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2-Silyl Group Effect on the Reactivity of Cyclopentane-1,3-diyls. Intramolecular Ring-Closure versus Silyl Migration

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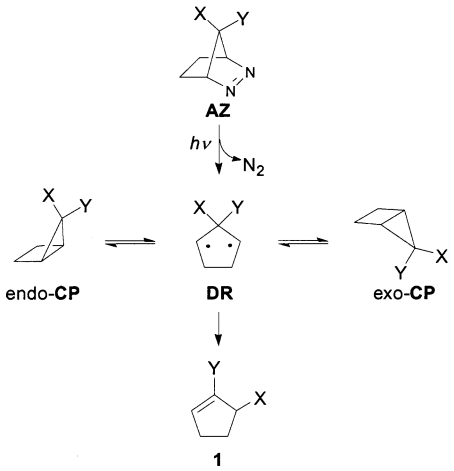
Received March 13, 2004

Generation of singlet and triplet 2-silylcyclopentane-1,3-diyls and their reactivity have been investigated in the thermal and photochemical denitrogenation of 2,3-diaza-7-silylbicyclo[2.2.1]-hept-2-ene. 5-Silylcyclopentene (silyl migration product) is quantitatively obtained, while 5-silylbicyclo-[2.1.0]pentane (intramolecular ring-closure product) is not detected in the denitrogenation reactions. Deuterium labeling studies clarify that 5-silylcyclopentene is formed by a suprafacial [1,2] silyl migration in singlet 2-silylcyclopentane-1,3-diyl. UDFT calculations closely reproduce the observed reactivity of the singlet diradical: The enthalpic barriers of the intramolecular ring-closure are calculated to be $\Delta H^{\ddagger \mathrm{exo}}_{468} = 5.8$ kcal/mol and $\Delta H^{\ddagger \mathrm{endo}}_{468} = 6.7$ kcal/mol, which are much higher than the energy barrier for the [1,2] silyl migration, $\Delta H^{\ddagger}_{468} = 2.7$ kcal/mol. The notable effect of the silyl group on raising the energy barrier of the intramolecular cyclization is rationalized by an electronic configuration of the lowest singlet state of 2-silylcyclopentane-1,3-diyls.

Introduction

Cylopentane-1,3-diyls **DR**[1] are promising intermediates in thermal interconversion of bicyclo[2.1.0]pentanes **CP** and their structural isomerization to cyclopentenes **1** (Scheme 1). The parent bicyclo[2.1.0]pentane (X = Y = H) isomerizes to cyclopentene with an Arrhenius activation barrier of 46.0 kcal/mol,[2] which is 8.2 kcal/mol higher than that for the interconversion (E_a = 37.8 kcal/mol)[3]. Herman and Goodman experimentally determined the heat of formation of cyclopentane-1,3-diyl by using time-resolved photoacoustic calorimetry.[4] Taken together with the activation energies and the heat of formation of bicyclo[2.1.0]pentane, the enthalpies of activation for the ring-closure and hydrogen migration from cyclopentane-1,3-diyl are determined to be 1−2 kcal/mol and 8 kcal/mol, respectively. Carpenter and co-workers closely reproduced the reaction profile using high-level ab initio calculations.[5] Thus, it is quite reasonable to observe the fact that the ring-closure to bicyclo[2.1.0]pentane is much faster than the hydrogen migration to cyclopentene from cyclopentane-1,3-diyl. In contrast, in 1973, Ashe reported that thermolysis of *endo*- and *exo*-5-silylbicyclo[2.1.0]-pentane **CP** (X = $SiMe_3$, Y = H) exclusively afforded 5-silylcyclopentene **1a** (X = $SiMe_3$, Y = H) with activation energies of 35.8 and 39.2 kcal/mol.[6] He did not observe any *endo*−*exo* interconversion in the thermolysis reactions. If one believes that 2-silylcyclopentane-1,3-diyl is an intermediate in the thermal isomerization reactions, the following question is quickly raised: Why does the silyl migration pathway overcome the intramolecular ring-closure, producing 5-silylbicyclo[2.1.0]pentane? Because thermal sigmatropic shift of silicon has been observed preferentially to that of hydrogen in 5-silylcy-

SCHEME 1. Generation of Cyclopentane-1,3-diyls and Their Reactivity



(1) (a) Baldwin, J. E.; Andrews, G. D. *J. Org. Chem.* **1973**, *38*, 1063−1064. (b) Buchwalter, S. L.; Closs, G. L. *J. Am. Chem. Soc.* **1975**, *97*, 3857−3858. (c) Buchwalter, S. L.; Closs, G. L. *J. Am. Chem. Soc.* **1979**, *101*, 4688−4694. (d) Sherrill, C. D.; Seidl, E. T.; Schaefer, H. F. *J. Phys. Chem.* **1992**, *96*, 3712−3716.

(2) (a) Halberstadt, M. L.; Chesick, J. P. *J. Am. Chem. Soc.* **1962**, *84*, 2688−2691. (b) Steel, C.; Zand, R.; Hurwitz, P.; Cohen, S. G. *J. Am. Chem. Soc.* **1964**, *86*, 679−684.

(3) (a) Cohen, J. P. *J. Am. Chem. Soc.* **1962**, *84*, 3250−3253. (b) Jorgenson, M. J.; Clark, T. J.; Corn, J. *J. Am. Chem. Soc.* **1968**, *90*, 7020−7024. (c) Baldwin, J. E.; Ollerenshaw, J. *J. Org. Chem.* **1981**, *46*, 2116−2119.

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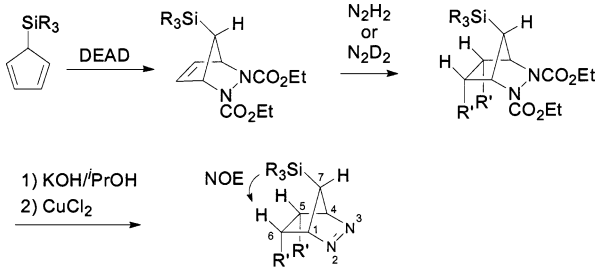
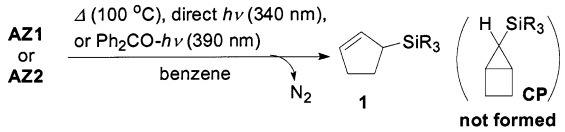
10.1021/jo049580z CCC: $27.50
Published on Web 07/24/2004

SCHEME 2. Synthesis of Azoalkanes AZ1, AZ2, and AZ1-d_2



AZ1: SiR_3 = $SiPhMe_2$, R' = H
AZ2: SiR_3 = Si^tBuMe_2, R' = H
AZ1-d_2: SiR_3 = $SiPhMe_2$, R' = D (53%-*d*)

SCHEME 3. Thermal and Photochemical Denitrogenation Reactions of Azoalkanes

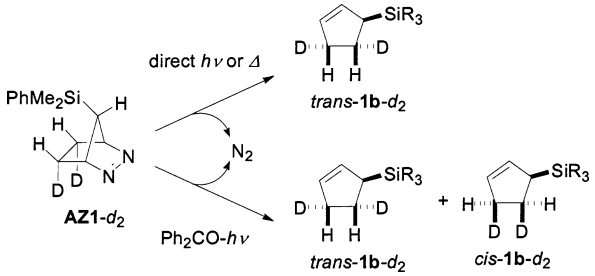


b: SiR_3 = $SiPhMe_2$, **c**: SiR_3 = Si^tBuMe_2

clopentadiene[7] and 1-silylindene,[8] it is expected that an energy barrier for the silyl migration in 2-silylcyclopentane-1,3-diyl is lower than the energy (8 kcal/mol) for the hydrogen migration in the parent cyclopentane-1,3-diyl. However, the activation energy of the silyl migration is unknown. If the energy barrier from 2-silylcyclopentane-1,3-diyl to 5-silylbicyclo[2.1.0]pentane is comparable to the barrier (1−2 kcal/mol) from cyclopentane-1,3-diyl to bicyclo[2.1.0]pentane, it could be natural that the intramolecular ring-closure competes with the silyl-migration reaction. In 1999, Borden and co-workers predicted a high enthalpic barrier to ring-closure of $\Delta H^{\ddagger}_{298} = 13.5$ kcal/mol at the CASPT2/6-31G* level of theory for 2,2-disilylcyclopentane-1,3-diyl (X = Y = SiH_3).[9] If the dramatic effect of the silyl group on raising the energy barrier is applied to the effect of the silyl group in monosilyl-substituted cyclopentane-1,3-diyls, then the exclusive formation of 5-silylcyclopentene from 5-silylbicyclo[2.1.0]pentane would be understandable. However, the effect of the monosilyl group on the energy barrier to ring-closure is still unknown and thus open to debate.

To clarify the puzzling effect of the silyl group on the mechanism for the exclusive formation of 5-silylcyclopentene in the thermal isomerization of 5-silylbicyclo[2.1.0]pentane, one should generate 2-silylcyclopentane-1,3-diyl using a different method and investigate the reactivity in detail. To this end, we have synthesized 7-silyl-2,3-diazabicyclo[2.2.1]hept-2-enes **AZ1**, **AZ2**, and **AZ1**-d_2 (Scheme 2), and the thermal and photochemical denitrogenation reactions were performed in this study (Schemes 3 and 4). Computational work on the reactivity of 2-trimethylsilylcyclopentane-1,3-diyl was also carried out at the UDFT level of theory. A rational mechanism is herein proposed with the support of both experimental and computational investigations to account for the exclusive formation of 5-silylcyclopentene from 2-silylcyclopentane-1,3-diyl.

SCHEME 4. Deuterium Labeling Studies in the Silyl-Migration Reactions



Results

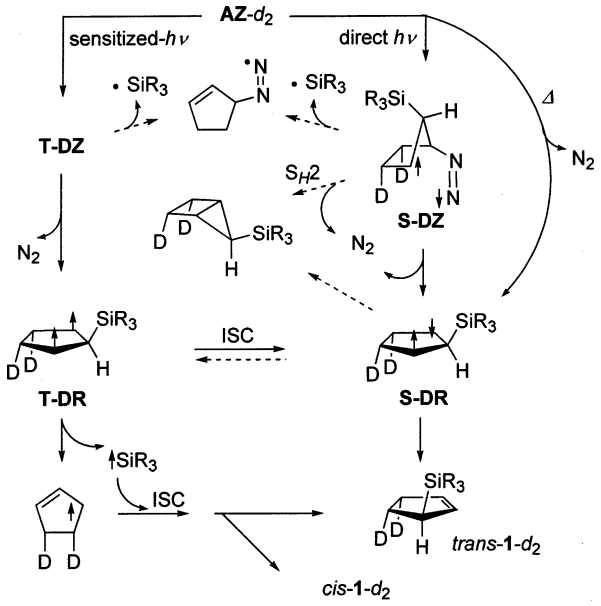
Synthesis of Azoalkanes AZ1 and AZ2. Azoalkanes **AZ1**, **AZ2**, and *endo*-selectively dideuterated **AZ1**-d_2 were prepared according to the method described in Scheme 2. Detailed experimental procedures and spectroscopic data are in the Supporting Information. The diastereoselective cycloaddition (>97% de) of 5-silylcyclopentadiene with diethyl azodicarboxylate (DEAD) was unveiled by the ^{1}H NMR (600 MHz) NOE measurements in the azoalkane structures. The NOE measurements also clarified the chemical shifts of *endo*- (δ 0.80 ppm) and *exo*-hydrogen atoms (δ 1.23 ppm) at C5 and C6 positions in **AZ1**. The deuterium contents (53 ± 3% -*d*) of the *endo*-hydrogen atoms in **AZ1**-d_2 were determined by the comparison of the peak areas of the ^{1}H NMR (600 MHz) spectrum. The *endo*-selective deuteration is probably due to the steric repulsion between the bulky silyl group and the diimide (N_2D_2) in the hydrogenation step.

Denitrogenation of Azoalkanes AZ1 and AZ2. The direct (340 ± 10 nm) photodenitrogenation of azoalkanes **AZ1** (λ_{max} = 342 nm, ϵ 221 in C_6H_6) and **AZ2** (λ_{max} = 342 nm, ϵ 159 in C_6H_6) in degassed C_6D_6 with a 500 W Xenon lamp (a monochromator was used for wavelength selection) led to the quantitative formation of 5-silylcyclopentenes **1b** (SiR_3 = $SiPhMe_2$) and **1c** (SiR_3 = Si^tBuMe_2) at room temperature (ca. 20 °C), see Supporting Information. We could not detect any trace of 5-silylbicyclo[2.1.0]-pentane **CP** under the reaction conditions (Scheme 3). Benzophenone-sensitized photodenitrogenations ($h\nu$ = 390 ± 10 nm) also afforded **1b** or **1c** (>97%) at the stage of ca. 30% conversion of the starting azoalkanes. In the absence of benzophenone, cyclopentenes **1b** and **1c** were not observed: Thus, the cyclopentenes formed in the presence of benzophenone must be derived from the triplet-excited azo chromophores. Because 5-silylbicyclo-[2.1.0]pentane **CP** is stable below the temperature of ca. 150 °C,[6] it is strongly proposed that 5-silylbicyclo[2.1.0]-pentane **CP** was not formed in the photodenitrogenation reaction of the azoalkanes **AZ1** and **AZ2**. Thermal denitrogenation of **AZ1** in a degassed benzene solution was also performed in a sealed tube at 100 °C. The results were similar to those in the photodenitrogenation reactions: The quantitative formation of 5-silylcyclopentene **1b** was observed.

Deuterium Labeling Studies of Silyl Migration. To get information regarding the mechanism for the silyl

(7) Fritz, H. P.; Kreiter, C. G. *J. Organomet. Chem.* **1965**, *4*, 313−319.
(8) Davison, A.; Rakita, P. E. *J. Organomet. Chem.* **1970**, *23*, 407−426.
(9) Johnson, W. T. G.; Hrovat, D. A.; Skancke, A.; Borden, W. T. *Theor. Chem. Acc.* **1999**, *102*, 207−225.

SCHEME 5. Mechanism of Thermal and Photochemical Denitrogenation of Azoalkanes



migration reaction, we performed deuterium labeling studies in the photochemical and thermal denitrogenation of deuterated azoalkane **AZ1**-d_2 (53 ± 3% -*d* in the *endo*-hydrogen atoms). The direct photodenitrogenation reaction quantitatively gave the dideuterated 5-silylcyclopentene **1b**-d_2 (Scheme 4), for which we have assigned the configurations of all the hydrogen atoms by means of C,H-COSY and NOE measurements (600 MHz NMR). The spectral data allowed one to distinguish unequivocally between all of the four hydrogen atoms in the methylene carbons. Careful ^{1}H NMR (600 MHz) spectroscopic analysis revealed that only the hydrogen atoms that were *trans* to the silyl group contained deuterium atoms (53 ± 3% -*d*, see Supporting Information). Thus, the suprafacial migration of the silyl group, which produces *trans*-**1b**-d_2 with 100% retention of configuration in the starting azoalkane **AZ1**-d_2, was observed in the direct irradiation conditions. In contrast, the benzophenone-sensitized denitrogenation afforded a mixture of *trans*- and *cis*-dideuterated cyclopentene **1b**-d_2 with 72% retention of configuration in the starting azoalkane (Scheme 4). The stereoselectivity was determined by the deuterium content in the *trans*- and *cis*-hydrogen atoms (39% and 15% -*d*, respectively) in **1b**-d_2. A control experiment with labeled cyclopentene *trans*-**1b**-d_2 showed that no deuterium scrambling occurred under the benzophenone-sensitized irradiation conditions. The results clearly signify that the stereochemical course of cyclopentene formation depends on the spin state of the excited azo-chromophore. The deuterium labeling study was also performed in the thermal decomposition of azoalkane **AZ1**-d_2 (Scheme 4). The perfect retention of the configuration, the suprafacial migration of the silyl group, was found to give *trans*-**1b**-d_2, as observed under direct irradiation conditions.

Discussion

Mechanism. The mechanism in Scheme 5 is proposed to account for the experimental observations in the denitrogenation reaction of silyl-substituted azoalkanes. It is generally accepted that diazenyl diradicals **DZ** are the first intermediates in photodenitrogenation of azoalkanes.[10] In our case, the singlet or triplet diazenyl diradical **S**- or **T-DR** may also be the initial intermediate from the singlet- or triplet-excited azo-chromophore. Because it is known that the lifetime of diazenyl radical (Me−N=N•) is ca. 100 fs,[11] and a β-silyl radical lives long enough to be detected by EPR,[12] the denitrogenation from **S**- and **T-DZ** should be faster than the desilylation from **DZ**.[13] The alternative option of S_H2 denitrogenation in **S-DZ**,[10] producing 5-silylbicyclo[2.1.0]pentane, is also excluded, because the housane was not observed in the photochemical process at room temperature.[14] Consequently, under direct irradiation conditions, the singlet diazenyl diradical **S-DZ** preferentially expels nitrogen to generate the *trans*-deuterated diradical **S-DR**, followed by the suprafacial silyl migration[15] producing the observed *trans*-**1**-d_2 configuration with complete retention of the initial configuration of the azoalkane. The singlet diradical **S-DR** may also be generated in the thermal decomposition of azoalkanes via concerted denitrogenation.[5]

In contrast to the singlet pathway (direct irradiation and thermal decomposition), a small but significant randomized distribution of the deuterium atoms in 5-silylcyclopentene **1b** was observed in the triplet-sensitized photodenitrogenation of azoalkane **AZ1**-d_2 (Scheme 4). From the triplet-excited azoalkane, again the diazenyl diradical **T-DZ** is generated first, which upon denitrogenation produces the triplet 1,3-diradical **T-DR**. Desilylation, intersystem crossing to a singlet radical pair, and subsequent C−Si bond formation produce 5-silylcyclopentene **1** (Scheme 5). Thus, the initial *trans*-configuration between the silyl group and deuterium atoms in the deuterated azoalkane is lost during the chemical processes.[16] However, as mentioned already (Scheme 4), the stereochemical randomization is not perfect. Thus, ca. 70% retention of the initial configuration was observed in **1b**-d_2. The competitive isc process of the **T-DR** to **S-DR** might be the reason for the partial randomization of the configuration (Scheme 5).[17]

As mentioned already, 2-silylcyclopentane-1,3-diyl **DR** is strongly proposed to be the intermediate for the selective formation of 5-silylcyclopentene **1** in the deni-

(10) (a) Sinicropi, A.; Page, C. S.; Adam, W.; Olivucci, M. *J. Am. Chem. Soc.* **2003**, *125*, 10947−10959. (b) Adam, W.; Trofimov, A. V. *Acc. Chem. Res.* **2003**, *36*, 571−579.

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(13) The energy barrier of the desilylation from the diazenyl diradical **S-DZ** (SiR$_3$ = SiMe$_3$) was calculated to be ca. 20 kcal/mol higher than the energy of the denitrogenation in the diazenyl diradical at the UB3LYP/6-31G* level of theory; see Figure S1 in the Supporting Information.

(14) Potential energy surface analysis found that the S_H2 process in **S-DZ** (SiR$_3$ = SiMe$_3$) has an energy barrier of ca. 15 kcal/mol at the UB3LYP/6-31G* level of theory; see Figure S2 in the Supporting Information.

(15) Suprafacial [1,2] oxygen migration in cyclopentane-1,3-diyl derivative, see: Abe, M.; Adam, W.; Ino, Y.; Nojima, M. *J. Am. Chem. Soc.* **2000**, *122*, 6508−6509.

(16) A CIDNP effect should be observed in the cyclopentene product, although we have no ability to measure it.

(17) Desilylation from **T-DR** (SiR$_3$ = SiMe$_3$) was calculated to possess an activation energy of 12.6 kcal/mol at the UB3LYP/6-31G* level of theory; Figure S3 in the Supporting Information.

trogenation reaction of azoalkanes **AZ**. Thus, it is concluded that the suprafacial silyl migration is much faster than the intramolecular cyclization process producing 5-silylbicyclo[2.1.0]pentane. To understand quantitatively the 2-silyl group effect on the reactivity of cyclopentane-1,3-diyl, UDFT calculations were performed for 2-trimethylsilylcyclopentane-1,3-diyl **DR1** (X = $SiMe_3$, Y = H) as a model compound.

UDFT Computations. Substituent effects on the spin-multiplicity of diradicals have been a topic of current interest.[18−20] First of all, the ground-state spin-multiplicity of **DR1** was computed at the UB3LYP/6-31G*[21] level of theory with the Gaussian 98 suite of programs.[22] In contrast to the triplet ground state of the parent cyclopentane-1,3-diyl (X = Y = H, $\Delta E_{ST} = E_S - E_T = +1.2$ kcal/mol),[1c,23] the singlet **DR1** was calculated to lie slightly below the triplet by 0.1 kcal/mol ($\Delta E_{ST} = -0.1$) in C_1 symmetry. The calculated energy gap is much smaller than that of 2,2-disilylcyclopentane-1,3-diyl (X = Y = SiH_3, $\Delta E_{ST} = -5.2$ kcal/mol, C_2 symmetry) at the same level of theory.[24] The significant effect of the silyl group on the singlet preference is attributed to the hyperconjugative stabilization of the singlet state, i.e., electron delocalization from the C−Si σ bond at C2 to the in-phase combination (ψ_S) of the p−π AOs at C1 and C3 (Figure 1).[9,23−25]

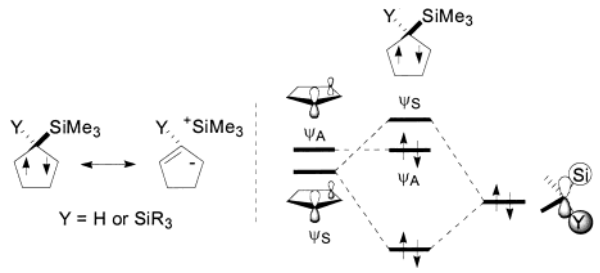


FIGURE 1. Hyperconjugative stabilization of singlet 2-silyl-substituted cyclopentane-1,3-diyls.

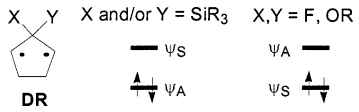
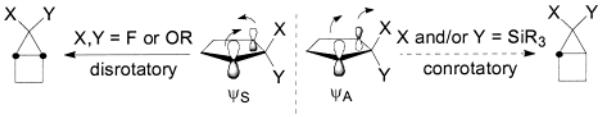


FIGURE 2. Substituent effect on the electronic configuration in the lowest singlet state of **DR**.

SCHEME 6. Substituent Effect on the Mode (Disrotatory versus Conrotatory) of Ring Closure in the Lowest Singlet State of 1,3-Diradicals



As illustrated in Figure 1, the dominant interaction of the in-phase ψ_S NBMO is with the filled pseudo-π orbital at the C2 position.[26] The orbital interaction leads to the destabilization of ψ_S and the preferred occupancy of the out-of-phase ψ_A NBMO. The ratio of the occupation number of the ψ_A and ψ_S NBMOs in the singlet **DR1** was calculated to be 1.17/0.83 = 1.40 using (2/2)CASSCF/6-31G*//UB3LYP/6-31G* computation. Thus, a 40% deviation from unity was computed. In sharp contrast, the preferred occupancy of ψ_S NBMO has been found for 2,2-difluoro-[27] and dialkoxy-substituted 1,3-diradicals[28] (Figure 2). In the case of the electron-withdrawing-group-substituted diradicals, the dominant interaction of the ψ_S NBMO with the unfilled C−X (X = F, OR) σ* orbital leads to the stabilization of the ψ_S NBMO; as a result, the ψ_S NBMO possesses the greater occupation number. The dramatic substituent effect at the C2 position on the electronic configuration in the lowest singlet states of 1,3-diradicals predicts the different reactivity between the silyl-substituted diradicals and the electron-withdrawing-group-substituted diradicals (Scheme 6). Thus, fast disrotatory ring-closure is expected to give *cis*-fused bicyclo[2.1.0]pentanes for dialkoxy-substituted singlet diradicals (X = Y = OR). In fact, the singlet states of 2,2-difluoro- and dialkoxycyclopentane-1,3-diyls are calculated to be transition-state structures rather than minima.[23,25a] The preferred formation of bicyclo[2.1.0]pentane derivatives was experimentally confirmed by the quantitative formation of the intramolecular cyclization product in the denitrogenation reaction of dialkoxy-substituted azoal-

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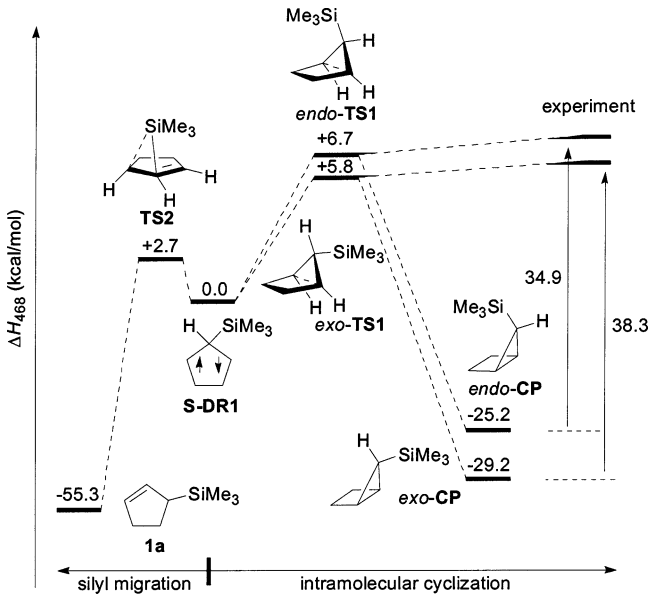

FIGURE 3. Computed and experimental relative enthalpies of stationary points in the reaction of 2-trimethylsilylcyclopentane-1,3-diyl **DR1**.

kanes.[29] In contrast, the conrotatory ring-closure to the highly strained *trans*-fused bicyclopentane is required from the electronic configuration of the lowest singlet state of the silyl-substituted diradicals, whose activation energy should be extremely high.[9] The *cis*-fused bicyclopentane may be formed from the energetically unfavored electronic configuration of the singlet silyl-substituted diradicals, i.e., the occupancy of ψ_S NBMO. In any event, the intramolecular cyclization in 2-silylcyclopentane-1,3-diyl needs a considerably high energy barrier.

UDFT calculations were performed to estimate quantitatively the energy barriers of the intramolecular cyclization and the silyl-migration reaction from the singlet **DR1** (Figure 3). It is quite difficult to obtain the values experimentally. We have also been interested in whether such a relatively low-cost method may be used to study the reaction profiles of open-shell singlet molecules, because, in general, multi-configuration self-consistent field methods, such as CASSCF and CASPT2 calculations, are needed for homolytic bond-breaking and -making processes.[30] Figure 3 summarizes the computed enthalpy profile (including zero-point energy corrections) of the reaction of singlet **DR1** at 195 °C (a typical temperature used in the experimental thermolysis of 5-silylbicyclo[2.1.0]pentane derivatives)[5] and compares the results with experimental values. Full Cartesian coordinates and vibrational frequencies for all the stationary points are listed in the Supporting Information. It is clear that the suprafacial silyl migration, $\Delta H^{\ddagger}_{468}$ = 2.7 kcal/mol, from the singlet diradical **S-DR1** is predicted to be an energetically more favorable process than the intramolecular cyclization, $\Delta H^{\ddagger endo}_{468}$ = 6.7 kcal/mol and $\Delta H^{\ddagger exo}_{468}$ = 5.8 kcal/mol, producing the *endo*- and *exo*-5-silylbicyclo[2.1.0]pentane. The electronic effect (the selective occupation of the out-of-phase ψ_A NBMO in the lowest singlet state of **S-DR1**) rationalizes the much higher activation enthalpies for the ring-closures, compared to the small activation enthalpy for the parent cyclopentene-1,3-diyl ($\Delta H^{\ddagger}_{413}$ = 1.2 kcal/mol)[5] and the nearly zero activation energy for 2,2-dialkoxycyclopentane-1,3-diyl. The accuracy of the UDFT calculations was confirmed by comparison with the available experimental values. From the activation energies of thermal decompositions of *endo*- and *exo*-5-silylbicyclo[2.1.0]-pentane,[6] the activation enthalpies ($\Delta H^{\ddagger}_{468}$'s) at 195 °C can be calculated to be 34.9 and 38.3 kcal/mol (Figure 3). Thus, the UDFT calculations closely reproduced the experimental results with some underestimation, ca. 3 kcal/mol.

Conclusions

The thermal and photochemical denitrogenation of azoalkanes **AZ1**, **AZ2**, and **AZ1**-d_2 have revealed the notable silyl group effect at the C2 position on the reactivity of singlet cyclopentane-1,3-diyls. Thus, the suprafacial [1,2] silyl migration to 5-silylcyclopentene was found to be much faster than the intramolecular cyclization to 5-silylbicyclo[2.1.0]pentane from singlet 2-silylcyclopentane-1,3-diyl. The observation provided valuable information regarding the mechanism for the selective formation of 5-silylcyclopentene in the thermal decomposition of *endo*- and *exo*-5-silylbicyclo[2.1.0]pentane, which has been debated until now. Benzophenone-sensitized photodenitrogenation of azoalkanes and the deuterium labeling study in the denitrogenation of **AZ1**-d_2 have signified that the triplet 2-silylcyclopentane-1,3-diyls also give the silyl migration product, exclusively. The computational studies have provided a reasonable answer to the substituent effect of the silyl group at the C2 position on the reactivity of singlet cyclopentane-1,3-diyls **DR**. The high energy barrier to ring closure is due to the electronic configuration of the lowest singlet state of the silyl-substituted diradical, i.e., the selective occupation of the out-of-phase ψ_A NBMO.

Acknowledgment. We thank Mrs. T. Muneishi at the Analytical Center of Faculty of Engineering, Osaka University, for measuring the 600 MHz NMR spectra.

Supporting Information Available: Experimental details, Cartesian coordinates, energies, and harmonic vibrational frequencies for all stationary points in the calculations, and ^{1}H NMR spectra for **AZ1**, **AZ2**, **1b**, and **1c**. This material is available free of charge via the Internet at http://pubs.acs.org.

JO049580Z

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