Organometallics **2002,** *21,* 2033−2035

Silicon−Carbon Unsaturated Compounds. 65. Thermal and Photochemical Isomerization of Trimethylsiloxy- and Bis(trimethylsilyl)-Substituted Silacyclobut-3-enes[†]

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Received January 2, 2002

Summary: Heating silacyclobut-3-ene ***2*** *at 250 °C afforded the trans-silacyclobut-3-ene* ***4****, via the silyl-substituted cycloprop-2-ene* ***3****. The photolysis of* ***4*** *gave a 1:1 mixture of* ***4*** *and the cis isomer* ***6****, which was transformed into* ***4*** *at 250 °C, quantitatively. Preliminary results of the theoretical treatment for the isomerization of* ***2′*** *to* ***3′*** *are described.*

Acylpolysilanes are useful precursors for the synthesis of silenes, and various types of the silenes are prepared by the photochemical, thermal, and Peterson-type reactions of these compounds.[1−7] Many papers concerning the reactions of the silenes thus formed with various substrates have been reported to date. Recently, we have found that the thermolysis of pivaloyl- and adamantoyltris(trimethylsilyl)silane with silyl-substituted acetylenes at 120 °C affords formal [2 + 2] cycloadducts, 1-silacyclobut-3-enes, which undergo isomerization cleanly to give the ring-opened products 1-(trimethylsiloxy)-1,1-bis(trimethylsilyl)-3-(silyl)propadienes at 160 °C.[8,9] In this paper we report the novel isomerization of 2,3-di-*tert*-butyl-2-(trimethylsiloxy)-1,1-bis(trimethylsilyl)-1-silacyclobut-3-ene (**2**),[10] obtained from the thermolysis of pivaloyltris(trimethylsilyl)silane (**1**) with *tert*-butylacetylene, to a silyl-substituted cyclopropene and then to the silacyclobut-3-ene system.

When a mixture of **1** and *tert*-butylacetylene was heated in a sealed tube at 140 °C for 24 h, compound **2** was obtained in 94% yield, as a single isomer (Scheme 1). The structure of **2** was verified by spectrometric and elemental analysis. The location of the substituents on the silacyclobut-3-ene ring for **2** was confirmed by NOE-FID difference experiments at 300 MHz. Thus, irradiation of the olefinic proton at δ 6.19 ppm on the sp^2 carbon atom in the four-membered ring resulted in a strong enhancement of the signal at 1.15 ppm, attributed to the *tert*-butyl protons on the sp^2 carbon of the ring, as well as the signals at 0.19 and 0.20 ppm due to two trimethylsilyl protons on the ring silicon atom.

Furthermore, saturation of the *tert*-butyl protons on the sp^3 ring carbon led to enhancement of the signals at 0.18 and 0.20 ppm due to trimethylsiloxy and trimethylsilyl protons, respectively.

When **2** was heated in a sealed glass tube at 250 °C for 5 h, its isomer, *trans*-2,4-di-*tert*-butyl-1-(trimethylsiloxy)-1,2-bis(trimethylsilyl)-1-silacyclobut-3-ene (**4**),[11] was produced in quantitative yield. In this reaction, one might consider that another stereoisomer of **4**, the cis isomer, should be formed. However, no cis isomer was detected in the reaction product by spectrometric analysis.

To learn more about the isomerization of **2** leading to compound **4**, we investigated the thermolysis of **2** under various conditions and found that **2** isomerizes at 190 °C cleanly to give 1,2-di-*tert*-butyl-3-[bis(trimethylsilyl)-(trimethylsiloxy)silyl]cycloprop-2-ene (**3**).[12] As expected, compound **3** thus formed was transformed cleanly into

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(10) Compound **2**: mp 69−70 °C; MS *m/z* 414 (M$^+$); IR 2954, 2900, 1252, 1101, 1043, 899, 835, 748, 685 cm^{-1}; ^{1}H NMR δ (CDCl$_3$) 0.18 (s, 9H, Me$_3$Si), 0.19 (s, 9H, Me$_3$Si), 0.20 (s, 9H, Me$_3$Si), 1.12 (s, 9H, *t*-Bu), 1.15 (s, 9H, *t*-Bu), 6.19 (s, 1H, HC=C); ^{13}C NMR δ (CDCl$_3$) 1.07, 1.30, 3.11 (Me$_3$Si), 31.66 (Me$_3$C) (2C), 37.72 (CMe$_3$) (2C), 96.04 (CO), 129.05, 174.74 (olefinic carbons); ^{29}Si NMR δ (CDCl$_3$) −24.5, −18.3, −13.5, 4.9. Anal. Calcd for C$_{20}$H$_{46}$Si$_4$O: C, 57.89; H, 11.17. Found: C, 57.70; H, 11.14.

(11) Compound **4**: mp 135−136 °C; MS *m/z* 414 (M$^+$); IR 2958, 2898, 1245, 1076, 1039, 844, 788, 755, 684 cm^{-1}; ^{1}H NMR δ (CDCl$_3$) 0.10 (s, 9H, Me$_3$Si), 0.15 (s, 9H, Me$_3$Si), 0.22 (s, 9H, Me$_3$Si), 1.02 (s, 9H, *t*-Bu), 1.08 (s, 9H, *t*-Bu), 6.45 (s, 1H, HC=C); ^{13}C NMR δ (CDCl$_3$) 0.30, 3.05, 3.72 (Me$_3$Si), 31.07, 32.13 (Me$_3$C), 33.64, 34.59 (CMe$_3$), 48.84 (CSi), 139.33, 165.07 (olefinic carbons); ^{29}Si NMR δ (CDCl$_3$) −27.8, −20.0, 1.5, 6.1. Anal. Calcd for C$_{20}$H$_{46}$Si$_4$O: C, 57.89; H, 11.17. Found: C, 57.81; H, 11.21.

(12) Compound **3**: MS *m/z* 414 (M$^+$); ^{1}H NMR δ (C$_6$D$_6$) 0.28 (s, 9H, Me$_3$Si), 0.36 (s, 18H, Me$_3$Si), 1.18 (s, 1H, CH), 1.27 (s, 18H, *t*-Bu); ^{13}C NMR δ (C$_6$D$_6$) 0.28, 2.75 (Me$_3$Si), 12.47 (CH), 29.38 (Me$_3$C), 31.16 (CMe$_3$), 116.73 (olefinic carbons); ^{29}Si NMR δ (CDCl$_3$) −20.8, 1.4, 5.4; exact mass calcd for C$_{20}$H$_{46}$Si$_4$O ([M$^+$]) 414.2626, found 414.2598.

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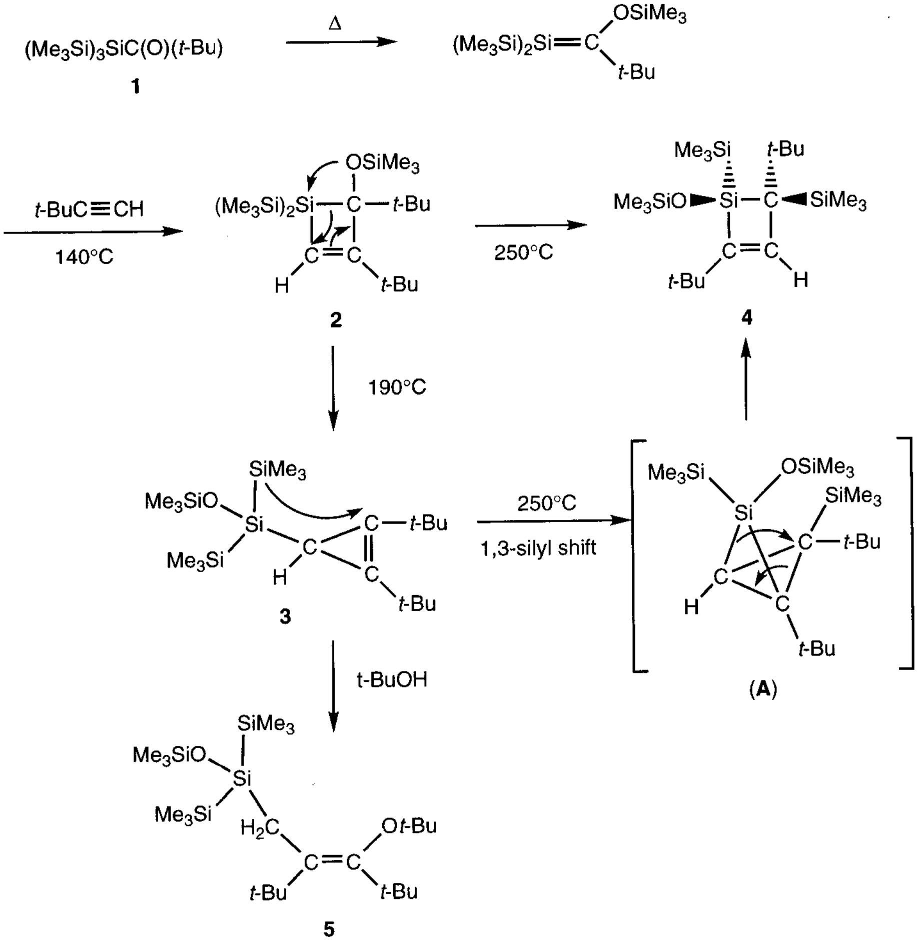
Scheme 1



4 at 250 °C. Product **3** is labile in air and decomposes slowly to unidentified materials.

The ^{1}H NMR spectrum for **3** shows two signals at δ 0.28 and 0.36 ppm, due to trimethylsiloxy protons and two equivalent trimethylsilyl protons, and two signals at 1.18 and 1.27 ppm, attributed to a proton and two equivalent *tert*-butyl protons, respectively. ^{13}C and ^{29}Si NMR spectra are also consistent with the structure proposed for **3**.

The thermolysis of **2** in the presence of *tert*-butyl alcohol in a sealed tube at 210 °C for 36 h afforded (*Z*)-1-*tert*-butoxy-1,2-di-*tert*-butyl-2-[((trimethylsiloxy)bis(trimethylsilyl)silyl)methyl]ethene (**5**),[13] arising from the scission of a carbon−carbon bond in the cyclopropene ring, in 35% yield, in addition to a 44% yield of **4**. The structure of **5** was verified by mass and ^{1}H, ^{13}C, and ^{29}Si NMR spectrometric analysis. The *Z* geometry of **5** was confirmed by NOE-FID difference experiments at 300 MHz. The formation of **5** clearly indicates that isomerization from **2** to **3** does not involve a carbene intermediate, proposed as the reactive intermediate in the cothermolysis of **1** with acetone reported previously.[14]

Scheme 1 illustrates a possible mechanistic interpretation for the isomerization of **2** to **4**. The mechanism involves the formation of silyl-substituted cyclopropene **3** as observed experimentally. Compound **3** thus formed would isomerize to give a silabicyclobutane intermediate (**A**), which is transformed into the final product **4**, although evidence for the formation of this intermediate has not yet been obtained.

The activation energy for the transformation from 2,3-dimethyl-2-siloxy-1,1-disilyl-1-silacyclobut-3-ene (**2′**) to 1,2-dimethyl-3-(siloxydisilylsilyl)cycloprop-2-ene (**3′**) was computed with the Gaussian 98 program[15] to be 34.8 kcal/mol with a zero-point energy correction at the B3LYP/6-31G* level[16,17] of density functional theory. Figure 1 shows optimized geometries of **2′**, **TS**$_{2'/3'}$, **3′**, and **A′**. We confirmed from an intrinsic reaction coor-

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[13] Compound **5**: MS *m*/*z* 488 (M$^+$); ^{1}H NMR δ (CDCl$_3$) 0.19 (s, 18H, Me$_3$Si), 0.27 (s, 9H, Me$_3$Si), 1.18 (s, 9H, *t*-Bu), 1.24 (s, 9H, *t*-Bu), 1.25 (s, 9H, *t*-Bu), 2.02 (s, 2H, CH$_2$); ^{13}C NMR δ (CDCl$_3$) 0.86, 3.04 (Me$_3$Si), 21.30 (CH$_2$), 30.99, 31.77, 31.92 (Me$_3$C), 35.59, 37.89, 72.02 (CMe$_3$), 124.45, 150.72 (olefinic carbons); ^{29}Si NMR δ (CDCl$_3$) −18.9, −2.6, 8.8. Anal. Calcd for $C_{24}H_{56}Si_4O_2$: C, 58.94; H, 11.54. Found: C, 58.83; H, 11.20.

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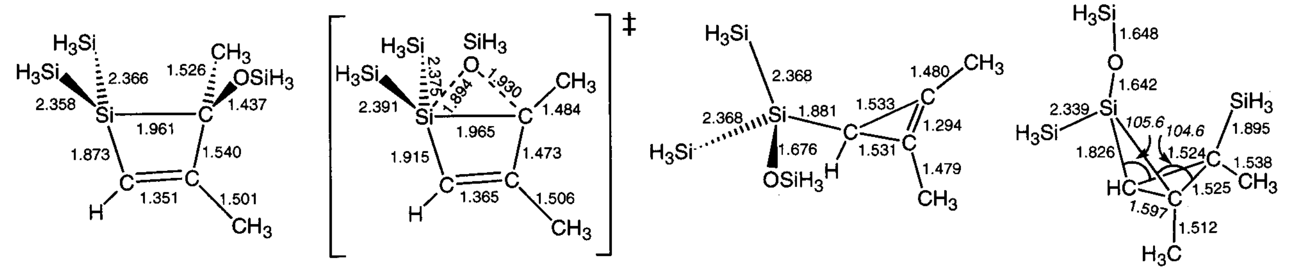
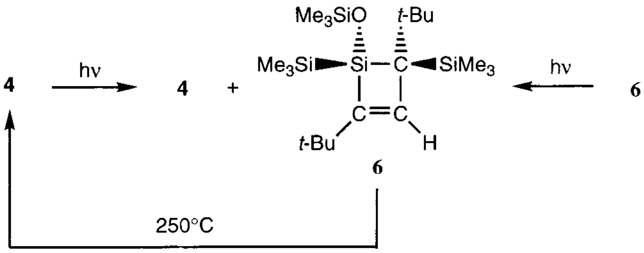


2' **TS$_{2'/3'}$** **3'** **(A')**

Figure 1. Optimized geometries of **2′**, **TS$_{2'/3'}$**, **3′**, and **A′** at the B3LYP/6-31G* level.

Scheme 2



dinate (IRC) analysis[18] that **TS$_{2'/3'}$** correctly connects **2′** and **3′**. This interesting process is a typical 1,2-siloxyl shift with a triangle geometry in the transition state, which results in the formation of a cyclopropene ring. We first assumed that a reaction intermediate that involves a five-coordinated silicon species should take place in this thermal reaction as a result of the 1,2-siloxyl shift, but this assumption was unsuccessful in our DFT computations, despite our best efforts. The cyclopropene structure is a reasonable intermediate, rather than a five-coordinate silicon intermediate, in that its valency is fully satisfied. The calculated activation energy shows that this process can reasonably occur under thermolysis conditions. We propose from DFT computations that intermediate **A** is involved during the isomerization of **3** to **4**. We are now optimizing the transition states connecting **A** with **3** and **4**. Detailed theoretical analyses on the entire reaction pathway will be reported in due course.

Interestingly, irradiation of **4** in a hexane solution with a low-pressure mercury lamp afforded an equilibrium mixture consisting of **4** and its stereoisomer, *cis*-2,4-di-*tert*-butyl-1-(trimethylsiloxy)-1,2-bis(trimethylsilyl)-1-silacyclobut-3-ene (**6**),[19] in a ratio of 1:1 (Scheme 2). Pure isomer **6** was separated from **4** by recycling preparative HPLC. That the photochemical reaction reaches a true equilibrium is confirmed by the observation that equal amounts of **4** and **6** are also obtained by the photolysis of pure **6**. To our surprise, when compound **6**, and also a 1:1 mixture of **4** and **6**, was heated in a sealed tube at 250 °C for 7 h, the trans isomer **4** was obtained quantitatively. No cis isomer **6** was detected in the resulting product. At present, the mechanism for the exclusive formation of **4** from **6** in the thermal process is not clear, but some interaction between the oxygen of a trimethylsiloxy group and the trimethylsilyl silicon located on the same side of the silacyclobut-3-ene ring might be present.

Configurations of **4** and **6** were verified by NOE-FID difference experiments at 300 MHz.[20] For **4**, saturation of hydrogen at 6.45 ppm on the sp^2 carbon led to the enhancement of two *tert*-butyl protons at 1.02 and 1.08 ppm, as well as trimethylsilyl protons at 0.10 ppm, as expected. Similar saturation of the protons at 1.02 ppm due to the *tert*-butyl group on the sp^3 carbon showed the enhancement of two trimethylsilyl protons at 0.10 and 0.22 ppm and hydrogen on the silacyclobutene ring. For **6**, irradiation of hydrogen at 6.71 ppm resulted in a strong enhancement of the protons at 1.04 and 1.06 ppm, due to two nonequivalent *tert*-butyl groups, as well as the protons at 0.07 ppm, attributed to the trimethylsilyl group on the sp^3 carbon. Irradiation of the *tert*-butyl protons at 1.04 ppm on the sp^3 carbon led to the enhancement of hydrogen on the silacyclobutene ring and the trimethylsilyl protons and trimethylsiloxy protons at 0.07 and 0.15 ppm, respectively. Similar irradiation of the trimethylsilyl protons at 0.20 ppm resulted in the enhancement of the trimethylsilyl protons, trimethylsiloxy protons, and *tert*-butyl protons on the sp^3 carbon at 0.07, 0.15, and 1.06 ppm, respectively. These results clearly indicate that compound **4** must have a trans configuration and **6** must be a cis form.

We are continuing to explore this and related systems.

Acknowledgment. This work was supported by a Grant-in-Aid for Scientific Research (No. 12650858) from the Ministry of Education, Science, Sports, and Culture of Japan, to which our thanks are due.

Supporting Information Available: Text giving experimental details and characterization data for all new compounds and figures giving ^{1}H$-^{29}$Si COSY spectra for **4** and **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM020001V

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(19) Compound **6**: mp 96−97 °C; MS *m/z* 414 (M$^+$); IR 2954, 2898, 2861, 1469, 1251, 1072, 1043, 840, 754 cm^{-1}; ^{1}H NMR δ (CDCl$_3$) 0.07 (s, 9H, Me$_3$Si), 0.15 (s, 9H, Me$_3$Si), 0.20 (s, 9H, Me$_3$Si), 1.04 (s, 9H, *t*-Bu), 1.06 (s, 9H, *t*-Bu), 6.71 (s, 1H, HC=C); ^{13}C NMR δ (CDCl$_3$) 0.51, 3.05, 3.50 (Me$_3$Si), 30.53, 31.82 (Me$_3$C), 33.58, 35.44 (CMe$_3$), 45.05 (CSi), 145.38, 164.71 (olefinic carbons); ^{29}Si NMR δ(CDCl$_3$) −21.7, −5.6, −1.7, 6.5; exact mass calcd for C$_{20}$H$_{46}$Si$_4$O ([M$^+$]) 414.2626, found 414.2631.

(20) Proton chemical shifts for **4** and **6** were determined by ^{1}H$-^{29}$Si COSY experiments.

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