

Ab Initio Calculations on the Preferred Mode of Ring Opening in Silacyclopropane

Per N. Skancke,^{*,†} David A. Hrovat, and Weston Thatcher Borden^{*}

Contribution from the Department of Chemistry, Box 351700, University of Washington, Seattle, Washington 98195-1700

Received December 23, 1996. Revised Manuscript Received June 16, 1997[⊗]

Abstract: CASSCF and CASPT2N/6-31G* calculations on silacyclopropane (**1**) find that the transition state for hydrogen migration in concert with ring opening, leading to ethylsilylene (**2**), has an energy that is significantly lower than the energies of the 1-sila- and 2-silatrimethylene diradicals (**6** and **7**), formed by ring opening alone. (12/12)CASPT2N calculations, corrected for differences in zero-point energies, give barriers of 24.7 and 13.2 kcal/mol, respectively, for the silacyclopropane to ethylsilylene reaction and its reverse. These values are in reasonable agreement with experimental estimates of 23–28 and 10.4 kcal/mol, respectively, for the corresponding reactions of alkylsilacyclopropanes. Diradicals **6** and **7**, which are transition states, are computed to be ca. 20 kcal/mol higher in energy than the transition state leading to ethylsilylene (**2**). The barrier to the conversion of **2** to 1-silapropene (**3**) is calculated to be 30.7 kcal/mol. The strong preference for opening of silacyclopropane (**1**) to ethylsilylene (**2**), which contrasts with the opening of cyclopropane to the trimethylene diradical, is interpreted in terms of the relative Si–H and C–H BDE's in primary silyl and alkyl radicals.

Modes, mechanisms, and energetics of ring-opening reactions of cyclopropanes have been studied extensively, both by calculations and by different experimental techniques.^{1,2} For silacyclopropane (**1**) similarly detailed studies are lacking. In analogy with the cyclopropane reaction, the ring opening of **1** could lead to either or both of the diradicals (**6** and **7**) in Scheme 1, depending on which of the ring bonds is broken. However, as discussed in this paper, *ab initio* calculations find that the energies of these two diradicals are significantly higher than that of the transition state leading to ethylsilylene (**2**).

Theoretical studies of silylene insertions into a variety of chemical bonds have been published.³ However, the intramolecular silylene insertion into a β C–H bond of **2**, which is the reverse of the ring-opening reaction of **1** that would lead to **2**, has, to our knowledge, not been investigated computationally. Since ring opening of silacyclopropanes to silylenes by retrograde C–H insertion has been postulated in experimental studies,⁴ we have performed *ab initio* calculations on the mechanism and the energetics for the interconversion of **1** and **2**. For the sake of completeness, we have included in our computational study all the species (**1**–**9**) shown in Scheme 1.

Computational Methodology

The geometries of closed-shell molecules **1**, **3**, **5**, and **9** were optimized, using RHF calculations, and single-point energies were

[†] On leave from the Chemistry Department, The University of Tromsø, N-9037, Tromsø, Norway.

[⊗] Abstract published in *Advance ACS Abstracts*, August 1, 1997.

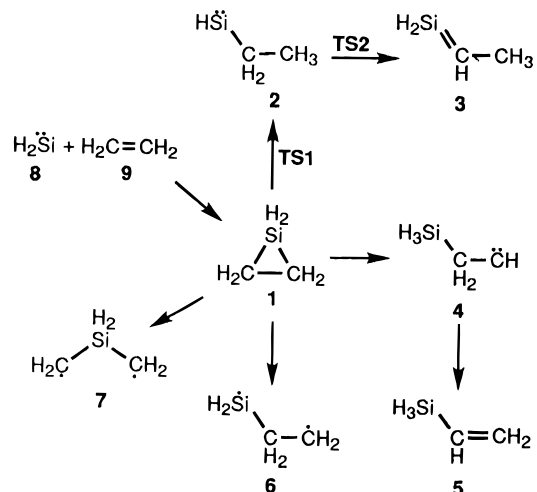
(1) An extensive list of references prior to 1992 can be found in the following: Getty, S. J.; Davidson, E. R.; Borden, W. T. *J. Am. Chem. Soc.* **1992**, *114*, 2085.

(2) The following theoretical and experimental papers have appeared since 1992: (a) Baldwin, J. E.; Yamaguchi, Y.; Schaefer, H. F., III *J. Phys. Chem.* **1994**, *98*, 7513. (b) Pedersen, S.; Herek, J. L.; Zewail, A. H. *Science* **1994**, *266*, 1359. (c) Doubleday, C., Jr. *J. Phys. Chem.* **1996**, *100*, 3520. (d) Doubleday, C., Jr.; Bolton, K.; Peshherbe, G. H.; Hase, W. L. *J. Am. Chem. Soc.* **1996**, *118*, 9923. (e) Doubleday, C., Jr.; Bolton, K.; Hase, W. L. *J. Am. Chem. Soc.* **1997**, *118*, 5251. (f) Hrovat, D. A.; Fang, S.; Borden, W. T.; Carpenter, B. K. *J. Am. Chem. Soc.* **1997**, *119*, 5253.

(3) Apeloig, Y. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1989; Vol. 1, pp 57–226.

(4) Dickinson, A. P.; O'Neal, H. E.; Ring, M. A. *Organometallics* **1991**, *10*, 3513 and references therein.

Scheme 1



obtained by MP2 calculations.⁵ The geometries of **2**, **4**, and **6**–**8** were optimized by (2/2)CASSCF calculations, and single-point energies were evaluated, using (2/2)CASPT2N calculations.⁶ (4/4)CASSCF calculations were used to locate two transition states, **TS1** and **TS2**, and (4/4)CASPT2N energies were computed at these geometries. The 6-31G* basis set⁷ was used for all the calculations.

Analytical vibrational frequencies were calculated at each stationary point, using the same level of theory at which the geometry was optimized. Differences in zero-point energies (ΔZPE) were computed from the unscaled vibrational frequencies. All of the calculations were performed with the programs contained in Gaussian 94⁸ or MOLCAS.⁹

The RMP2 and (2/2)- and (4/4)CASPT2N relative energies obtained from these calculations are given in Table 1, and the geometries of

(5) Møller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618.

(6) CASPT2N uses second-order, multi-reference perturbation theory to recover the correlation energy that is not recovered variationally in the active space. See: (a) Anderson, K.; Malmqvist, P.-Å.; Roos, B. O.; Sadlej, A.; Wolinski, K. *J. Phys. Chem.* **1990**, *94*, 5483. (b) Anderson, K.; Malmqvist, P.-Å.; Roos, B. O. *J. Chem. Phys.* **1992**, *96*, 1218.

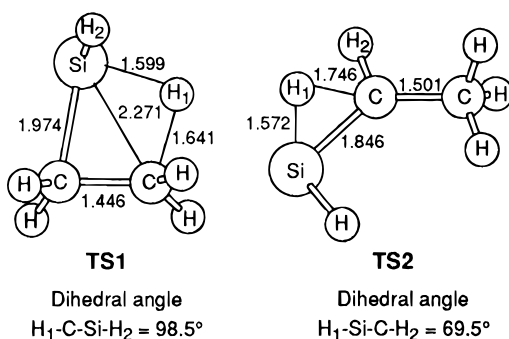
(7) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213.

(8) Gaussian 94, Revision B.3, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Peng,

Table 1. Relative Energies (ΔE , kcal/mol) for the Structures in Scheme 1, Calculated with the 6-31G* Basis Set at the (n/n)CASPT2N ($n = 0-4$)^a and (12/12)CASPT2N Levels and Including ΔZPE

species	$\Delta E_{(n/n)CASPT2N}$	$\Delta E_{(12/12)CASPT2N}$
1 ^b	0	0
2 ^c	11.1	11.5
3 ^b	9.5	
4 ^e	62.0	
5 ^b	-7.9	
6 ^{e,e}	42.5	41.1
7 ^{e,f}	42.4	43.6
8 ^g + 9 ^b	42.6	40.5
TS1 ^{d,g}	23.3	24.7
TS2 ^{d,h}	41.8	

^a n for (n/n)CASPT2N is the same as the number of electrons and orbitals in the active space for geometry optimization. ^b RHF/6-31G* optimized geometry. ^c (2/2)CASSCF/6-31G* optimized geometry. ^d (4/4)CASSCF/6-31G* geometry. ^e Imaginary frequency = 285i cm⁻¹. ^f Imaginary frequency = 68i cm⁻¹. ^g Imaginary frequency = 1152i cm⁻¹. ^h Imaginary frequency = 1546i cm⁻¹.

**Figure 1.** Some structural parameters for **TS1** and **TS2**, found by using (4/4)CASSCF/6-31G* calculations. Bond lengths are in angstroms.

TS1 and **TS2** are shown in Figure 1. The complete geometries, energies, and ΔZPE corrections for all the species in Scheme 1 are available as Supporting Information.

In order to confirm the reliability of the CASPT2N relative energies that were computed with only the chemically active electrons and orbitals placed in the active space for each species in Scheme 1, we carried out larger CASPT2N calculations. It was not possible to perform calculations that correlated all 18 valence electrons in 18 orbitals, but we were able to carry out (12/12)CASSCF and (12/12)CASPT2N calculations. The electrons that were correlated by these calculations were the 12 electrons that occupied the six valence orbitals of highest energy at each geometry. As shown in Table 1, the (12/12)CASPT2N energies of **2**, **6-9**, and **TS1**, relative to that of **1**, differ by less than 5% from the relative energies obtained by the smaller CASPT2N calculations, which used different sized active spaces for different species.

Results and Discussion

As shown by the data in Table 1, our calculations find that silylene **2** has significantly lower energy than carbene **4** and than diradicals **6** and **7**,¹⁰ which could also be formed from **1**. The (12/12)CASPT2N barrier to ring opening of **1**, leading to silylene **2** in a concerted, retrograde C-H insertion reaction, is calculated to be 24.7 kcal/mol. The barrier to reaction in the opposite direction is found to be 13.2 kcal/mol. The transition state for this reaction (**TS1**) has a much lower energy than either

diradical **6** or **7**.¹⁰ These silatrimethylene diradicals are both computed to have energies that are ca. 20 kcal/mol higher than that of **TS1**. Thus, the ring opening of silacyclopropane has a preferred reaction path that is completely different from that of cyclopropane.

In an experimental study⁴ of the isomerization kinetics of butyl- and pentylsilylenes, Arrhenius parameters were deduced for ring opening and ring closure of the silacyclopropanes that were presumed to be the intermediates formed by addition of H₂Si: to 1-butene and to 1-pentene. The barrier to ring closure of 10.4 kcal/mol, found experimentally, is in reasonable agreement with our (12/12)CASPT2N value of 13.2 kcal/mol.

For the barrier to ring opening, an "experimental" value of 64.3 kcal/mol, minus the ring strain in silacyclopropane, was obtained.⁴ Estimates of ring strain in **1** have been made by the use of different homodesmotic reactions and at different levels of *ab initio* theory. Values, obtained from two different reactions by calculations that included electron correlation, are 35.9^{11a} and 41.4^{11b} kcal/mol. These strain energies give values for the "experimental" barrier to ring opening of 2-alkylsilacyclopropanes of respectively 28 and 23 kcal/mol, which compare well with our (12/12)CASPT2N value of 24.7 kcal/mol for the barrier to opening of **1** to **2**.

We do not find a transition state for the addition of H₂Si: to ethylene to form **1**. The addition reaction is energetically a continuously downhill process, with a small plateau at a silicon carbon distance of about 2.7 Å. This is in accord with the results of previous calculations¹² which have demonstrated that the barrier to the addition, predicted at the RHF level, is an artifact. Our (12/12)CASPT2N reaction energy of 45.1 kcal/mol, uncorrected for $\Delta ZPE = -4.6$ kcal/mol, is in good agreement with a value of 47.9 kcal/mol obtained by previous MP2 calculations.¹²

The geometry of **TS1** (Figure 1) resembles that calculated¹³ for the insertion of H₂Si: into CH₄, where the optimized Si-C distance is 2.267 Å, and the Si-H and C-H distances are 1.501 and 1.507 Å, respectively. The unbroken Si-C bond in **TS1** is found to be significantly longer than those in both **1** ($r = 1.851$ Å) and **2** ($r = 1.915$ Å). Along the intrinsic reaction coordinate (IRC), which was followed at the (4/4)CASSCF level, this bond was elongated further before closure to **1** began. A (6/6)CASSCF geometry optimization of **TS1**, in which the pair of electrons in the Si-C bond was correlated, gave results similar to those obtained with (4/4)CASSCF calculations. Interestingly, following the IRC from **TS1** toward **1** at the RHF level led to loss of H₂Si: rather than to ring closure. This finding is consistent with the artifactual RHF barrier to formation of **1** from addition of H₂Si: (**8**) to ethylene (**9**).¹²

Since carbene **4** has an energy that is significantly higher than that of **TS1**, we have not attempted to locate the transition state for ring opening of **1** to **4**. We have, however, located **TS2** (also shown in Figure 1), which links silylene **2** and silene **3**. The barrier to the rearrangement of **2** to **3** is computed to be 30.7 kcal/mol, which is considerably higher than the barrier between **2** and **1**. The high barrier computed for the rearrangement of **2** to **3** is consistent with the experimental finding that intermolecular reactions of silylenes compete with their intramolecular rearrangements to silenes.⁴

C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; and Pople, J. A.; Gaussian, Inc.: Pittsburgh, PA, 1995.

(9) MOLCAS version 3, Anderson, K.; Blomberg, M. R. A.; Fülischer, M. P.; Kellö, V.; Lindh, R.; Malmqvist, P.-Å.; Noga, J.; Olsen, J.; Roos, B. O.; Sadlej, A. J.; Siegbahn, P. E. M.; Urban, M.; Widmark, P.-O.; University of Lund: Lund, Sweden, 1994.

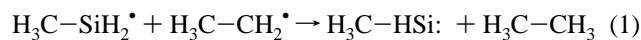
(10) Several different conformational isomers were optimized for each diradical. The structures for **6** and **7** that were of lowest energy at both the (2/2)CASSCF and (2/2)CASPT2N levels were each found to be a transition state by CASSCF vibrational analyses.

(11) (a) Skancke, A.; Van Vechten, D.; Liebman, J. F.; Skancke, P. N. *J. Mol. Struct.* **1996**, *376*, 461. (b) Boatz, J. A.; Gordon, M. S.; Hilderbrandt, R. L. *J. Am. Chem. Soc.* **1988**, *110*, 352

(12) Anwari, F.; Gordon, M. S. *Isr. J. Chem.* **1983**, *23*, 129.

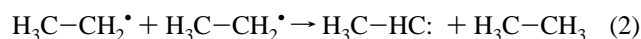
(13) Gordon, M. S.; Truong, T. N. *Chem. Phys. Lett.* **1987**, *142*, 110.

The most important finding of this computational study is that silacyclopropane **1** undergoes ring opening to silylene **2** rather than to diradicals **6** or **7**. The reason for this strong preference, which contrasts with the preference for ring opening of cyclopropane to a trimethylene diradical,^{1,2} is easily understood. The CASPT2N/6-31G* energy¹⁴ of -35.1 kcal/mol, calculated for the reaction



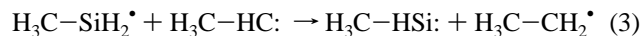
indicates that the Si–H BDE of a primary silyl radical in forming a singlet silylene is lower by this amount than the energy liberated upon forming a C–H bond from a primary alkyl radical.

The preference for opening of cyclopropane to trimethylene, rather than to ethylcarbene, is equally easy to understand. The CASPT2N energy¹⁴ of 14.7 kcal/mol for the reaction, analogous to that in eq 1,



shows that the C–H BDE of a primary alkyl radical in forming a singlet carbene is significantly larger than the energy liberated in forming a C–H bond from a primary alkyl radical.¹⁵

The difference between the reactions in eqs 1 and 2, which is given by the reaction in eq 3,



(14) MP2 for closed-shell species, UMP2 for radicals, and (2/2)-CASPT2N for silylenes and carbenes, uncorrected for ΔZPE .

(15) In contrast, the C–H BDE of a primary vinyl radical in forming a singlet vinylidene is much less than the energy liberated in forming a C–H bond from a primary alkyl radical. It is for this reason that propenylidene was calculated to be lower in energy than propene-1,3-diyl (singlet vinylmethylene) and that cyclopropene was predicted to undergo ring opening to propenylidene by retrograde, C–H insertion. [Yoshimine, M.; Pacansky, J.; Honjou, N. *J. Am. Chem. Soc.* **1989**, *111*, 4198 and references cited therein.] The prediction of ring opening of cyclopropene to propenylidene has subsequently been confirmed by several different experiments. [(a) Walsh, R.; Wolf, C.; Untiedt, S.; de Meijere, A. *J. Chem. Soc., Chem. Commun.* **1992**, 421. (b) Hopf, H.; Plagens, A.; Walsh, R. *J. Chem. Soc., Chem. Commun.* **1994**, 1467. (c) Likhovtorik, I. R.; Brown, D. W.; Jones, M., Jr. *J. Am. Chem. Soc.* **1994**, *116*, 6175. (d) Hopf, H.; Graf von der Schulenberg, W.; Walsh, R. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 381.]

resides in the relative BDE's of primary silyl and alkyl radicals. The reaction in eq 3 is calculated to be exothermic by nearly 49.8 kcal/mol at the CASPT2N/6-31G* level.¹⁴ This difference of nearly 50 kcal/mol between the C–H and Si–H BDE's in the ethyl and methylsilyl radicals is many times larger than the 11 kcal/mol difference between the experimental¹⁶ C–H and Si–H BDE's in ethane¹⁷ and in methylsilane.¹⁸

The Si–H bonds in a silyl radical are much weaker than the C–H bonds in an alkyl radical for two reasons, both of which are related to the fact that unshared electrons on silicon occupy atomic orbitals with much larger amounts of s character than unshared electrons on carbon.¹⁹ First, this difference between silicon and carbon results in much less s character in the Si–H bonds at the highly pyramidalized silicon centers of silyl radicals than in the C–H bonds at the nearly planar carbons of alkyl radicals. Second, and probably more important, upon breaking an Si–H bond to form a singlet silylene from a silyl radical, both lone pair electrons occupy an orbital with much more s character than in a singlet carbene.

The resulting weakness of Si–H bonds in silyl radicals is responsible for the preference, predicted by our calculations and found experimentally,⁴ for silacyclopropanes to undergo ring opening by retrograde C–H insertion, forming silylenes, rather than by ring opening without hydrogen migration, forming silatrimethylene diradicals.

Acknowledgment. We thank the National Science Foundation for support of this research. One of us (P.N.S.) thanks the Norwegian Research Council for the financial support that made his stay at the University of Washington possible.

Supporting Information Available: Optimized geometries for all the species in Scheme 1 and the energies calculated at these geometries (4 pages). See any current masthead page for ordering and Internet access instructions.

JA964384Y

(16) Without correcting for zero-point energies, CASPT2N finds 15 kcal/mol for this difference in C–H versus Si–H BDEs.

(17) Parmar, S. S.; Benson, S. W. *J. Am. Chem. Soc.* **1989**, *111*, 57.

(18) Walsh, R. *Acc. Chem. Res.* **1981**, *14*, 246.

(19) The different spatial extents of 3s and 3p orbitals result in unshared electrons on atoms in the second row of the periodic table generally occupying AO's with much more s character than unshared electrons on atoms in the first row. Kutzelnigg, W. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 272.