



Synthesis and thermal behavior of *cis*- and *trans*-1-*tert*-butyl-4,5-dimethyl-2-phenyl-2-(trimethylsiloxy)-1-(trimethylsilyl)-1-silacyclohex-4-ene

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ABSTRACT

The cothermolysis of benzoyl(*tert*-butyl)bis(trimethylsilyl)silane with 2,3-dimethylbutadiene in a sealed tube at 140 °C for 24 h afforded *cis*- and *trans*-1-*tert*-butyl-4,5-dimethyl-2-phenyl-2-(trimethylsiloxy)-1-(trimethylsilyl)-1-silacyclohex-4-ene (**2** and **3**) in a ratio of approximately 1:1 in 66% combined yield. When *cis*-silacyclohex-4-ene **2** was heated in a sealed tube at 250 °C for 24 h, dyotropic ring contraction took place to give 1-[(*tert*-butyl)(trimethylsiloxy)(trimethylsilyl)silyl]-3,4-dimethyl-1-phenylcyclopent-3-ene (**4**), but not *trans*-2-*tert*-butyl-4,5-dimethyl-2-phenyl-1-(trimethylsiloxy)-1-(trimethylsilyl)-1-silacyclohex-4-ene (**6**). The thermolysis of *trans*-silacyclohex-4-ene **3** under the same conditions, however, afforded two products, 1-silyl-1-phenylcyclopent-3-ene **4** and *trans*-1-*tert*-butyl-4,5-dimethyl-2-phenyl-1-(trimethylsiloxy)-2-(trimethylsilyl)-1-silacyclohex-4-ene (**5**). The theoretical calculations were carried out to characterize the transition states and other local minima, and to evaluate the activation energies for the dyotropic rearrangement of **2** to **4** and **6**, and **3** to **4** and **5**. The energy barriers between **2** and **4**, between **3** and **4**, and between **3** and **5** were evaluated to be 188, 191, 192 kJ mol⁻¹, respectively. The energy barrier between **2** and **6**, however, was calculated to be 201 kJ mol⁻¹ or higher. These results are consistent with the experimental finding that the thermal isomerization of **2** affords only **4**, but **3** produces both **4** and **5**.

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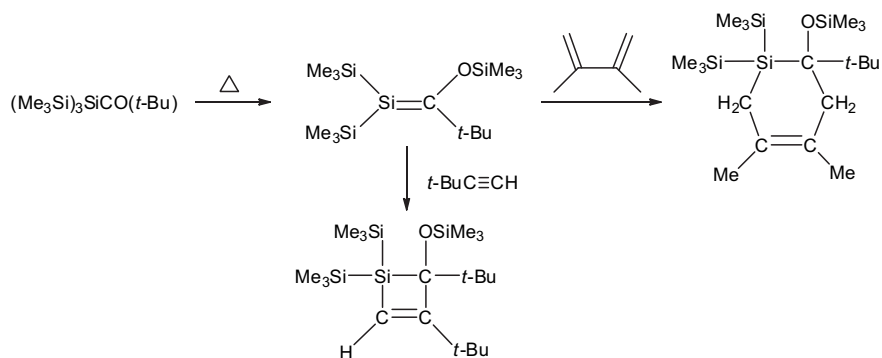
1. Introduction

A wide variety of silenes can be readily produced by the photolysis, thermolysis, and Peterson type reaction of arylpolysilanes, and many papers concerning the reactions of the silenes thus formed with various substrates have been published to date [1]. Recently, considerable attention has been focused on the formation and reactions of silacyclobutenes and silacyclohexenes, arising from cycloaddition of the silenes to alkynes [2–5] and butadienes [6–8]. On the other hand, it has been reported that these silacycloalkenes readily undergo thermal isomerization to give various types of the products, whose structures depend highly on the substituents on the silicon atom and also the adjacent carbon atom in the ring [2,6b]. Theoretical investigations to elucidate the mechanism for the formation and reactions of these compounds have also been carried out [2c–e,h,5,6b].

During the course of our investigation concerning the thermal behavior of the silacycloalkenes, we found that the thermolysis of the silacyclohexenes formed by the reactions of the silenes generated thermally from pivaloyl- and adamantoyltris(trimethylsilyl)silane with butadienes undergo cleanly dyotropic rearrangement [9] to give the isomerization products, in which two migrating groups, trimethylsiloxy and trimethylsilyl groups on the stationary carbon and silicon atoms in the six-membered ring are mutually exchanged. In these rearrangements, the trimethylsiloxy group is introduced to the silicon atom from the opposite side of the leaving trimethylsilyl group. As the result, two migrating groups are located in a *trans* fashion in the resulting products [6b]. Obviously, the driving force of the rearrangement is thought to be the formation of an energetically stable Si–O–Si bond. For examples, the thermolysis of 2-*tert*-butyl- and 2-adamantyl-4,5-dimethyl-2-(trimethylsiloxy)-1,1-bis(trimethylsilyl)-1-silacyclohex-4-ene proceeded cleanly to give *cis*-2-*tert*-butyl- and *cis*-2-adamantyl-4,5-dimethyl-1-(trimethylsiloxy)-1,2-bis(trimethylsilyl)-1-silacyclohex-4-ene, respectively. However, similar thermolysis of 4,5-dimethyl-2-mesityl-2-(trimethylsiloxy)-1,1-bis(trimethylsilyl)-1-silacyclohex-4-ene produced a ring-contracted compound, 3,4-dimethyl-1-mesityl-1-[trimethylsiloxy]bis

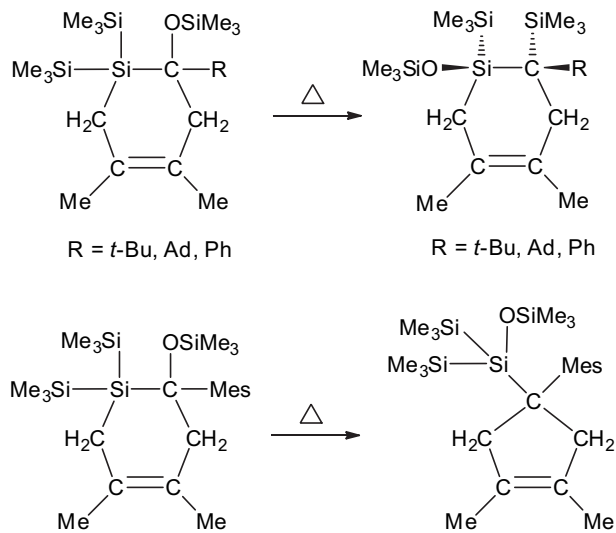
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(trimethylsilyl)silyl]cyclopent-3-ene. No 1-silacyclohex-4-ene derivative was detected in the product. In contrast to the behavior of this mesityl-substituted derivative, the thermolysis of the phenyl-substituted derivative, 4,5-dimethyl-2-phenyl-2-(trimethylsilyloxy)-1,1-bis(trimethylsilyl)-1-silacyclohex-4-ene afforded the 1-silacyclohex-4-ene derivative as the sole product.

In order to learn more about the thermal behavior of the 1-silacyclohex-4-ene bearing a phenyl group on the carbon atom at the 2-position in the ring, we have synthesized *cis*- and *trans*-1-*tert*-butyl-2-phenyl-4,5-dimethyl-2-(trimethylsilyloxy)-1-(trimethylsilyl)-1-silacyclohex-4-ene, by the cothermolysis of benzoyl (*tert*-butyl)(trimethylsilyl)silane with 2,3-dimethylbutadiene and investigated their thermal behavior. We have also carried out theoretical treatment to get more about information on the dyotropic rearrangement.



2. Results and discussion

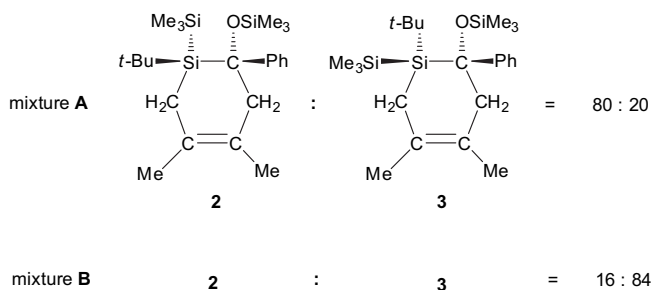
The cothermolysis of benzoyl(*tert*-butyl)bis(trimethylsilyl)silane (**1**) with 2,3-dimethylbutadiene at 140 °C for 24 h gave a mixture consisting of *cis*- and *trans*-1-*tert*-butyl-2-phenyl-2-(trimethylsilyloxy)-1-(trimethylsilyl)-1-silacyclohex-4-ene (**2** and **3**), as shown in Scheme 1. No other products were detected in the reaction mixture by spectrometric analysis. The ratio of the two products was determined to be 1:1 by ¹H NMR spectrometric analysis. Unfortunately, all attempts to separate the product **2** from **3** were unsuccessful. The fractions separated by using the recycling

HPLC were always shown to be a mixture consisting of **2** and **3**. Although we could not isolate **2** and **3** in a pure form, the mixtures with different ratio of **2** and **3** could be obtained. Therefore, we carried out the thermal reactions, using the mixture with a different ratio of **2** and **3**, **A** (**2/3** = 80/20) and **B** (**2/3** = 16/84), as the starting compound.

The structures of **2** and **3** were verified by spectrometric analysis, as well as by elemental analysis, using the mixtures **A** and **B**, respectively. The locations of the substituents on the silacyclohexenyl ring for **2** and **3** were confirmed by differential NOE experiments at 300 MHz. Thus, in the differential NOE experiments for **2**, saturation of the trimethylsilyloxy protons on the ring carbon atom at 0.10 ppm led to enhancement of the signal at 0.35 ppm, attributed to the trimethylsilyl protons, as well as the ring methylene proton at 2.78 ppm and the phenyl ring protons at 7.50 ppm. Furthermore, irradiation of the trimethylsilyl protons on the silicon atom in the six-membered ring at 0.35 ppm resulted in a strong enhancement of the signals at 0.10 and 0.77 ppm, due to the trimethylsilyloxy protons on the ring carbon and the *tert*-butyl protons on the ring silicon, and of the signal at 1.48 ppm, attributable to the ring methylene protons. These results clearly indicate that the trimethylsilyl group on the ring silicon atom and the trimethylsilyloxy group on the adjacent carbon atom for **2** are located in a *cis* fashion. The *trans* configuration for **3** was also confirmed by differential NOE experiments at 300 MHz. Thus, saturation of the *tert*-butyl protons on the ring silicon atom at 1.08 ppm resulted in enhancement of the signals at 0.06 and 0.13 ppm, attributable to the trimethylsilyloxy protons and trimethylsilyl protons, as well as the ring methylene protons.

When the mixture **A** was heated in a degassed sealed tube at 250 °C for 24 h, two products, 1-[(*tert*-butyl)(trimethylsilyloxy)(trimethylsilyl)silyl]-3,4-dimethyl-1-phenylcyclopent-3-ene (**4**) and *trans*-1-*tert*-butyl-2-phenyl-1-trimethylsilyloxy-2-trimethylsilyl-1-silacyclohex-4-ene (**5**) were obtained in 43% and 12% yields, respectively, in addition to the unchanged starting compounds **2** (40%) and **3** (5%) (Scheme 2). No other products were detected in the reaction mixture by GLC analysis and also by spectrometric analysis. The true product yield, obtained from each starting compound **2** or **3**, in the reaction mixture was determined on the basis of the following assumptions: compound **2** undergoes isomerization to give only 1-silyl-1-phenylcyclopent-3-ene **4**, but compound **3** affords two products, **4** and *trans*-silacyclohex-4-ene **5**, respectively. If this idea is correct, compound **2** produces **4** in 40% yield, and compound **3** affords **4** and **5** in 3% and 12% yields, respectively.

We also carried out the reaction using the mixture consisting of **2** and **3** in a ratio of 1:1. Thus, the thermolysis of this mixture under the same conditions afforded the products **4** and **5** in 32% and 30% yields, respectively, together with the unchanged starting compounds **2**



(25%) and **3** (13%). Again the yields of the products **4** and **5** from each starting compound are calculated to be 25% for the formation of **4** from **2** in the mixture, and 7% and 30% for **4** and **5** from **3**. These results are consistent with those obtained from the thermolysis of the mixture **A**.

In fact, the idea is based on the results obtained from the dyotropic rearrangement of the 2-*tert*-butyl- and 2-adamantyl-2-(trimethylsilyloxy)-1,1-bis(trimethylsilyl)-1-silacyclohex-4-ene derivatives. We have found that the dyotropic rearrangement of these compounds proceeds to give *cis*-1-(trimethylsilyloxy)-1,2-bis(trimethylsilyl)-1-silacyclohex-4-ene derivatives, via the transition state involving a pentacoordinate silicon atom [6b]. In this rearrangement, a trimethylsilyloxy shift from the carbon atom at the 2-position in the silacyclohexenyl ring to the ring silicon atom takes place from the opposite side of the leaving trimethylsilyl group. As a result, both migrating trimethylsilyloxy and trimethylsilyl groups from the stationary carbon and silicon atoms in the silacyclohexenyl ring are located at the *trans* position. In compound **2**, the trimethylsilyl group on the ring silicon atom and the trimethylsilyloxy group on the adjacent phenyl-substituted ring carbon atom are located at the *cis* position. Consequently, the formation of *trans*-silacyclohex-4-ene **5** in the thermal isomerization of **2** must involve inversion of the substituents on the ring silicon or adjacent carbon atom with scission of the silicon–carbon bond in the silacyclohexenyl ring. This process seems to be energetically unfavorable. In fact, theoretical treatment indicates that the energy of the TS for the reaction of **2** giving compound **5** is higher than that of the reaction leading to the product **4**.

One might consider the formation of a product, *trans*-2-*tert*-butyl-4,5-dimethyl-2-phenyl-1-(trimethylsilyloxy)-1-(trimethylsilyl)-1-silacyclohex-4-ene (**6**), in which a *tert*-butyl group on the ring silicon and a trimethylsilyloxy group on the carbon atom at the 2-position in the 1-silacyclohexenyl ring in **2** mutually interchange their positions. However, no product **6** was detected in the resulting mixture by spectrometric analysis. The theoretical study shown below also indicates that the formation of **6** is energetically unfavorable.

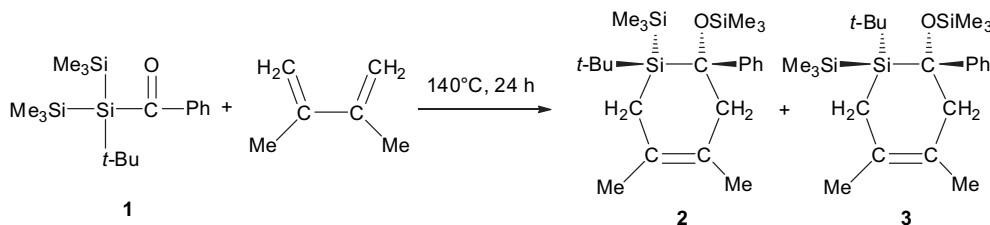
Products **4** and **5** were isolated by column chromatography. The structure of **4** was confirmed by spectrometric analysis, as well as by elemental analysis. The ¹H NMR spectrum of **4** shows two resonances at 0.23 and 0.26 ppm due to the trimethylsilyl protons

and trimethylsilyloxy protons, a single resonance at 0.79 ppm attributed to *tert*-butyl protons, and a resonance at 1.52 ppm due to the methyl protons on the sp²-ring carbons, as well as methylene protons and phenyl ring protons. The ¹³C NMR spectrum of **4** reveals two resonances at 1.5 and 2.4 ppm, attributed to the trimethylsilyl carbons, and a resonance at 13.7 ppm, due to the methyl carbons and a single resonance at 40.3 ppm attributable to the quaternary sp³-ring carbon, as well as the resonances due to the *tert*-butyl carbons, methylene carbons, and phenyl ring carbons. The ²⁹Si NMR spectrum shows three resonances at –21.8, 2.7, and 5.6 ppm, as expected. These results are wholly consistent with the structure proposed for **4**.

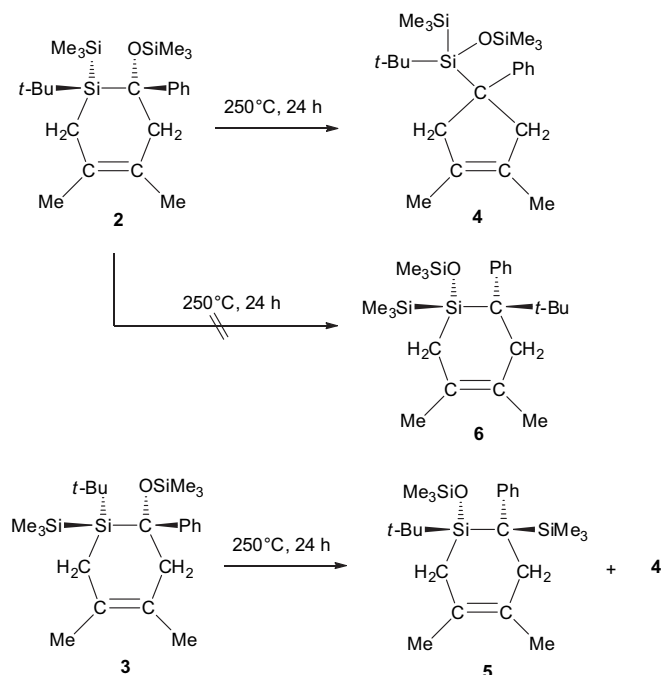
The structure of **5** was also confirmed by spectrometric analysis, as well as by elemental analysis (see Experimental Section), and its *trans* configuration was verified by differential NOE experiments at 300 MHz. Thus, irradiation of the *tert*-butyl (Scheme 2) protons on the ring silicon atom at 1.17 ppm led to enhancement of the signals at 0.09 and 0.14 ppm, attributable to the trimethylsilyloxy protons and the trimethylsilyl protons, as well as a signal at 0.95 ppm, due to the ring methylene proton. These results clearly indicate that compound **5** must have the structure with *trans* configuration. The thermolysis of **B** (ratio of **2/3** = 16/84) under the same conditions proceeded to give the rearranged product, **4** and **5** in 20% and 59% yields, in addition to the starting compounds **2** (9%) and **3** (12%). On the basis of the assumption described above, it may also be considered that compound **2** in the mixture **B** produced the product **4** in 7% yield, and compound **3** gave both of the products **4** and **5** in 13% and 59% yields, respectively.

The present dyotropic rearrangement indicates that *cis* isomer **2** undergoes isomerization to give the ring-contracted compound, silyl-substituted cyclopent-3-ene **4**, and *trans* isomer **3** affords *trans*-silacyclohex-4-ene **5** with the exchange of the Me₃SiO and Me₃Si group as a major product, along with **4** as a minor product.

Theoretical calculations. To obtain further information about the energy and structure changes in the dyotropic rearrangement of **2** and **3** to **4**, of **3** to **5**, and of **2** to **6**, respectively, shown in Scheme 2, theoretical calculations based on the density functional theory (DFT) method were carried out. First, we adopted “simplified models”, where all the methyl groups in the starting compounds and also in the products are replaced by the hydrogen atoms and the phenyl group by a methyl group, respectively. To distinguish real models and the corresponding simplified models, a prime is added to each number of the latter compounds. So the simplified models analogues to **2**, **3**, **4**, **5**, and **6**, are labeled as **2'**, **3'**, **4'**, **5'**, and **6'**, respectively. For each reaction, the transition state (TS) was characterized, and then the intrinsic reaction coordinate (IRC) analysis was carried out at the TS for both directions. The IRC calculation was restricted in the neighborhood of the TS. At the endpoint, the IRC was followed by normal optimization runs to confirm the continuity of the reaction coordinate to the reactant and product. Second, LMs and TSs were reexamined with the real models where the molecular structures are identical with those



Scheme 1. Synthesis of **2** and **3**.



Scheme 2. Thermolysis of 2 and 3.

used in the experiments. The activation energy is defined as energy of the TS measured from the corresponding reactant. The calculations were carried out with the hybrid B3LYP method [10,11] and the 6-31G(d) basis sets, which are implemented in the Gaussian 03 software [12].

Fig. 1 shows the structures and relative energies for four LMs, and 2', 3', 4', and 5', and for two TSs between 2' and 4', and between 3' and 5'. In the skeletal ring contraction of 2'–4', the siloxy group on the carbon atom in the six-membered ring migrates to the adjacent silicon atom, and simultaneously, the methylene–silicon bond in the six-membered ring is broken, and then the methylene group attacks the carbon atom adjacent to the silicon to form the five-membered ring. On the other hand, in the isomerization reaction of 3' to 5', the siloxy group on the carbon atom and the silyl group on the silicon atom migrate mutually to exchange their bonding atoms.

Fig. 2 shows the other TSs and LMs relating to the isomerization reactions illustrated in Scheme 2. The TS in the reaction of 3' leading to 4' is shown in Fig. 2(a). The structure of the product is the same as 4' described above, but it is the enantiomer. The isomerization reaction of 2' leading to the silacyclohex-4-ene, similar to that of 3' to 5', however, does not afford 5', but leads to a new product 6'. The TS in the conversion of 2' to 6', denoted as TS(2' to 6') and the virtual product 6' are shown in Fig. 2(b) and (c), respectively. The energy for the TS(2' to 6') is apparently higher than those for the three reactions mentioned above. This result is consistent with the fact that the product 6 was not detected experimentally (The energetics is discussed later, again.).

A possible route for the isomerization of 2' leading to the formation of 5' involves homolytic scission of the silicon–carbon bond in the six-membered ring. Once the silicon–carbon bond in the ring was cleaved, the methyl and silyl groups on the silicon atom, and the methyl and siloxy groups on the carbon atom can rotate freely. Recombination of the silicon–carbon bond after rotation of the methyl and silyl groups on the silicon obviously produces 3'. Thus, the resulting 3' isomerizes to give 5' as described

above. Fig. 2(d) shows the TS which is formed in homolytic scission of the silicon–carbon bond. The electronic structure for this TS was obtained by the spin polarized solution.

All the TS energies are compared for both simplified and real models as shown in Fig. 3. With the real models, the energies for TS(2 to 4), TS(3 to 4), TS(3 to 5), TS(2 to 6), and TS(2 to biradical species (BS)) arising from homolytic scission of the ring silicon–carbon bond, are calculated to be 188, 191, 192, 201 and 204 kJ mol⁻¹, respectively. Comparing the five TS energies, the latter two are larger than the former three. For more quantitative discussion, we used “the threshold energy” which is defined as the difference between the highest energy among TS(2 to 4), TS(3 to 4), and TS(3 to 5) and the lower energy between TS(2 to 6) and TS(2 to BS). The threshold energy was calculated to be 6 and 9 kJ mol⁻¹ for the simplified and real models, and this difference is too small to explain the result observed experimentally. We carried out the frequency analysis to obtain the Gibbs free energy, and the MP2 calculation. In the free energy calculation, TS(2 to BS) was more stable than the TSs for the allowed reactions, and the threshold energy could not be improved to explain the experimental results at all. TS(2 to BS) has an open structure with the Si–C bond length of 3.8 or 4.2 Å for the simplified and real model, and the major spin density localizes on the Si and C atoms. The relative stability for TS(2 to BS) with the real model increased remarkably compared to the simplified model. We feel that the stability of radical species may be overestimated with the B3LYP functional, and the entropy correction becomes more significant for the open structures like TS(2 to BS). We estimated the MP2 energy for the TSs optimized by the B3LYP functional. The energy for TS(2 to BS) was calculated to be much higher than those for the other TSs. The threshold energy also increased to 19 kJ mol⁻¹. These results agree well with the experimental finding that 3 produces both 4 and 5, but 2 affords 4, as the sole product.

In conclusion, the thermolysis of *cis*-2-trimethylsilyloxy-1-trimethylsilyl-1-silacyclohex-4-ene 2 at 250 °C underwent dyotropic rearrangement to give the ring-contracted product, silyl-substituted cyclopent-3-ene 4 as the sole product. No product, *trans*-2-*tert*-butyl-1-trimethylsilyloxy-1-silacyclohex-4-ene 6, arising from mutual exchange of the trimethylsilyl group and *tert*-butyl group on the silacyclohexenyl ring, was detected in the reaction mixture. Similar thermolysis of *trans*-2-trimethylsilyloxy-1-trimethylsilyl-1-silacyclohex-4-ene 3 afforded two products, 4 and *trans*-1-trimethylsilyloxy-2-trimethylsilyl-1-silacyclohex-4-ene 5.

The theoretical calculation showed that 3 produced both 4 and 5, but 2 afforded only 4 through the comparison of the TS energies, which was consistent with the experimental results. The border line whether the reaction is allowed or forbidden is rather subtle. However, our most reliable estimate, which was obtained by using the B3LYP optimized structure and the MP2 single point energy, indicated the threshold energy of 19 kJ mol⁻¹.

3. Experimental

3.1. General procedure

All reactions of the 1-silacyclohex-3-ene derivatives were carried out in a degassed sealed glass tube (1.0 × 15 cm). NMR spectra were recorded on JNM-LA300 spectrometer and JNM-LA500 spectrometer. Low-resolution mass spectra were measured on a JEOL Model JMS-700 instrument. Column chromatography was performed by using Wakogel C-300 (WAKO). Gel permeation

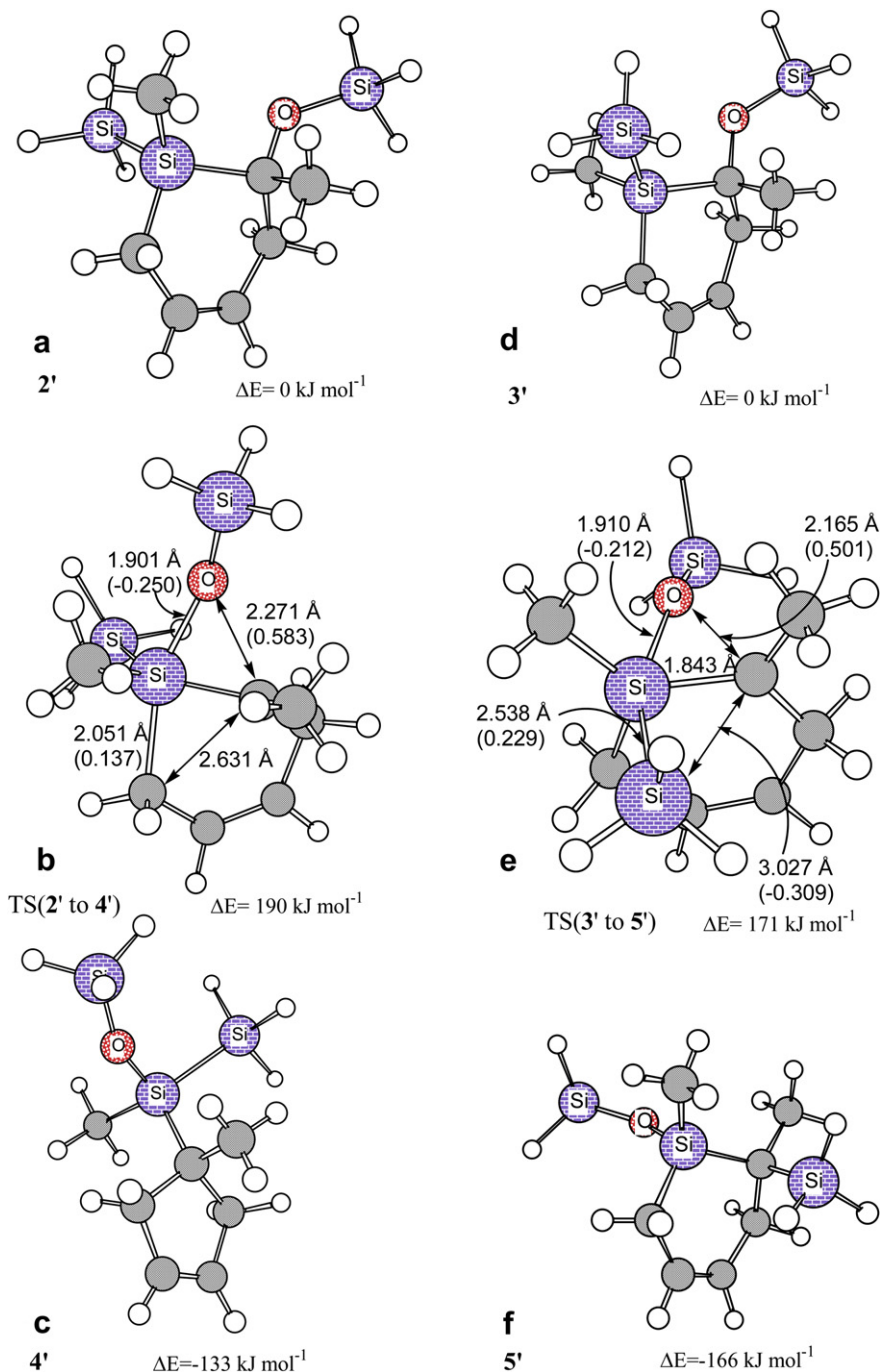


Fig. 1. Optimized structures for 2' (a), TS(2' to 4') (b), 4' (c), 3' (d), TS(3' to 5') (e), and 5' (f) with simplified models. 2', 3', 4', and 5' are simplified models corresponding to 2, 3, 4, and 5, respectively. ΔE means the relative energy of TS and product measured from the corresponding reactant.

chromatography separation was performed with a Model LC-908 Recycling Preparative HPLC (Japan Analytical Industry Co. Ltd.).

3.2. Synthesis of benzoyl(*tert*-butyl)bis(trimethylsilyl)silane (**1**)

In a 200 mL two-necked flask was placed 5.035 g (18.7 mmol) of *tert*-butyltris(trimethylsilyl)silane and 2.265 g (20.2 mmol) of potassium *tert*-butoxide. To this was added 100 mL of THF at room temperature. The solution turned yellow immediately. The mixture was stirred for 43 h at room temperature. The resulting solution was added slowly to a solution of 2.624 g (18.7 mmol) of

benzoylchloride in 50 mL of THF at $-78\text{ }^{\circ}\text{C}$ by the use of dropping funnel. The mixture was stirred for 30 min at $-78\text{ }^{\circ}\text{C}$ and allowed to stand at room temperature for 12 h. After the mixture was hydrolyzed with water, the organic layer was separated and the aqueous layer was extracted with ether. The solvent ether was evaporated and the residue was chromatographed on silica gel eluting with hexane:ethyl acetate/1:1, to give 3.095 g (56% yield) of **1**: Anal. Calcd for $\text{C}_{17}\text{H}_{32}\text{OSi}_3$: C, 60.64; H, 9.58. Found: C, 60.33; H, 9.44. MS m/z 336 (M^+); ^1H NMR δ (CDCl_3) 0.26 (s, 18H, Me_3Si), 1.15 (s, 9H, *t*-Bu), 7.41–7.53 (m, 3H, phenyl ring protons), 7.69 (d, 2H, phenyl ring protons, $J = 7.1$ Hz); ^{13}C NMR δ (CDCl_3) 1.5 (Me_3Si ,

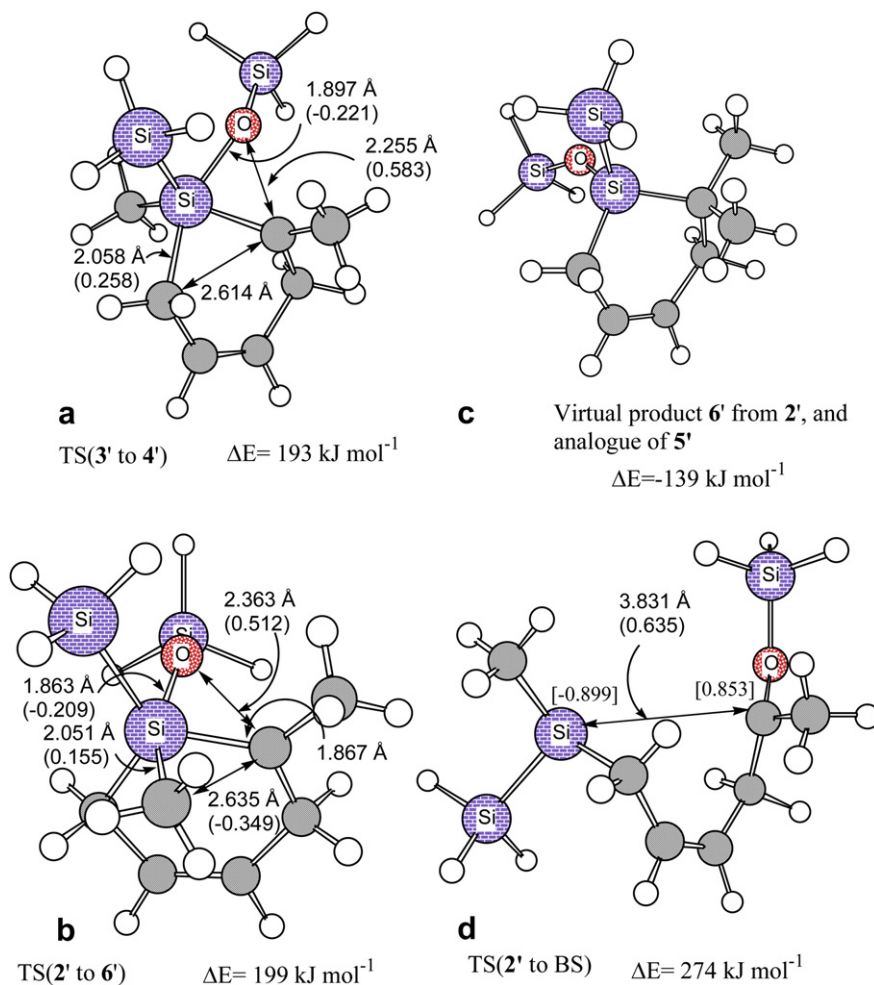


Fig. 2. Optimized structures for TS(3' to 4') (a), TS(2' to 6') (b), virtual product 6' (c), and TS(2' to BS), i.e., TS for the Si–C bond breaking (d). See the caption of Fig. 1, and 6' is a simplified model corresponding to 6.

21.8 (CMe₃), 30.9 (Me₃C), 127.1, 128.2, 132.1, 144.8 (phenyl ring carbons), 237.7 (CO); ²⁹Si NMR δ (CDCl₃) –25.9 (SiSiMe₃), –15.1 (Me₃SiSi).

3.3. Synthesis of 2 and 3

A mixture of 0.461 g (1.37 mmol) of 1 and 0.392 g (4.78 mmol) of 2,3-dimethyl-1,3-butadiene was heated in a sealed tube at

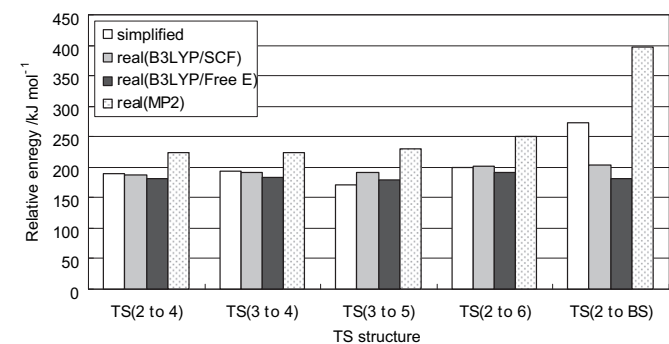


Fig. 3. Comparison of the five TS energies evaluated for the simplified and real models. For real models, the SCF energy, Gibbs free energy through the frequency analysis, and MP2 energy are shown. The MP2 energy was estimated by a single point calculation with the B3LYP optimized structure. Primes for simplified models are omitted for clarity.

140 °C for 24 h. The reaction mixture was chromatographed on silica gel using hexane as the eluent to give a mixture of products 2 and 3 (0.352 g, 66% combined yield). The ratio of the isomers was calculated to be approximately 1:1 by the ¹H NMR spectroscopic analysis. All attempts to separate one isomer from the other were unsuccessful. But the isolated mixture showed different ratios of the isomers by the use of the recycling HPLC. For 2: Anal. Calcd for C₂₃H₄₂OSi₃: C, 65.96; H, 10.11. Found: C, 65.99; H, 10.00. MS *m/z* 418 (M⁺); ¹H NMR δ (CDCl₃) 0.10 (s, 9H, Me₃Si), 0.35 (s, 9H, Me₃Si), 0.77 (s, 9H, *t*-Bu), 1.48 (br s, 2H, ring protons), 1.71 (s, 3H, Me), 1.81 (s, 3H, Me), 2.78 (d, 1H, ring proton, *J* = 16.8 Hz), 2.96 (d, 1H, ring proton, *J* = 16.8 Hz), 7.00–7.52 (m, 5H, phenyl ring protons); ¹³C NMR δ (CDCl₃) 1.3, 3.1 (Me₃Si), 16.3 (CH₂Si), 19.8 (CMe₃), 21.5, 23.7 (Me), 28.5 (Me₃C), 48.9 (CH₂), 76.9 (CO), 125.4, 125.6, 125.9, 126.0, 127.6, 149.2 (phenyl ring and olefinic carbons); ²⁹Si NMR δ (CDCl₃) –18.4 (SiSiMe₃), –9.2 (Me₃SiSi), 11.9 (OSiMe₃). For 3: MS *m/z* 418 (M⁺); ¹H NMR δ (CDCl₃) 0.06 (s, 9H, Me₃Si), 0.13 (s, 9H, Me₃Si), 1.08 (s, 9H, *t*-Bu), 1.29 (d, 1H, ring proton, *J* = 16.5 Hz), 1.65 (s, 3H, Me), 1.78 (s, 3H, Me), 1.80 (d, 1H, ring proton, *J* = 16.5 Hz), 2.68 (d, 1H, ring proton, *J* = 17.4 Hz), 2.88 (d, 1H, ring proton, *J* = 17.4 Hz), 6.99–7.51 (m, 5H, phenyl ring protons); ¹³C NMR δ (CDCl₃) 0.8, 2.7 (Me₃Si), 16.5 (CH₂Si), 20.5 (CMe₃), 21.1, 23.7 (Me), 29.1 (Me₃C), 49.4 (CH₂), 77.5 (CO), 125.2, 125.3, 125.5, 126.6, 127.8, 149.4 (phenyl ring and olefinic carbons); ²⁹Si NMR δ (CDCl₃) –19.5 (SiSiMe₃), –10.1 (Me₃SiSi), 10.8 (OSiMe₃).

3.4. Thermolysis of **2** and **3** in a ratio of 80:20

Compounds **2** and **3** (0.0138 g, 0.0329 mmol) were heated in a sealed tube at 250 °C for 24 h. The reaction mixture was analyzed by ¹H NMR spectrum as being the products **4** (43%) and **5** (12%), in addition to the starting compounds **2** (40%) and **3** (5%). Products **4** and **5** were isolated by column chromatography. For **4**: Anal. Calcd for C₂₃H₄₂OSi₃: C, 65.96; H, 10.11. Found: C, 66.01; H, 9.98. MS *m/z* 418 (M⁺); ¹H NMR δ (CDCl₃) 0.23 (s, 9H, Me₃Si), 0.26 (s, 9H, Me₃Si), 0.79 (s, 9H, *t*-Bu), 1.52 (s, 6H, Me), 2.87 (d, 1H, ring proton, *J* = 16.5 Hz), 2.93 (br s, 2H, ring protons), 3.17 (d, 1H, ring proton, *J* = 16.5 Hz), 7.02 (tt, 1H, phenyl ring proton, *J* = 7.3 Hz, 1.2 Hz), 7.20 (t, 2H, phenyl ring protons, *J* = 7.3 Hz), 7.39 (dd, 2H, phenyl ring protons, *J* = 7.3 Hz, 1.2 Hz); ¹³C NMR δ (CDCl₃) 1.5, 2.4 (Me₃Si), 13.7 (Me), 23.1 (CMe₃), 27.7 (Me₃C), 40.3 (quarternary ring carbon), 47.6, 49.8 (CH₂), 124.4, 127.4, 127.7, 129.2, 129.7, 149.2 (phenyl ring and olefinic carbons); ²⁹Si NMR δ (CDCl₃) -21.8 (Me₃Si), 2.7 (SiMe₃), 5.6 (OSiMe₃). For **5**: Anal. Calcd for C₂₃H₄₂OSi₃: C, 65.96; H, 10.11. Found: C, 65.86; H, 9.79. MS *m/z* 418 (M⁺); ¹H NMR δ (CDCl₃) 0.09 (s, 9H, Me₃Si), 0.14 (s, 9H, Me₃Si), 0.95 (d, 1H, ring proton, *J* = 17.1 Hz), 1.05 (d, 1H, ring proton, *J* = 17.1 Hz), 1.17 (s, 9H, *t*-Bu), 1.60 (s, 3H, Me), 1.67 (s, 3H, Me), 2.61 (d, 1H, ring proton, *J* = 18.3 Hz), 2.83 (d, 1H, ring proton, *J* = 18.3 Hz), 7.03 (tt, 1H, phenyl ring proton, *J* = 7.3 Hz, 1.2 Hz), 7.22 (t, 2H, phenyl ring protons, *J* = 7.3 Hz), 7.36 (dd, 2H, phenyl ring protons, *J* = 7.3 Hz, 1.2 Hz); ¹³C NMR δ (CDCl₃) 0.1, 2.3 (Me₃Si), 17.9 (CH₂Si), 20.17 (CMe₃), 20.22, 24.2 (Me), 28.3 (Me₃C), 29.6 (quarternary ring carbon), 39.1 (CH₂), 123.4, 124.9, 125.8, 127.4, 127.8, 145.9 (phenyl ring and olefinic carbons); ²⁹Si NMR δ (CDCl₃) -1.8 (ring Si), 3.5 (Me₃Si), 7.8 (OSiMe₃).

3.5. Thermolysis of **2** and **3** in a ratio of 50:50

Compounds **2** and **3** (0.2587 g, 0.618 mmol) were heated in a sealed tube at 250 °C for 24 h. The reaction mixture was analyzed by ¹H NMR spectrum as being the products **4** (32%) and **5** (30%), in addition to the starting compounds **2** (25%) and **3** (13%). Products **4** and **5** were isolated by column chromatography. All spectral data for **4** and **5** were identical with those of the authentic sample described above.

3.6. Thermolysis of **2** and **3** in a ratio of 16:84

Compounds **2** and **3** (0.0110 g, 0.0263 mmol) were heated in a sealed tube at 250 °C for 24 h. The reaction mixture was analyzed by ¹H NMR spectrum as being the products **4** (20%) and **5** (59%), in addition to the starting compounds **2** (9%) and **3** (12%). Products **4** and **5** were isolated by column chromatography. All spectral data for **4** and **5** were identical with those of the authentic samples described above.

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