A Model Study on The Photochemical Isomerizations of Cyclic Silenes

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Abstract

The mechanism for the photochemical isomerization reaction is investigated theoretically using a model system of a five-membered-ring silene with the CAS(8,8)/6-311G(d) and MP2-CAS-(8,8)/6-311++G(3df,3pd)//CAS(8,8)/6-311G(d) methods. These model investigations indicate that the preferred reaction route for a five-membered-ring silene, which leads to the photorearrangement product, is as follows: reactant → Franck-Condon region → conical intersection → photoproduct. In other words, the direct mechanism is a one-step process that has no barrier. These theoretical results agree with the available experimental observations.

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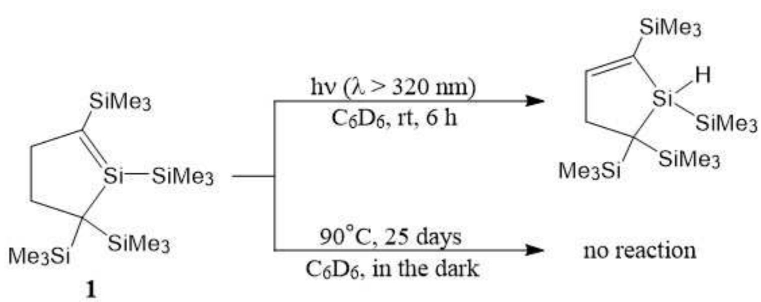
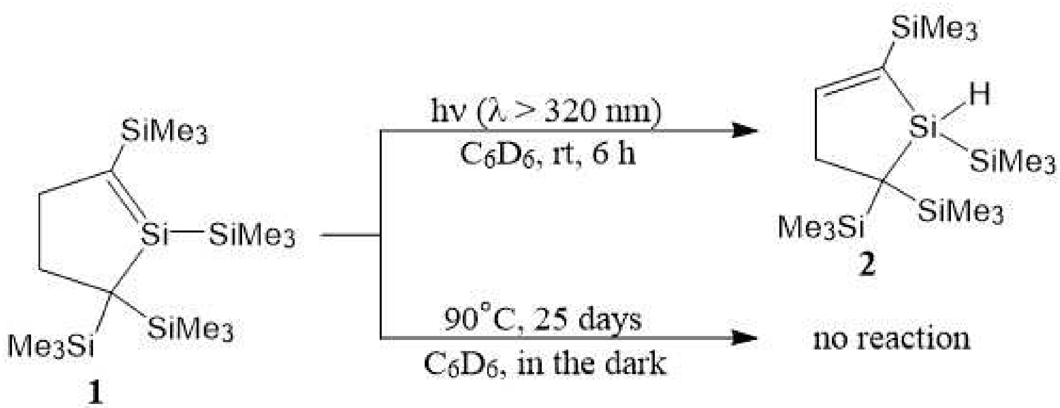
The photomigration reaction mechanism for a five-membered-ring silene **1** was theoretically studied using the CAS/6-311G(d) and MP2-CAS/6-311++G(3df,3pd) methods. The model computations conclude that the conical intersection mechanism plays an important role in such a photochemical reaction. That is, the conical intersection mechanism is a one-step process that has no barrier.



I. Introduction

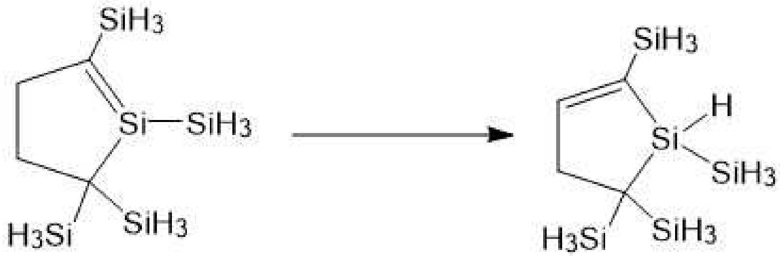
Recently, Iwamoto, Kira and coworker reported that irradiation of silene **1** in benzene using a filtered light (λ > 320 nm) at room temperature yielded an isomeric cyclic alkene **2** via an interesting 1,3-hydrogen shift.[1] See Scheme 1. Also, it was found that silene **1** is thermally very stable. That is, no reaction occurred when **1** was heated in benzene at 90°C for 25 days.[1] Although there have been several photochemical 1,3-sigamatropic rearrangements known,[2] this experimental finding constitutes the first silene-to-alkenylsilane rearrangement via 1,3-hydrogen sigmatropy. Nevertheless, as far as we are aware, until now neither experimental nor theoretical studies have been performed on the photorearrangement mechanism of such a five-membered-ring silene **1**.



Scheme 1)

In this paper we give a deeper insight into the unknown photorearrangement mechanism of five-membered-ring silene **1**. In particular, it will be shown below that the Conical Intersections (CIs)[3] play a crucial role in the photochemical rearrangements of five-membered-ring silene species. We envision that the present combination of observed experimental work and theoretical examination will provide a comprehensive understanding of the excited state behavior of five-membered-ring silene **1**.

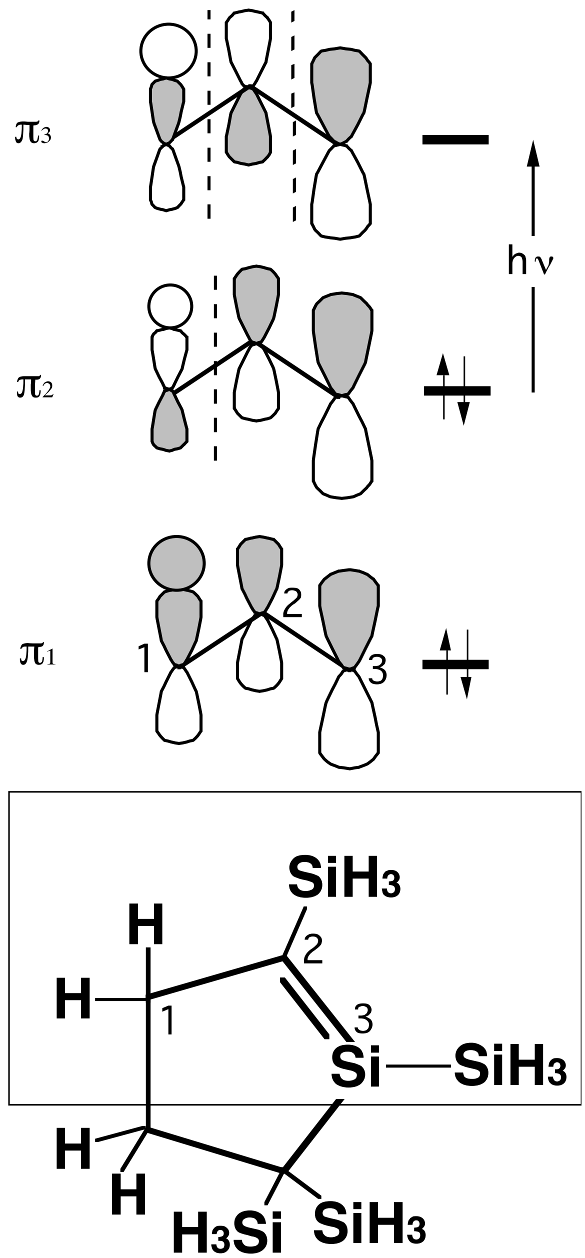
Therefore, in this work we use the multiconfigurational self-consistent field (MCSCF) program released in GAUSSIAN 09[5.6] to explore the potential energy surface and mechanism of the following reaction (eq 1):



Rea-3 **Pro-4** (1)

II. General Consideration

In order to easily find out the CI, the five-membered ring silylene (**Rea-3**) was simplified to be a three-atom system, i.e., H_2C^1–$C^2(SiH_3)$–$Si^3(SiH_3)$ as shown in Scheme 2.[7] It is clear from Scheme 2 that in the highest occupied molecular orbital (π_2), the HOMO is occupied by two electrons, in which a nodal plane exists between the terminal carbon atoms. On the other hand, in the lowest unoccupied molecular orbital (π_3) antibonding interactions exist between the center and the terminal carbon as well as silicon atoms. As can be seen, the lowest singlet $\pi \rightarrow \pi^*$ excitation is the singlet π_2 (HOMO) $\rightarrow$ π_3 (LUMO) transition. It is noteworthy that mixing the π and π^* levels in the three-atom system redistributes the electron density.



Scheme 2

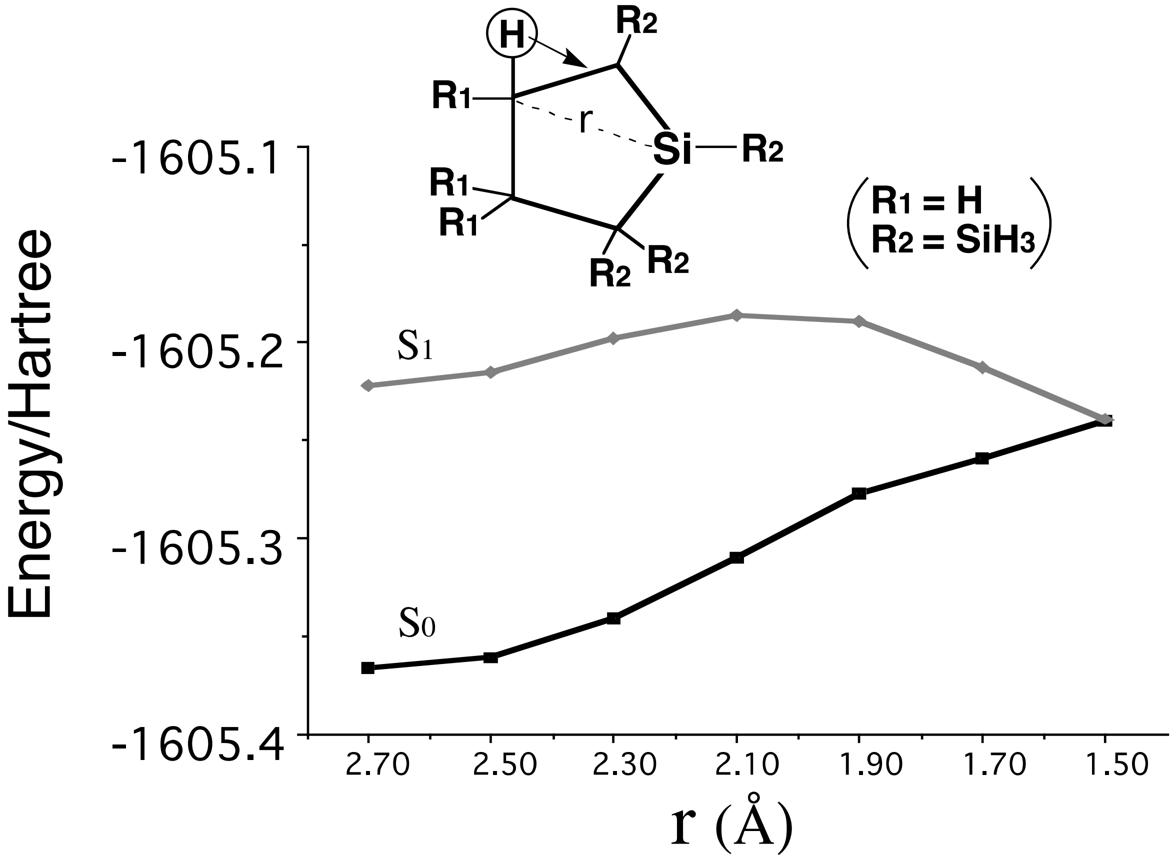


Figure 1: The minimum-energy pathway of a 1,3-hydrogen migration in reactant (**Rea-3**) along the distance r coordinate optimized for the S_0 and S_1 states at the CAS(8,8)/6-311G(d) level of theory. Also see ref. (10) and Supporting Information.

Figure 1 shows the qualitative potential energy surfaces for the S_0 and S_1 states of **Rea-3** as a function of distance r along the C^1——Si^3 direction. Although the distance r was obtained without full optimization of **Rea-3**, they at least give us a hint that a degeneracy between HOMO and LUMO can exist as a result of the distance along the C^1——Si^3 direction. Moreover, the formation of such a degenerate point provides further evidence for an enhanced intramolecular migration in the five-membered ring geometry, and possibly the existence of a CI, where decay to the ground state can be fully efficient. Accordingly, we shall utilize the above result to interpret the mechanism for the photochemical isomerization reaction of **Rea-3** in the following section.

III. Results and Discussion

The relative energies of the stationary points for eq 1 based on the CAS(8,8)/6-311G(d) and MP2-CAS(8,8)/6-311++G(3df,3pd)//CAS(8,8)/6-311G(d) levels are collected in Figure 2. Also, the calculated geometrical parameters for the stationary points are given in Figure 2. Cartesian coordinates and energetics calculated for the various points at the CASSCF and MP2-CAS levels of theory are available as Supporting Information.

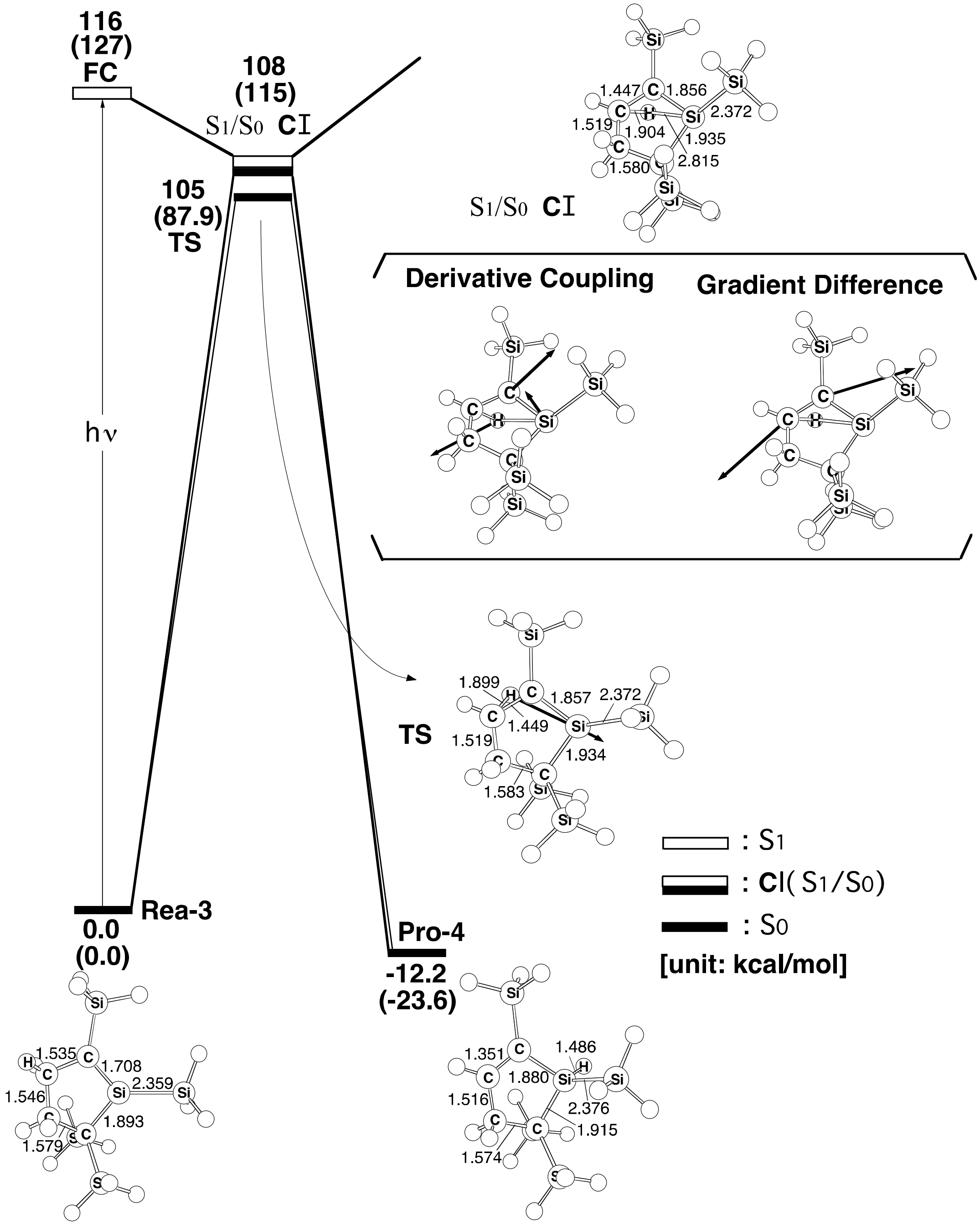


Figure 2: Energy profiles for the photochemical isomerization mode of silene (**Rea-3**). The abbreviations **FC**, **TS,** and **CI** stand for Frank–Condon, transition state, and conical intersection, respectively. The relative energies were obtained at the MP2-CAS-(8,8)/6-311++G(3df,3pd)//CAS(8,8)/6-31G(d) and CAS(10,10)/6-311G(d) (in parentheses) levels of theory. The selected geometrical parameters of CASSCF optimized structures of the stationary points are also given. Hydrogens are omitted for clarity. The heavy arrow in **TS** indicates the main atomic motion in the transition state eigenvector. The derivative coupling and gradient difference vectors — those which lift the degeneracy — computed with CASSCF at the conical intersection S_1/S_0 **CI**. For more information see the text.

In the first step the reactant (**Rea-3**) is excited to its excited singlet state by a vertical excitation as shown in Figure 2. The vertical excitation energy (**FC**) is calculated to lie 127 kcal/mol above the ground-state surface at the CAS(8,8)/6-311G(d) optimized reactant geometry **Rea-3**. This value drops to 116 kcal/mol after correction using MP2-CAS calculations. To keep the CPU times acceptable, we take **Rea-3**, using the SiH_3 substituents rather than the $SiMe_3$ groups, as a model for our calculations. In fact, alkyl substitutions in **Rea-3** may change the energy of excited states slightly because of, for example, alkyl hyperconjugations, but the basic photo-excitation features should not change significantly.[8,9]

Based on Scheme 2, the [1,3] sigmatropic shift mechanism has been proposed to account for the exclusive formation of **Pro-4** on direct photolysis of **Rea-3**. According to this concept, the search for a conical crossing point between S_0 and S_1 surfaces was performed by scanning both the ∠HCC bending angle and the C–H bond length. The relaxation reaches a conical intersection (i.e., S_1/S_0 **CI**) where the photoexcited system decays nonradiatively to S_0. Then, according to the results outlined in Figure 2, funneling through S_1/S_0 **CI** leads to two different reaction paths on the ground-state surface, via either the derivative coupling vector or the gradient difference vector.[3] The derivative coupling vector for S_1/S_0 **CI** corresponds to a [1,3] hydrogen migration, while the gradient difference vector corresponds to a C–C bond stretching motion, which leads to a vibrationally hot species at the S_0 configuration. As seen in Figure 2, the MP2-CAS result suggests that S_1/S_0 **CI** is lower than **FC** by only 8.0 kcal/mol in energy. Accordingly, our computations predict that the photochemical rearrangement reaction of **Rea-3** should be a barrierless process. That is, starting from the **FC** point, five-membered-ring silene (**Rea-3**) enters an efficient decay channel, S_1/S_0 **CI**. After decay at this conical intersection point, the doubly-bonded cyclic photoproduct **Pro-4** as well as the initial reactant **Rea-3** can be reached via a barrierless ground-state relaxation pathway. Thus, our theoretical calculations demonstrate that photoreaction of reactant **Rea-3** can be represented as:[10]

Rea-3 (S_0) + hν → FC → CI → Pro-4

The dark reaction on the ground-state potential energy surface is also examined. Although photo-excitation raises **Rea-3** into an excited electronic state, the products of the photochemical process are controlled by the ground-state (thermal) potential surface.[3] The search for transition states on the S_0 surface near the structure of S_1/S_0 **CI** gives **TS**. As seen in Figure 2, for the dark reaction, the energy of the **TS** connecting **Rea-3** and **Pro-4** on the S_0 surface lies 3.0 kcal/mol below the energy of the S_1/S_0 **CI**. It should be noted that the computational results indicate the energy barriers for **Rea-3** → **Pro-4** and **Pro-4** → **Rea-3** are predicted to be 105 and 117 kcal/mol, respectively. This finding suggests that it would be difficult to produce the five-membered-ring molecule **Pro-4** using the thermal (dark) reaction, which is in good agreement with the experimental observations.[3]

In conclusion, from the present results, we can elaborate on the standard model of the photochemistry of five-membered-ring silene species. It is found that knowledge of the conical intersection of the silene molecules is of great importance in understanding its reaction mechanism since it can affect the driving force for photochemistry. For instance, a five-membered-ring silene is vertically excited to the S_1 state. Then, radiationless decay from S_1 to S_0 of silene occurs via a conical intersection, which results in a rapid 1,3-H migration. Starting from this conical intersection, the products of the photorearrangement as well as the initial reactant can be reached on a barrier-less ground-state relaxation path. As a result, these findings, based on the conical intersection viewpoint, have helped us to better understand the photochemical reactions, and to support the experimental observations.

Acknowledgments

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(1) Ishida, S.; Iwamoto, T.; Kira, M. *Organometallics* **2009**, *28*, 919.

(2) For instance, see: (a) Sakurai, H.; Kamiyama, Y.; Nakadaira, Y. *J. Am. Chem. Soc.* **1976**, *98*, 7424. (b) Ishikawa, M.; Fuchikami, T.; Kumada, M. *J. Orgonomet. Chem.* **1978**, *249*, 37. (c) Turro, N. J., *Modern Molecular Photochemistry.* Benjamin Publishing: Reading, MA, 1978. (d) Conlin, R. T.; Bobbit, K. L. *Organometallics* **1987**, *6*, 1406. (e) Kira, M.; Maruyama, T.; Sakurai, H. *J. Am. Chem. Soc.* **1991**, *113*, 3986. (f) Bernardi, F.; Olivucci, M.; Robb, M. A.; Tonachini, G. *J. Am. Chem. Soc.* **1992**, *114*, 5805. (g) Takahashi, M.; Kira, M. *J. Am. Chem. Soc.* **1997**, *119*, 1948.

(3) For instance, see: (a) Bernardi, F.; Olivucci, M.; Robb, M. A. *Isr. J. Chem.* **1993**, 265. (b) Klessinger, M. *Angew. Chem. Int. Ed. Engl*. **1995**, *34*, 549. (c) Bernardi, F.; Olivucci, M.; Robb, M. A. *Chem. Soc. Rev*. **1996**, 321. (d) Bernardi, F.; Olivucci, M.; Robb, M. A. *J. Photochem. Photobio. A: Chem.* **1997**, *105*, 365. (e) Klessinger, M. *Pure Appl. Chem.* **1997**, *69*, 773. (f) Klessinger, M.; Michl J. In Excited *States and Photochemistry of Organic Molecules,* VCH Publishers, New York, 1995.

(4) Frisch, M. J., et al. Gaussian, Inc., Wallingford CT, 2010.

(5) The active space for describing the photorearrangement of a five-membered-ring silene (**1**) comprises eight electrons in eight orbitals. i.e., three *p*-π orbitals plus one σ(C–C), one σ(Si–C), one σ*(C–C), one σ*(Si–C), and one σ*(C–H) orbitals. The CASSCF method was used with the 6-311G(d) basis sets for geometry optimization (vide infra). The optimization of conical intersections was achieved in the (f – 2)-dimensional intersection space using the method of Bearpark et al. (see ref. 6) implemented in the Gaussian 09 program. Every stationary point was characterized by its harmonic frequencies computed analytically at the CASSCF level. Localization of the minima and conical intersection minima was performed in Cartesian coordinates; therefore, the results are independent of any specific choice of internal variables. To correct the

energetics for dynamic electron correlation, we have used the multireference Møller-Plesset (MP2-CAS) algorithm as implemented in the program package GAUSSIAN 09. Unless otherwise noted, the relative energies given in the text are those determined at the MP2-CAS(8,8)/6-311++G(3df,3pd) level using the CAS(8,8)/6-311G(d) geometry.

(6) M. J. Bearpark, M. A. Robb, H. B. Schlegel, *Chem. Phys. Lett.* **1994**, *223*, 269.

(7) In order to emphasize how to obtain the conical intersection point, I chose only one variable (i.e., the C^1---Si^3 distance, r) and make the other geometrical parameters constant. The reason for choosing only one variable to search for the conical intersection is due to the fact that the big difference between the geometrical structures of **Rea-3** and **Pro-4** is one hydrogen atom is situated at the C^1 atom in the former and then this hydrogen atom is situated at the Si^3 atom in the latter. As a result, using only one variable (r) can easily examine the degenerate point between the ground state (S_0) and the excited state (S_1) surfaces. Moreover, the other fixed geometrical parameters in **Rea-3** were optimized at the CAS(8,8)/6-311G(d) level of theory, which are given in Supporting Information.

(8) As mentioned in ref. 1, the experimental data for **1**, using the $SiMe_3$ substituents, showed that the transition has absorption bands, whose wavenumbers are > 320 nm (= 89.3 kcal/mol).

(9) It has to be emphasized that due to considering the computational time as well as the available disk space, I chose the SiH_3 groups rather than the experimentally reported $SiMe_3$ substituents in the present theoretical study. Also, the theoretical data given in Figure 2 were computed in the gas phase rather then the experimentally observed solvent phase. As a result, the calculated results shown in Figure 2 are somewhat different from the available experimental data (see ref. 10). Nevertheless, the model used as well as the computational results obtained in this study can at least give a qualitative explanation.

(10) It should be pointed out that this singlet cycloalkene formation reaction would be essentially concerted, since decay via the S_1/S_0 (**CI**) conical intersection will occur within one vibrational period. See: Manthe, U.; Koppel, H. *J. Chem. Phys*. **1990**, *93*, 1658.