J. Phys. Chem. A **2005,** *109,* 11902−11906

The Mechanism of Photochemical 1,3-Silyl Migration of Allylsilane

Masae Takahashi*

Photodynamics Research Center, The Institute of Physical and Chemical Research (RIKEN), 519-1399, Aoba, Aramaki, Aoba-ku, Sendai 980-0845, Japan

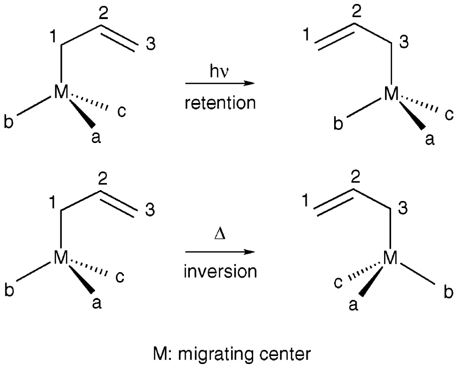
Received: July 20, 2005; In Final Form: October 7, 2005

The photochemical reaction mechanisms of model compounds for 4-*tert*-butyl-1-(4-phenylphenyl)-1-(1,1-dimethylallyl)silacyclohexane are investigated using a complete active space comprised of six electrons in six orbitals with the standard 6-31G(d) basis set. It is concluded that the stereochemistry in the photochemical 1,3-silyl migrations of allylsilanes has a retention preference, in accord with the Woodward−Hoffmann rules. The calculated conical intersection (CI) structure suggests a dissociation path to radicals in addition to a 1,3-shift path. The bulkiness and rigidness of a silacyclohexane moiety does not affect the stereochemistry, but a slightly elongated Si−C bond length in the CI structure would promote the dissociation path.

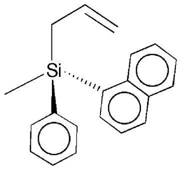
1. Introduction

The photochemical 1,3-silyl migrations from carbon to carbon are of particular interest from a mechanistic point of view. A large number of reactions involving the photochemical 1,3-silyl migrations from carbon to carbon,[1] or between heteroatoms,[2] have been reported in the literature. However, the description of the stereochemical and mechanistic details is scarce.[1c] The stereochemistry of a 1,3-sigmatropic rearrangement is explained systematically by the well-established Woodward−Hoffmann (W−H) rules, the basis of which is an orbital symmetry.[3] The migrating group moves according to a supra process in the photochemical 1,3-sigmatropic rearrangement, and the configuration is retained, whereas the thermal and suprafacial rearrangement occurs with an inversion of the configuration at the migrating center (Scheme 1). Although the W−H rules correctly predict the stereochemistry in the reactions of organic compounds with a carbon framework, it is of great interest to examine whether the rule is applicable to the stereoselection of organosilicon compounds. Following modern experiments and quantum chemical computations, it is noted that a low-lying crossing on the potential energy surface (conical intersection: CI) is a general feature of the excited states relevant to photochemical reactions.[4]

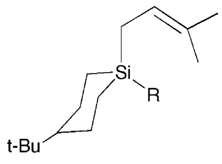
SCHEME 1. Suprafacial 1,3-Sigmatropic Migrations from Carbon to Carbon



The experiment by Kwart and Slutsky in 1972 showed experimentally that the thermal 1,3-silyl migration of optical active allylic methyl(naphthyl)phenylsilane (**1**) proceeds suprafacially with an inversion of the configuration at the silicon,[5] and the stereochemistry agrees with the prediction by the W−H rules. Since then, the thermal 1,3-silyl migration in allylic silanes was long believed to generally follow the W−H rules. More than 20 years after the experiment by Kwart and Slutsky,[5] we[6] and Yamabe et al.[7] have revealed simultaneously and independently, using advanced theoretical calculations, that the thermal 1,3-silyl migration of allylsilane and the derivatives prefers a retention pathway over an inversion one, which is against the W−H rules. As an example of the retention preference in thermal 1,3-silyl migration, the experiment of β-keto silanes on 1,3-silyl migration from carbon to oxygen was shown.[8] The reaction is, however, regarded from our theoretical investigation[9] as an intramolecular nucleophilic substitution, out of the conservation rules of orbital symmetry by Woodward and Hoffmann.[3] Many other 1,3-silyl migrations are attributed to the intramolecular nucleophilic substitutions proceeding with retention of the configuration at the silicon.[10,11] After two theoretical studies indicated the retention preference of the thermal 1,3-silyl migration in allylsilane,[6,7] the first experimental evidence for the retention preference was reported using stereochemically rigid 4-*tert*-butyl-silacyclohexane derivatives (**2**).[12]



1



2

The mechanistic study of the photochemical 1,3-silyl migration of allylic **1** was reported in 1986 by Kira, Taki, and Sakurai.[1c] The photochemical migration occurs with the inversion of the silyl configuration, against the W−H rules. The configuration of the photochemical products was identified by performing the thermal back reaction, which, according to Kwart

---

* Present address: Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan. E-mail: masae@imr.edu.

10.1021/jp053999r CCC: $30.25

et al.,[5] occurs with inversion. On the other hand, the thermal 1,3-silyl migration of allylic silanes with an inversion of the configuration was doubted by Brook.[10] In addition, the thermal 1,3-silyl migration of allylsilane prefers the retention of the configuration theoretically,[6,7] and, actually, the experiment with **2** (R = 4-phenylphenyl) has supported the retention preference.[12]

In this report, we investigate the photochemical 1,3-silyl migrations of allylsilanes theoretically, focusing on the stereochemistry and the reaction mechanism. A photochemical reaction consists of three successive processes: the vertical excitation by a photon, the relaxation on an excited-state potential surface, and the dark reaction on a ground-state potential surface. The first process determines the excited-state surface on which the following reaction proceeds, and thus should be investigated carefully. From the comparison between the calculated UV absorption wavelengths and the excitation wavelength usually used in experiments, the excited state is determined. Accurate calculations of UV absorption wavelengths are required. In our previous studies, we calculated UV absorption maxima of several organosilicon compounds[13−15] and found a good linear correlation between the experiments and calculations (correlation coefficient = 0.98). We carefully calculate the UV absorption wavelength to reveal the first event of photochemistry, and then we investigate the successive photochemical reaction using the complete active space self-consistent field (CASSCF) method.[4] The CASSCF method is currently the most appropriate ab initio method for examining the reaction paths on excited states. Since the report by Robb et al.,[16] several photochemical sigmatropic rearrangements have been extensively studied using the CASSCF method.[17] It is common understanding that the selection of correct orbitals for active space should be carefully carried out in the photochemical study by the CASSCF method. In our previous theoretical study on the photochemistry of silacyclopropenylidene, we experienced that, when using adequately selected orbitals for active space and enough large basis sets, the excitation energy calculated at the MP2−CAS level agrees very well with the experimentally observed UV absorption maximum.[18]

2. Calculations

Ab initio molecular orbital calculations were performed with the Gaussian 98 software package.[19,20]

UV absorption maxima were calculated at the TD/6-311++G(d,p)//MP2/6-31G(d) level as in our previous papers.[13−15] The geometries were fully optimized, and all optimized structures were confirmed to be minima by verifying the absence of imaginary vibrational frequencies in the harmonic approximation.

In the investigation of photochemical reaction pathways, the molecular geometries were fully optimized at the CASSCF level of calculations using the standard 6-31G(d) basis set[19] as implemented in the Gaussian series of programs.[4] The harmonic vibrational frequencies of all stationary points were computed to characterize them as minima (all frequencies are real) or transition states (TSs; only one imaginary frequency).

TABLE 1: Calculated UV Absorption Wavelengths, λ, and the Oscillator Strengths, f[a]

	λ_1/nm	f_1		λ_2/nm	f_2	
4	184.3	0.052	$\pi_{allyl} \rightarrow$ C 3s	178.7	0.433	$\pi_{allyl} \rightarrow \pi^*_{allyl}$
5	187.3	0.051	$\pi_{allyl} \rightarrow$ C 3s	180.6	0.424	$\pi_{allyl} \rightarrow \pi^*_{allyl}$
6	241.1	0.336	$\pi_{ph} \rightarrow \pi^*_{ph}$	223.2	0.003	$\pi_{ph} \rightarrow \pi^*_{ph}$
7	198.5	0.002	$\pi_{allyl} \rightarrow$ C 3s	185.9	0.436	$\pi_{allyl} \rightarrow \pi^*_{allyl}$
8	187.3	0.052	$\pi_{allyl} \rightarrow$ C 3s	180.6	0.431	$\pi_{allyl} \rightarrow \pi^*_{allyl}$
9	217.2	0.017	$\pi_{ph} \rightarrow \pi^*_{ph}$	217.1	0.009	$\pi_{ph} \rightarrow \pi^*_{ph}$
10	217.2	0.028	$\pi_{ph} \rightarrow \pi^*_{ph}$	216.8	0.004	$\pi_{ph} \rightarrow \pi^*_{ph}$
11	184.4	0.052	$\pi \rightarrow \pi^*$	183.2	0.057	$\pi_{allyl} \rightarrow$ C 3s
12	235.0	0.203	$\pi_{ph} \rightarrow \pi^*_{ph}$	220.0	0.001	$\pi_{ph} \rightarrow \pi^*_{ph}$

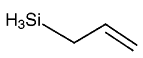
[a] Calculated at the TD/6-311++G(d,p)//MP2/6-31G(d) level.

To select correct orbitals for the active space in the photochemical study using CASSCF methods, we first examine the natural orbitals according to the tutorial[21] for examining the orbitals and planning the active space. We selected the six active orbitals, the π-, π^*-, σ-, and σ^*-orbitals in the C=C bond and the σ- and σ^*-orbitals in the Si−C bond that is cleaved. In the system with six active orbitals, two electrons are fully coupled in a σ_{CC} bond, leaving two possible spin couplings for the remaining four electrons. The driving force that controls the generation of ground-state photoproducts is expected to be provided by recoupling these four electrons in the partly fragmented bonds that occur when the system decays. We must give some justification for the use of six active orbitals. For the description of the photochemical 1,3-sigmatropic shifts in a carbon system, four electrons in four orbitals is the usual active space, as reported by Robb et al.[16] We found, however, as shown in the Results and Discussion section, that better Si−C bond lengths related to the possibility of the dissociation of an allyl group are given in CAS(6,6) than in CAS(4,4). CAS(8,8) including the other σ_{CC} bond would be better than CAS(6,6) to give better C−C bond lengths, but, with our computer system, six electrons in six orbitals was the maximum active space to complete the calculations in a reasonable time scale. In addition, the unbalanced choice of active space does not change the qualitative feature for the reaction mechanism. In the CASSCF calculations, the energies are somewhat overestimated because of the lack of dynamic correlation. In ref 18, we described how the energy is corrected using the MP2−CASSCF method. In this work, the MP2−CASSCF calculations were not performed because we had no experimental data for the present systems to compare to the calculations. The present calculations would give a qualitatively good indication of where the CIs locate in energy relative to the reactant.

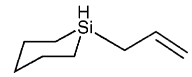
3. Results and Discussion

Photochemical reactions start from vertical excitation by a photon. From an experimental point of view, a target molecule is required to have an absorption band in the wavelength region of irradiation light. The biphenyl group absorbs 254-nm UV light. For comparison with the experimentally observed retention preference in the thermal 1,3-silyl migration of **2**, one of derivatives of **2**, 4-*tert*-butyl-1-(4-phenylphenyl)-1-(1,1-dimethylallyl)silacyclohexane (**3**; R = 4-phenylphenyl in **2**), is selected for the study of the photochemical 1,3-silyl migration in which the biphenyl moiety acts as a UV-absorber. First, the excited state produced by the irradiation of 254-nm light to **3** and the electronic nature is investigated. With our computer system, it is impossible to calculate the UV absorption maximum of **3** at the reliable calculation level because of the large molecular size; therefore, we calculate the related smaller compounds **4**−**12**. Table 1 represents the calculated UV absorption wavelengths of compounds **4**−**12**, in which λ_1 and λ_2 are the longest two wavelengths. λ_1 and λ_2 of **12** are $\pi_{ph} \rightarrow \pi^*_{ph}$ transitions in which one (λ_1) is allowed and the other (λ_2) is forbidden. The case is the same in λ_1 and λ_2 of **6**. A phenyl group gives a much shorter absorption wavelength and a weaker oscillator strength than does a biphenyl group: λ_1 and λ_2 of **9** and **10** are located around 220 nm and are the $\pi_{ph} \rightarrow \pi^*_{ph}$ transitions, but the oscillator strengths are weak compared with the λ_1 of **6** and **12**. The λ_1 and λ_2 of **4**, **5**, **7**, and **8** are the

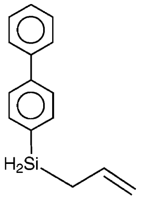
Rydberg $\pi_{\text{allyl}} \rightarrow$ C 3s (λ_1) and the valence $\pi_{\text{allyl}} \rightarrow \pi^*_{\text{allyl}}$ (λ_2) transitions. The absorption wavelengths are very close between λ_1 and λ_2, like in the case of nonconjugated alkenes.[22] It is found that, in comparison with allylsilane (**4**), the silacyclohexane moiety of 1-(allyl)silacyclohexane (**5**) and the methyl group at the silacyclohexane moiety of **8** do not affect the absorption wavelength of λ_1 and λ_2. Methyl substitution at the allyl group (**7**) causes a red shift in λ_1 and λ_2 by approximately 10 nm, but the peak positions are well separated from the λ_1 and λ_2 of **6** and **12**. Consequently, **6** is the best model compound to investigate the first event of the photochemical reaction of **3**, and the strong band from the $\pi_{\text{ph}} \rightarrow \pi^*_{\text{ph}}$ transition of the biphenyl moiety is obtained at 241.1 nm. It is concluded that the first event of the photochemical reaction of **3** by the irradiation of 254-nm UV light would be the excitation of the $\pi_{\text{ph}} \rightarrow \pi^*_{\text{ph}}$ of the biphenyl moiety.



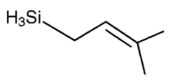
4



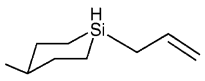
5



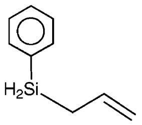
6



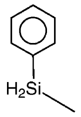
7



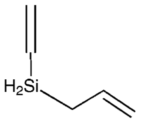
8



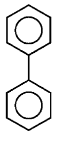
9



10



11



12

From the π_{ph} and π^*_{ph} orbitals of **12**, which mainly contribute to the $\pi_{\text{ph}} \rightarrow \pi^*_{\text{ph}}$ transition, the transition would cause the structural change from twisted to planar around the C−C axis connecting the two phenyl groups. The optimized structure of the trans isomer[23] of **3** (**3t**) at the B3LYP/6-31G(d) level shows a twisted structure for the biphenyl moiety, but the experimentally observed biphenyl part of **3t** is nearly planar in crystal.[12] The photochemical reaction is usually performed in hexane, but the structure of the biphenyl moiety of **3t** in solution is not known. A strong $\pi_{\text{ph}} \rightarrow \pi^*_{\text{ph}}$ transition is obtained at 258.2 nm in the calculation of planar **12** and would cause no substantial structural change. The 1,3-silyl migration is not expected from the $\pi_{\text{ph}} \rightarrow \pi^*_{\text{ph}}$ transition. The next step in photochemical 1,3-silyl migration is the path from the $^1(\pi_{\text{ph}} \rightarrow \pi^*_{\text{ph}})$ state to other excited states. At present, we could not reveal the path from the $^1(\pi_{\text{ph}} \rightarrow \pi^*_{\text{ph}})$ state to other excited states because the best model compound **6** is too large to perform the CASSCF calculations at the reliable level with our computer system, although the path is an important process.[2k] Simple nonconjugated alkenes possess a Rydberg $^1(\pi_{\text{allyl}} \rightarrow \text{C 3s})$ and valence $^1(\pi_{\text{allyl}} \rightarrow \pi^*_{\text{allyl}})$ that lie very close in energy. The $\pi_{\text{allyl}} \rightarrow \pi^*_{\text{allyl}}$ state gives predominantly $E-Z$ isomerization via an avoided crossing, but can also lead to a carbon and hydrogen sigmatropic shift.[22] Compounds **4**, **5**, **7**, and **8** have neither a phenyl nor a vinyl group, and the S_1 and S_2 are the Rydberg $^1(\pi_{\text{allyl}} \rightarrow \text{C 3s})$ and valence $^1(\pi_{\text{allyl}} \rightarrow \pi^*_{\text{allyl}})$, respectively. $\pi_{\text{allyl}} \rightarrow \sigma^*_{\text{SiC}}$ transition is mixed with $\pi_{\text{allyl}} \rightarrow$ C 3s in the S_1 excited state of **4**. The 1,3-silyl migration is expected to occur from the $\pi_{\text{allyl}} \rightarrow \sigma^*_{\text{SiC}}$ transition. Here we investigate the photochemical reaction pathway of **4** theoretically as the smallest model compound of the photochemical 1,3-silyl migrations of **3**. To check the effect of the bulkiness and stereochemical rigidness of silacyclohexane on the photochemical reaction pathways, compound **5** is examined. Compounds **7** and **8** have the same electronic nature of S_1 and S_2 as **4** and **5**, and no substantial difference in the photochemical reaction is expected.

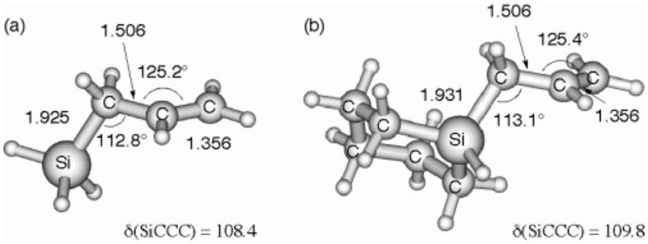


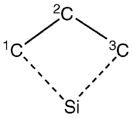
Figure 1. Optimized structures of (a) **4** and (b) **5** at the CAS(6,6)/6-31G(d) level. Bond lengths are given in Å. Bond angles are given in degrees.

The optimized structures of **4** and **5** at the CAS(6,6)/6-31G(d) level are shown in Figure 1. The silicon−carbon bond length of **5** (1.931 Å) is longer than that of **4** (1.925 Å), and the silicon−carbon−carbon bond angle (113.1°) of **5** is larger than that of **4** **(**112.8°**)**. This seems to be due to the bulkiness of the silacyclohexane in **5**. The optimized geometric parameters of the allylic part are the same between **4** and **5**: the single- and double-bond lengths are 1.506 and 1.356 Å, respectively, and the bond angle is 125°.

The effect of active-space size on the optimized CI structures of **4** is investigated (Table 2). Two S_1/S_0 CIs are obtained, one with retention and one with inversion of the configuration at the silicon. The stereochemistry is characterized by the structure of the silyl group, as in our previous report:[6] planar for inversion and pyramidal for retention. From the three Si−C bond lengths, the retention CI would lead to 1,3-silyl migrations, and the inversion CI would lead to 1,2-silyl migrations. The shorter bond length of Si−^{2}C relative to those of the Si−^{1}C and Si−^{3}C in the retention CI at the CAS(4,4)/6-31G(d) and CAS(6,6)/6-31G(d) levels is the same in the retention transition structure for the ground-state reaction[6] and in the H/allyl and alkyl/allyl conical intersections.[17f] The inversion CI lies much higher in energy by 11.4 and 28.5 kcal/mol than does the retention CI at the CAS(2,2)/6-31G(d) and CAS(4,4)/6-31G(d) levels, respectively. We rule out the inversion path from the present study because of the high energy. The maximum difference in bond length is small between the CAS(2,2) and CAS(4,4) geometries of inversion CI (0.062 Å) and among the geometries of the allyl moiety of retention CI at the CAS(2,2), CAS(4,4), and CAS(6,6) levels (0.049 Å), especially the C−C bond lengths of retention CI, which are nearly equal between the CAS(4,4) and CAS(6,6) methods. However, the Si−C bond lengths of retention CI are gradually shortened with enlarging the active space from CAS(2,2) to CAS(6,6). We use, hereafter, an active space comprised of six electrons in six orbitals.

Geometry optimization on the S_1 excited-state surface is performed from the ground-state structures of **4** and **5** optimized on the S_0 surface. The S_1 excited-state of **4** and **5** at the CAS(6,6)/6-31G(d) level is valence $^1(\pi_{\text{allyl}} \rightarrow \pi^*_{\text{allyl}})$, which is expected to give sigmatropic shift. The relaxation reaches an S_1/S_0 CI where the system decays nonradiatively to S_0. The CIs of **4** and **5** locate in energy by 99.4 and 100.0 kcal/mol above

TABLE 2: Optimized Structures of the CIs of 4[a]



configuration		$r(^1C-^2C)$	$r(^2C-^3C)$	$r(Si-^1C)$	$r(Si-^2C)$	$r(Si-^3C)$
retention	CAS(2,2)	1.386	1.385	2.811	2.814	2.818
	CAS(4,4)	1.414	1.413	2.779	2.708	2.791
	CAS(6,6)	1.435	1.411	2.701	2.668	2.709
inversion	CAS(2,2)	1.458	1.331	2.316	3.082	3.912
	CAS(4,4)	1.475	1.325	2.359	3.127	3.974

[a] The 6-31G(d) basis set is used.

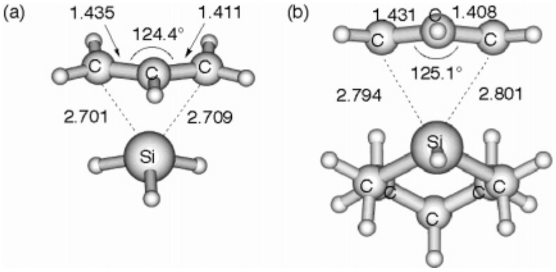


Figure 2. Optimized structures of S_0/S_1 CIs of (a) **4** and (b) **5** at the CAS(6,6)/6-31G(d) level. Bond lengths are given in Å. Bond angles are given in degrees.

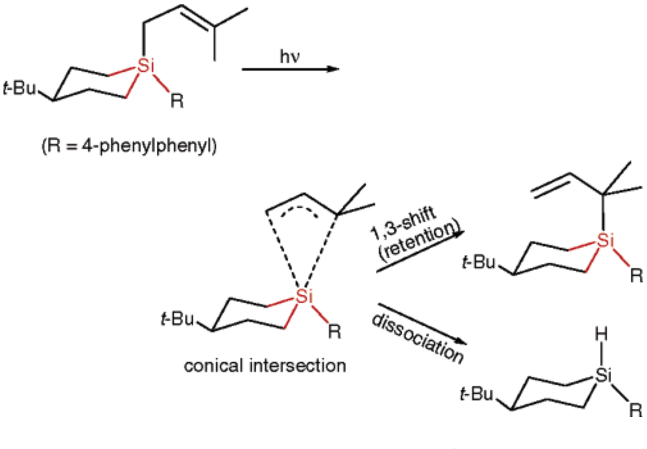
the ground-state minima, respectively. The characteristic of the CI structures (Figure 2) is common to the H/allyl and alkyl/allyl CIs reported as ubiquitous control elements in photochemical sigmatropic shift by Wilsey and Houk:[17f] above a nearly planar allylic part, a migrating atom interacts with two terminal allylic carbons. There are four quasi-unpaired electrons that can recouple in four different ways leading to a reactant, a trimethylene diradical (via a 1,2-shift), and an isomeric 1,3-shift product or dissociated radicals. Wilsey and Houk[17f] reported that two vectors at the H/allyl and alkyl/allyl CIs characterize the directions in which the excited-state and ground-state degeneracy is broken. The two vectors are gradient-different and nonadiabatic coupling vectors. The gradient-different vector leads to either a trimethylene diradical or to dissociated radicals. The nonadiabatic coupling vector leads to the reactant or to the 1,3-shift product. Similarly, the 1,3-shift and dissociation to radicals are anticipated from the CIs of **4** and **5**. From the pyramidal structure of silyl moiety, the configuration during the 1,3-shift is retained. The difference between the two C−C bond lengths seems to be an artifact selected by the active space containing one σ_{CC} bonding. However, the artifact does not affect the qualitative feature of our present interest. No substantial effect of the rigid substituent of **5** on the CI structure is found, but the Si−C bond length is a slightly elongated by 0.09 Å.

The ground-state potential surface of the sigmatropic rearrangement of allylsilanes has already been investigated.[6,7] The search for the TS of **5** on an S_0 surface near the structure of the S_1/S_0 CI gives a TS. The Si−C−C−C framework of the TS structure is nearly equal to the previously reported transition structure[6] for thermal 1,3-silyl migration with a retention of the configuration at the silicon: $r(^1C-^2C) = 1.404$, $r(^2C-^3C) = 1.405$, $r(^1C-Si) = 2.393$, $r(^2C-Si) = 2.133$, and $r(^1C-^2C) = 2.341$ Å. The Si−C bond lengths of the TS structure are much shorter than those of CI (2.7 Å for **4** and 2.8 Å for **5**). The longer bond length at CI would give the possibility of a dissociation pathway to radicals.

4. Conclusions

The stereochemistry of the photochemical 1,3-silyl migration of **4** is confirmed theoretically as retention, which agrees with the W−H rules. There are doubts about whether the experimental finding of inversion is correct. Our calculations support these doubts. The configuration of the photochemical products was experimentally identified[1c] by performing the thermal back reaction, which, according to Kwart et al.,[5] occurs with inversion. Brook doubted in his review of the thermal 1,3-silyl migration of allylic silanes with an inversion of the configuration.[10] In 1997, using the advanced theoretical calculations, we[6] and Yamabe et al.[7] revealed independently that the ground-state reaction prefers retention in contrast to the W−H rules. It was found in the previous paper[6] that the major stabilization in the TS with retention for the ground-state reaction is caused by a subjacent orbital control,[24] although the major stabilization of the TS with inversion is caused by the MO interaction between the low-lying lowest unoccupied molecular orbital (LUMO) and the allyl orbital, as predicted by the W−H rules.

The calculated CI structures are common to the ubiquitous control elements in the photochemical sigmatropic rearrangements with a carbon framework,[17f] indicating the possibility of a dissociation path to radicals in addition to the 1,3-shift path. The bulkiness and rigidness of the silacyclohexane moiety of **5** does not affect the stereochemistry, but the elongated Si−C bond lengths would promote the dissociation path. Experimental evidence using 4-*tert*-butyl-1-(4-phenylphenyl)-1-(1,1-dimethylallyl)silacyclohexane (**3**) is desired in future.



Acknowledgment. The author is grateful to the Hayashi Memorial Foundation. The author sincerely acknowledges the reviewers for their valuable suggestions and comments.

References and Notes

(1) (a) Ishikawa, M.; Nakagawa, K.; Ishiguro, M.; Ohi, F.; Kumada, M. *J. Organomet. Chem*. **1978**, *152*, 155. (b) Kira, M.; Yoshida, H.; Sakurai,

H. *J. Am. Chem. Soc*. **1985**, *107*, 7767. (c) Kira, M.; Taki, T.; Sakurai, H. *J. Org. Chem*. **1989**, *54*, 5647.

(2) (a) Ishikawa, M.; Fuchikami, T.; Sugaya, T.; Kumada, M. *J. Am. Chem. Soc*. **1975**, *97*, 5923. (b) Sakurai, H.; Kamiyama, Y.; Nakadaira, Y. *J. Am. Chem. Soc.* **1976**, *98*, 7424. (c) Ishikawa, M.; Fuchikami, T.; Kumada, M. *J. Organomet. Chem*. **1978**, *149*, 37. (d) Brook, A. G.; Harris, J. W.; Lennon, J.; Sheikh, M. E. *J. Am. Chem. Soc*. **1979**, *101*, 83. (e) Baines, K. M.; Brook, A. G. *Organometallics* **1987**, *6*, 692. (f) Wright, B. B. *J. Am. Chem. Soc.* **1988**, *110*, 4456. (g) Ishikawa, M.; Sakamoto, H. *J. Organomet. Chem*. **1991**, *414*, 1. (h) Ishikawa, M.; Nishimura, Y.; Sakamoto, H. *Organometallics* **1991**, *10*, 2701. (i) Takaki, K.; Sakamoto, H.; Nishimura, Y.; Sugihara, Y.; Ishikawa, M. *Organometallics* **1991**, *10*, 888. (j) Boske, J.; Niecke, E.; Krebs, B.; Lage, M.; Henkel, G. *Chem. Ber./Recl.* **1992**, *125*, 2631. (k) Kira, M.; Miyazawa, T.; Sugiyama, H.; Yamaguchi, M.; Sakurai, H. *J. Am. Chem. Soc.* **1993**, *115*, 3116. (l) Ohshita, J.; Niwa, H.; Ishikawa, M.; Yamabe, T.; Yoshii, T.; Nakamura, K. *J. Am. Chem. Soc.* **1996**, *118*, 6853. (m) Miyazawa, T.; Koshihara, S.; Liu, C.; Sakurai, H.; Kira, M. *J. Am. Chem. Soc.* **1999**, *121*, 3651.

(3) (a) Woodward, R. B.; Hoffmann, R. *J. Am. Chem. Soc*. **1965**, *87*, 395. (b) Hoffmann, R.; Woodward, R. B. *J. Am. Chem. Soc.* **1965**, *87*, 2046, (c) Woodward, R. B.; Hoffmann, R. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 781. (d) Woodward, R. B.; Hoffmann, R. *The Conservation of Orbital Symmetry*; Academic Press: New York, 1970.

(4) Bernardi, F.; Olivucci, M.; Robb, M. A. *Chem. Soc. Rev.* **1996**, *25*, 321.

(5) (a) Kwart, H.; Slutsky, J. *J. Am. Chem. Soc*. **1972**, *94*, 2515. (b) Slutsky, J.; Kwart, H. *J. Am. Chem. Soc*. **1973**, *95*, 8678.

(6) Takahashi, M.; Kira, M. *J. Am. Chem. Soc*. **1997**, *119*, 1948.

(7) Yamabe, T.; Nakamura, K.; Shiota, Y.; Yoshizawa, K.; Kawauchi, S.; Ishikawa, M. *J. Am. Chem. Soc.* **1997**, *119*, 807.

(8) Brook, A. G.; MacRae, D. M.; Limburg, W. W. *J. Am. Chem. Soc.* **1967**, *89*, 5493.

(9) Takahashi, M.; Kira, M. *J. Am. Chem. Soc*. **1999**, *121*, 8597.

(10) See ref 56 in Brook, A. G. *Acc. Chem. Res*. **1974**, *7*, 77−84.

(11) For a review, see Brook, A. G.; Bassingdale, A. R. *Rearrangements in Ground and Excited States*; de Mayo, P., Ed.; Academic Press: London, 1980; Vol. 2, Essay 9.

(12) Zhang, L. C.; Kabuto, C.; Kira, M. *J. Am. Chem. Soc.* **1999**, *121*, 2925.

(13) Takahashi, M.; Tsutsui, S.; Sakamoto, K.; Kira, M.; Müller, T.; Apeloig, Y. *J. Am. Chem. Soc*. **2001**, *123*, 347.

(14) Takahashi, M.; Kira, M.; Sakamoto, K.; Müller, T.; Apeloig, Y. *J. Comput. Chem.* **2001**, *22*, 1536.

(15) In refs 13 and 14, we reported erroneously that the UV calculations were carried out at the TD-B3LYP/6-311++G(d,p) level, while they were actually carried out at the TD/6-311++G(d,p) level.

(16) Bernardi, F.; Olivucci, M.; Robb, M. A.; Tonachini, G. *J. Am. Chem. Soc*. **1992**, *114*, 5805.

(17) (a) Rossi, I.; Bernardi, F.; Olivucci, M.; Robb, M. A. *J. Phys. Chem*. **1995**, *99*, 6757. (b) Freund, L.; Klessinger, M. *Int. J. Quantum Chem*. **1998**, *70*, 1023. (c) Wilsey, S.; Houk, K. N.; Zewail, A. H. *J. Am. Chem. Soc.* **1999**, *121*, 5772. (d) Steuhl, H.-M.; Bornemann, C.; Klessinger, M. *Chem.*—*Eur. J.* **1999**, *5*, 2404. (e) Bornemann, C.; Klessinger, M. *Org. Lett*. **1999**, *1*, 1889. (f) Wilsey, S.; Houk, K. N. *J. Am. Chem. Soc*. **2000**, *122*, 2651. (g) Bernardi, F.; Olivucci, M.; Robb, M. A.; Vreven, T.; Soto, J. *J. Org. Chem*. **2000**, *65*, 7847. (h) Fuss, W.; Schmid, W. E.; Trushin, S. A. *J. Am. Chem. Soc.* **2001**, *123*, 7101. (i) Wilsey, S.; Houk, K. N. *J. Am. Chem. Soc*. **2002**, *124*, 11182. (j) Garavelli, M.; Bernardi, F.; Cembran, A.; Castaño, O.; Frutos, L. M.; Merchán, M.; Olivucci, M. *J. Am. Chem. Soc.* **2002**, *124*, 13770.

(18) Takahashi, M.; Sakamoto, K. *J. Phys. Chem. A* **2004**, *108*, 7301.

(19) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley: New York, 1986.

(20) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A.; Stratmann, R. E., Jr.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.11; Gaussian, Inc.: Pittsburgh, PA, 1999.

(21) Foresman, J. B.; Frisch, Æ. *Exploring Chemistry with Electronic Structure Methods*; Gaussian, Inc.: Pittsburgh, PA, 1993.

(22) Kropp, P. J. *CRC Handbook of Organic Photochemistry and Phtobiology*; Horspool, W. M., Song, P.-S., Eds.; CRC Press: Boca Raton, FL, 1995; Chapter 2, pp 16−28 and references therein.

(23) The trans isomer is defined with respect to 4-*tert*-butyl and allyl groups.

(24) (a) Berson, J. A.; Salem. L. *J. Am. Chem. Soc*. **1972**, *94*, 8917. (b) Berson, J. A. *Acc. Chem. Res.* **1972**, *5*, 406.