

## Retention Stereochemistry of Thermal 1,3-Silyl Migration in Allylsilanes

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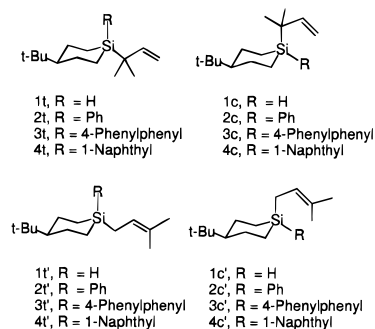
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Although thermal 1,3-silyl migration in allylic silanes has long been thought in general to proceed concertedly with inversion of configuration at the migrating silicon, according to the experiments with optical active allylic methyl(naphthyl)phenylsilanes by Kwart et al.,<sup>1</sup> recent theoretical studies by us<sup>2</sup> and Yamabe et al.<sup>3</sup> have revealed that for the thermal 1,3-silyl migration in  $\text{CH}_2=\text{CHCH}_2\text{SiH}_3$ , two concerted pathways which lead to retention and inversion at the silicon are allowed. The theoretical results have indicated that the activation energy for the retention pathway is even lower than that for the inversion pathway. There has been no experimental evidence for the existence of the retention pathway of the 1,3-silyl migration in allylic silanes so far.<sup>4,5</sup> We wish herein to report the first examples of the thermal 1,3-silyl migration with retention stereochemistry and the significant dependence of the stereochemical outcome on a substituent at silicon.<sup>6</sup>

As an appropriate aliphatic system to investigate the stereochemistry of the 1,3-silyl migration, we have chosen stereochemically rigid 4-*tert*-butylsilacyclohexane derivatives, which were first designed and synthesized by Sakurai et al.<sup>7,8</sup> (*E*)- and (*Z*)-4-*tert*-butyl-1-(1,1-dimethylallyl)silacyclohexane derivatives **1**–**4** were synthesized as follows; a reaction of a di-Grignard reagent of 1,5-dibromo-3-*tert*-butylpentane with (1,1-dimethylallyl)dichlorosilane<sup>9</sup> afforded a mixture of (*E*)- and (*Z*)-4-*tert*-butyl-1-(1,1-dimethylallyl)silacyclohexanes (**1t** and **1c**, respectively) with the cis/trans ratio of 1:2.<sup>10</sup> 1-Aryl-4-*tert*-butyl-1-(1,1-dimethylallyl)silacyclohexane derivatives **2**–**4** were obtained by the photochemical isomerization<sup>11</sup> of the corresponding 3,3-dimethylallylsilane derivatives **2'**–**4'**. They were synthesized by the reactions of the corresponding aryllithium reagents with 4-*tert*-butyl-1-chloro-1-(3,3-dimethylallyl)silacyclohexanes obtained by the reaction of the di-Grignard reagent with (3,3-dimethylallyl)trichlorosilane. The cis and trans isomers of **1**–**4** were separated from the mixture by means of HPLC. The stereoisomers of **1** were

assigned by comparing the  $^3J_{\text{HH}}$  values for H–Si–C–H between the two isomers. Thus, an isomer of **1** showed the  $^3J_{\text{HSiCH}}$  values of 7.4 and 1.5 Hz, while the corresponding values of the other isomer were 2.4 and 1.2 Hz. Comparison of the coupling constants with those for 4-*tert*-butyl-1-methylsilacyclohexanes studied by Sakurai et al.<sup>5</sup> and other silacyclohexane derivatives<sup>12</sup> led to the unambiguous assignment of the stereoisomers: the isomer with the large  $^3J_{\text{HSiCH}}$  of 7.5 Hz to **1t** and the other isomer to **1c**.



The stereochemistries of **3t** and **3t'** were confirmed by X-ray crystallography. The molecular structures of **3t** and **3t'** are shown in Figure 1.<sup>13</sup> The stereoisomers of **2**, **2'**, **4**, and **4'** were identified unambiguously by comparing proton chemical shifts of these compounds with those of **3t** and **3c** and those of **3t'** and **3c'**; <sup>1</sup>H NMR resonances of *tert*-butyl protons in trans-isomers of **2**–**4** and **2'**–**4'** appear always at higher fields than those of the corresponding cis-isomers; <sup>1</sup>NMR resonances of allylic protons of **2t'**, **3t'**, and **4t'** appear at higher fields than those of the cis-isomers.<sup>15</sup>

When **1t** and **1c** were heated in sealed tubes without solvents at 350 °C for 10 min, facile 1,3-silyl migration took place to give the corresponding 3,3-dimethylallylsilane derivatives **1t'** and **1c'**, respectively, in almost quantitative yields, with complete retention of configuration, as shown in Table 1; allylic silanes **1t'** and **1c'** were configurationally stable at 350 °C for more than 1 h, while partial decomposition to the unidentified products was observed during the prolonged reaction time. The assignment of the stereochemistry of the products was confirmed on the basis of the  $^3J_{\text{HSiCH}}$  values; the product from **1t** showed  $^3J_{\text{HSiCH}}$  values of 7.4 and 1.5 Hz, while the  $^3J_{\text{HSiCH}}$  values of the product from **1c** were 2.4 and 1.2 Hz. The present results constitute the first observation of the 1,3-silyl migration in allylic silanes with retention of configuration at the silicon atom, which is predicted by theoretical calculations.<sup>1,16</sup>

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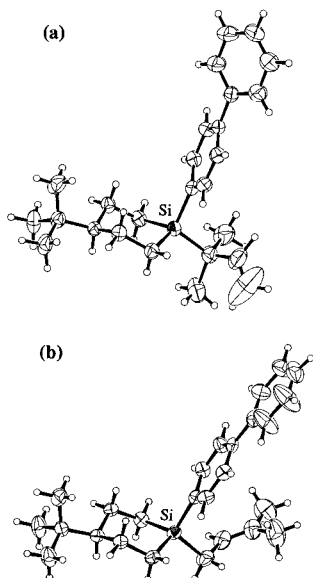
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(13) The reflection intensities were collected on a Rigaku AFC-5R diffractometer with a rotating anode (45 kV, 200 mA), using graphite-monochromated Cu K $\alpha$  radiation ( $\lambda = 1.54178$  Å). The structure was solved by direct methods, using SIR-92,<sup>14</sup> and refined by full-matrix least squares on  $F^2$ . **3t**:  $\text{C}_{26}\text{H}_{36}\text{Si}$ ; colorless, prismatic; orthorhombic; space group  $P_{21}$  (No. 61);  $a = 23.884(4)$  Å,  $b = 18.457(2)$  Å,  $c = 10.867(1)$  Å,  $V = 4790.7(9)$  Å<sup>3</sup>;  $Z = 8$ ;  $r_{\text{calcd}} = 1.044$  g/cm<sup>3</sup>;  $\mu(\text{Cu K}\alpha) = 8.90$  cm<sup>-1</sup>; 150 K.  $R = 0.052$  (data with  $I > 3\sigma(I)$ ),  $R_w = 0.045$ , and  $\text{GOF} = 2.78$ . **3t'**:  $\text{C}_{26}\text{H}_{36}\text{Si}$ ; colorless, prismatic; triclinic; space group  $P_1$  (No. 1);  $a = 19.809(4)$  Å,  $b = 21.540(5)$  Å,  $c = 6.271(3)$  Å,  $\alpha = 94.20(3)^\circ$ ,  $\beta = 91.30(3)^\circ$ ,  $\gamma = 117.37(1)^\circ$ ;  $V = 2365(1)$  Å<sup>3</sup>;  $Z = 4$ ;  $r_{\text{calcd}} = 1.058$  g/cm<sup>3</sup>;  $\mu(\text{Cu K}\alpha) = 9.02$  cm<sup>-1</sup>; 286 K.  $R = 0.075$  (data with  $I > 3\sigma(I)$ ),  $R_w = 0.074$ , and  $\text{GOF} = 6.94$ .

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(15) Details of the experimental data of all of these allylic silanes are given in the Supporting Information.

(16) Alternative isomerization pathways including homolytic cleavage of the silicon–carbon (allyl) bond cannot compete with the concerted 1,3-silyl migration on the basis of the experimental bond dissociation energy (BDE) of 73 kcal/mol (305 kJ/mol) for the Si–C(allyl) bond;<sup>17</sup> a half-life for the bond homolysis is estimated to be around 10<sup>9</sup> s at 350 °C, if the A factor is reasonably assumed as 10<sup>16</sup> s<sup>-1</sup>.

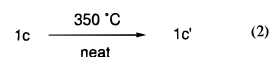
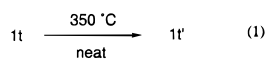


**Figure 1.** ORTEP drawings of **3t** (a) and **3t'** (b).

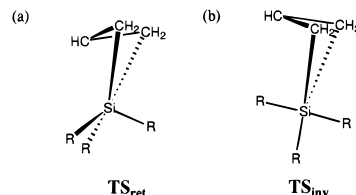
**Table 1.** Thermal Isomerization of 4-*tert*-Butyl-1-(1,1-dimethylallyl)silacyclohexanes to the Corresponding 4-*tert*-Butyl-1-(3,3-dimethylallyl)silacyclohexanes in Sealed Tubes at 350 °C<sup>a</sup>

starting allylsilane	cis/trans ratio	reaction time (min)	conversion (%)	product		
				major isomer	cis/trans ratio	yield (%)
<b>1t</b> (R = H)	0/100	10	36	<b>1t'</b>	0/100	95
<b>1c</b> (R = H)	100/0	10	45	<b>1c'</b>	100/0	94
<b>2t</b> (R = Ph)	0/100	10	65	<b>2t'</b>	0/100	99
<b>2c</b> (R = Ph)	92/8	10	65	<b>2c'</b>	92/8	98
<b>3t</b> (R = Biph) <sup>b</sup>	0/100	5	60	<b>3t'</b>	33/67	98
<b>3c</b> (R = Biph) <sup>b</sup>	100/0	5	73	<b>3c'</b>	60/40	98
<b>4t</b> (R = Naph) <sup>c</sup>	0/100	5	50	<b>4t'</b>	31/69	97
<b>4c</b> (R = Naph) <sup>c</sup>	100/0	5	66	<b>4c'</b>	70/30	100

<sup>a</sup> The cis/trans ratios of the starting and produced allylic silanes, conversion, and product yields were determined by NMR. <sup>b</sup> Biph = 4-phenylphenyl, Naph = 1-naphthyl.



Interestingly, the stereochemical outcome of the 1,3-silyl migration in the allylic silanes varied depending on the substituents at the silicon atom. Thus, as shown in Table 1, hydrido- and phenyl-substituted allylic silanes (**1** and **2**) showed the complete retention of the stereochemistry, while the stereochemistry of the starting materials was lost to a significant extent in



**Figure 2.** Schematic representation of the retention (TS<sub>ret</sub>, a) and inversion transition states (TS<sub>inv</sub>, b) in the 1,3-silyl migration of CH<sub>2</sub>=CHCH<sub>2</sub>SiR<sub>3</sub>.

the case of 4-phenylphenyl and 1-naphthyl-substituted allylic silanes (**3** and **4**).

In our theoretical paper,<sup>2</sup> two transition states, the retention (TS<sub>ret</sub>) and the inversion transition states (TS<sub>inv</sub>), have been found in the 1,3-silyl migration of allylsilane (CH<sub>2</sub>=CHCH<sub>2</sub>SiH<sub>3</sub>); the structures TS<sub>ret</sub> and TS<sub>inv</sub> are pentacoordinate square pyramidal and trigonal bipyramidal around silicon atom, respectively, as shown schematically in Figure 2. Furthermore, it has been suggested that (i) a  $\pi$ -type substituent on silicon like a vinyl group stabilizes more TS<sub>inv</sub> than TS<sub>ret</sub> and (ii) since the TS<sub>ret</sub> is stabilized by subjacent orbital control through significant overlap between a silicon 3p orbital and a 2p $\pi$  orbital of the central carbon, the extent of destabilization by bulky substituents in TS<sub>ret</sub> will be larger than that in the TS<sub>inv</sub>. With these two effects, in the allylic silanes with a relatively bulky aromatic substituent, the inversion pathway may participate competitively or even preferably to the retention pathway. The observed stereochemical outcome is in good accord with the theoretical prediction, but it is necessary to elucidate the transition structures in the allylsilacyclohexane systems in more detail. Allylic silanes **1** with a less bulky hydrido substituent showed complete retention of configuration in the thermal 1,3-silyl migration, while **4** bearing a relatively large aromatic substituent gave low stereoselectivity. Since a difference in the steric hindrance at the transition states between **2** and **3** is unlikely to exist, the observed difference in the stereochemical outcome may be ascribed to the difference in the electronic effects between **2** and **3**. The inversion stereochemistry for the 1,3-silyl migration in optically active allylic silanes bearing phenyl and naphthyl substituents observed by Kwart et al.<sup>1</sup> is understood by extrapolating the above discussion.

**Supporting Information Available:** Experimental details for the preparation and characterization of various allylic silacyclohexane derivatives, X-ray structural information on **3t** and **3t'**, and <sup>1</sup>H NMR spectra of several allylic silacyclohexanes (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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