a in the Presence of Acetone-d₆. A mixture of 0.3160 g (1.118 mmol) of **1a** and 0.7540 g (12.982 mmol) of acetone-d₆ 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 for 20 min at room temperature. After evaporation of the solvent, the residue was chromatographed on a silica gel column, with hexane as eluent, to give 0.1265 g (0.371 mmol) of **4a-d₆** (33%), 0.0221 g (0.074 mmol) of **5-d** (7%), and 0.0362 g (0.128 mmol) of the starting compound **1a** (12%). Pure **4a-d₆** and **5-d** were separated by recycling preparative HPLC. Data for **4a-d₆**: MS *m/z* 326 (M⁺ - Me); IR 3066, 3045, 2954, 2902, 2867, 2227, 1427, 1253, 1139, 1118, 1083, 1047, 939, 788, 736 cm⁻¹; ¹H NMR (CDCl₃) δ 0.44 (s, 3H, MeSi), 0.55 (s, 3H, MeSi), 0.96–1.01 (m, 1H, CH₂), 1.12–1.23 (m, 2H, CH₂), 1.51–1.60 (m, 2H, CH₂), 1.84–2.07 (m, 2H, CH₂), 3.89 (s, 1H, OCH), 7.32–7.50 (m, 7H, phenyl and phenylene ring protons), 7.61 (dd, 1H, phenylene ring protons, *J* = 6.7 Hz, 1.3 Hz), 7.86 (dd, 1H, phenylene ring protons, *J* = 6.7 Hz, 1.3 Hz); ¹³C NMR (CDCl₃) δ -1.18, -0.44 (MeSi), 16.72, 16.94, 17.63 (CH₂Si), 24.67 (sep, CD₃, *J* = 19.9 Hz), 64.95 (CO), 127.67, 127.96, 128.22, 128.78, 134.36, 134.86, 135.95, 139.10, 143.92, 146.02 (phenyl and phenylene ring carbons); ²⁹Si NMR (CDCl₃) δ -4.3, 6.2; ²H NMR (CDCl₃) δ 1.00, 1.06. Data for **5-d**: MS *m/z* 300 (M⁺ - H); IR 3297, 3068, 3010, 2917, 2875, 2113, 1427, 1114, 908, 833, 732 cm⁻¹; ¹H NMR (CDCl₃) δ 0.31 (d, 3H, MeSi, *J* = 3.7 Hz), 0.35 (br s, 3H, MeSi), 0.89–0.98 (m, 4H, CH₂), 1.55 (quint, 2H, CH₂, *J* = 8.0 Hz), 1.77 (br s, 1H, OH), 4.34 (sext, 1H, SiH, *J* = 3.7 Hz), 7.34–7.40 (m, 6H, phenyl ring protons), 7.49–7.57 (m, 4H, phenyl ring protons); ¹³C NMR (CDCl₃) δ -5.67 (MeSi), -1.87 (CDH₂, *J* = 18.3 Hz), 17.55, 18.20, 20.47 (CH₂), 127.84, 127.87, 129.16, 129.57, 133.19, 134.29, 136.57, 138.41 (phenyl ring carbons); ²⁹Si NMR (CDCl₃) δ -14.5, 7.0; ²H NMR (CDCl₃) δ 0.38.

Photolysis of 1b in the Presence of Acetone-d₆. A mixture of 0.4063 g (1.438 mmol) of **1b** and 0.9917 g (17.023 mmol) of acetone-d₆ 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 for

20 min at room temperature. After evaporation of the solvent, the residue was chromatographed on a silica gel column, with hexane as eluent, to give 0.0660 g (0.220 mmol) of **5-d** (15%) and 0.0740 g (0.262 mmol) of the starting compound **1a** (18%). Pure **5-d** was separated by recycling preparative HPLC. All spectral data for **5-d** were identical with those of an authentic sample obtained from the above reaction.

Photolysis of 1a in the Presence of *tert*-Butyl Alcohol.

A mixture of 0.3069 g (1.086 mmol) of **1a** and 0.8248 g (11.129 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 for 10 min at room temperature. After evaporation of the solvent, the residue was chromatographed on a silica gel column, with hexane as eluent, to give 0.1140 g (0.322 mmol) of **6a** and **6b** (in a ratio of 4:1, 30%), 0.0556 g (0.156 mmol) of **7** (14%), and 0.0768 g (0.263 mmol) of the starting compound **1a** (24%). Pure **6a**, **6b**, and **7** were separated by recycling preparative HPLC. Data for **6a**: MS m/z 339 ($M^+ - Me$); IR 3045, 2973, 2927, 1427, 1363, 1251, 1195, 1108, 1045, 908, 809, 779, 736 cm^{-1} ; 1H NMR ($CDCl_3$) δ 0.43 (s, 3H, MeSi), 0.51 (s, 3H, MeSi), 1.07–1.12 (m, 2H, CH_2), 1.15 (s, 9H, *t*-Bu), 1.53–1.62 (m, 2H, CH_2), 1.81–2.02 (m, 2H, CH_2), 7.29–7.47 (m, 7H, phenyl and phenylene ring protons), 7.54 (dd, 1H, phenylene ring protons, $J = 7.3$ Hz, 1.1 Hz), 7.85 (dd, 1H, phenylene ring protons, $J = 7.3$ Hz, 1.1 Hz); ^{13}C NMR ($CDCl_3$) δ -1.36, 1.96 (MeSi), 16.61, 17.16, 19.44 (CH_2Si), 32.03 (Me_3C), 72.81 (CMe_3), 127.65, 127.85 (2C), 128.70, 134.38, 134.82, 135.95, 139.48, 143.58, 148.11 (phenyl and phenylene ring carbons); ^{29}Si NMR ($CDCl_3$) δ -4.2, 0.7. Anal. Calcd for $C_{21}H_{30}Si_2O$: C, 71.12; H, 8.53. Found: C, 71.47; H, 8.24. Data for **6a**: MS m/z 339 ($M^+ - Me$); IR 3045, 2973, 2904, 1427, 1363, 1249, 1193, 1108, 1056, 811, 736 cm^{-1} ; 1H NMR ($CDCl_3$) δ 0.30 (s, 3H, MeSi), 0.55 (s, 3H, MeSi), 0.83–0.93 (m, 2H, CH_2), 1.05–1.14 (m, 2H, CH_2), 1.27 (s, 9H, *t*-Bu), 1.78–2.08 (m, 2H, CH_2), 7.28–7.48 (m, 8H, phenyl and phenylene ring protons), 7.83 (dd, 1H, phenylene ring protons, $J = 6.8$ Hz, 1.0 Hz); ^{13}C NMR ($CDCl_3$) δ -1.28, 1.91 (MeSi), 17.10, 17.63, 20.15 (CH_2Si), 32.15 (Me_3C), 72.98 (CMe_3), 127.69, 127.90 (2C), 128.80, 134.50, 134.77, 135.93, 139.09, 143.57, 147.56 (phenyl and phenylene ring carbons); ^{29}Si NMR ($CDCl_3$) δ -3.4, -0.4. Anal. Calcd for $C_{21}H_{30}Si_2O$: C, 71.12; H, 8.53. Found: C, 70.82; H, 8.59. Data for **7**: MS m/z 299 ($M^+ - t$ -Bu); IR 3048, 2973, 2917, 2875, 2113, 1427, 1363, 1251, 1195, 1114, 1049, 908, 877, 823, 800, 732 cm^{-1} ; 1H NMR ($CDCl_3$) δ 0.33 (d, 3H, MeSi, $J = 3.9$ Hz), 0.41 (s, 3H, MeSi), 0.89–0.99 (m, 4H, CH_2), 1.25 (s, 9H, *t*-Bu), 1.54 (quint, 2H, CH_2 , $J = 8.3$ Hz), 4.38 (sext, 1H, SiH, $J = 3.9$ Hz), 7.34–7.42 (m, 6H, phenyl ring protons), 7.52–7.61 (m, 4H, phenyl ring protons); ^{13}C NMR ($CDCl_3$) δ -5.66, -0.58 (MeSi), 17.54, 18.40, 21.66 (CH_2), 32.07 (Me_3C), 72.62 (CMe_3), 127.56, 127.78, 128.98, 129.06, 133.59, 134.29, 136.77, 139.82 (phenyl ring carbons); ^{29}Si NMR ($CDCl_3$) δ -14.6, -3.3. Anal. Calcd for $C_{21}H_{32}Si_2O$: C, 70.72; H, 9.04. Found: C, 70.45; H, 9.26.

Photolysis of 1a in the Presence of Different Concentrations of *tert*-Butyl Alcohol. A hexane solution (65 mL) containing **1a** (0.01 M) and *tert*-butyl alcohol (0.04 M) was photolyzed with a low-pressure mercury lamp for 20 min. The mixture was chromatographed on a silica gel column, with hexane as eluent, to give **1a** (20%), a mixture of **6a** and **6b** (22% combined yield), and **7** (22% yield). The ratio of **6a** and **6b** was determined by 1H NMR spectrometric analysis to be 4:1.

Similar photolysis of a hexane solution (65 mL) containing **1a** (0.17 M) and *tert*-butyl alcohol (0.34 M) afforded **1a** (25%),

a mixture of **6a** and **6b** (22% combined yield, **6a:6b** = 4:1), and **7** (30% yield).

Photolysis of 1b in the Presence of *tert*-Butyl Alcohol.

A mixture of 0.2964 g (1.049 mmol) of **1b** and 0.7818 g (10.548 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 for 10 min at room temperature. After evaporation of the solvent, the residue was chromatographed on a silica gel column, with hexane as eluent, to give 0.0802 g (0.322 mmol) of **6a** and **6b** (in a ratio of 1:4, 22%), 0.0545 g (0.153 mmol) of **7** (15%), and 0.0783 g (0.266 mmol) of the starting compound **1a** (26%). Pure **6a**, **6b**, and **7** were separated by recycling preparative HPLC. All spectral data for **6a**, **6b**, and **7** were identical with those of authentic samples obtained from the above reaction.

Photolysis of 1a in the Presence of *tert*-Butyl Alcohol-*d*.

A mixture of 0.4085 g (1.446 mmol) of **1a** and 0.6580 g (8.877 mmol) of *tert*-butyl alcohol-*d* 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 for 15 min at room temperature. After evaporation of the solvent, the residue was chromatographed on a silica gel column, with hexane as eluent, to give 0.1242 g (0.350 mmol) of **6a** and **6b** (in a ratio of 4:1, 24%), 0.0954 g (0.267 mmol) of **7-d** (19%), and 0.0824 g (0.292 mmol) of the starting compound **1a** (20%). Pure **6a**, **6b** and **7-d** were separated by recycling preparative HPLC. Data for **7-d**: MS m/z 300 ($M^+ - t$ -Bu); IR 3068, 2973, 2917, 2875, 2113, 1427, 1363, 1251, 1195, 1114, 1049, 906, 877, 821, 721 cm^{-1} ; 1H NMR ($CDCl_3$) δ 0.33 (d, 3H, MeSi, $J = 3.9$ Hz), 0.40 (br s, 2H, CH_2DSi), 0.87–0.99 (m, 4H, CH_2), 1.25 (s, 9H, *t*-Bu), 1.54 (quint, 2H, CH_2 , $J = 8.6$ Hz), 4.37 (sext, 1H, SiH, $J = 3.9$ Hz), 7.34–7.39 (m, 6H, phenyl ring protons), 7.51–7.61 (m, 4H, phenyl ring protons); ^{13}C NMR ($CDCl_3$) δ -5.66 (MeSi), -0.86 (CDH_2 , $J = 18.3$ Hz), 17.55, 18.41, 21.66 (CH_2), 32.08 (Me_3C), 72.63 (CMe_3), 127.56, 127.78, 128.98, 129.07, 133.60, 134.30, 136.79, 139.84 (phenyl ring carbons); ^{29}Si NMR ($CDCl_3$) δ -14.6, -3.3; 2H NMR ($CDCl_3$) δ 0.45. All spectral data for **6a** and **6b** were identical with those of authentic samples obtained from the above reaction.

Photolysis of 1b in the Presence of *tert*-Butyl Alcohol-*d*.

A mixture of 0.3056 g (1.082 mmol) of **1b** and 0.7790 g (10.510 mmol) of *tert*-butyl alcohol-*d* 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 for 12 min at room temperature. After evaporation of the solvent, the residue was chromatographed on a silica gel column, with hexane as eluent, to give 0.0921 g (0.260 mmol) of **6a** and **6b** (in a ratio of 4:1, 24%), 0.0670 g (0.188 mmol) of **7-d** (17%), and 0.0792 g (0.280 mmol) of the starting compound **1a** (26%). Pure **6a**, **6b** and **7-d** were separated by recycling preparative HPLC. All spectral data for **6a**, **6b** and **7-d** were identical with those of authentic samples obtained from the above reaction.

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