J. Am. Chem. Soc. **1998,** *120,* 7079−7084

Ab Initio Calculations of the Effects of Geminal Silyl Substituents on the Stereomutation of Cyclopropane and on the Singlet−Triplet Splitting in Trimethylene

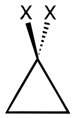
Anne Skancke,*,† David A. Hrovat, and Weston Thatcher Borden*

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

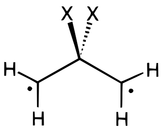
Received March 4, 1998. Revised Manuscript Received May 21, 1998

Abstract: (10/10)CASSCF and CASPT2N/6-31G* calculations predict that geminal silyl substituents at C(2) of the (0,0)-trimethylene diradical (**2c**) should strongly stabilize the lowest singlet state by hyperconjugative electron donation to the in-phase combination of p-π AOs at C(1) and C(3). After correction for zero point energy differences, singlet **2c** is found to be an energy minimum, with a barrier to closure to 1,1-disilylcyclopropane (**1c**) of 6.4 kcal/mol, and to lie below triplet **2c** by 11.1 kcal/mol. The conrotatory transition state that connects **1c** to **2c** is computed to be 8.5 kcal/mol lower in energy than the transition state for cleavage of the C(2)−C(3) ring bond in **1c** by rotation of just one of these methylene groups and 6−7 kcal/mol lower in energy than the transition states for breaking one of the ring bonds to C(1) by methylene rotation. Coupled conrotation of C(2) and C(3) is therefore predicted to dominate rotation of just one of these methylene groups in the stereomutation of **1c**.

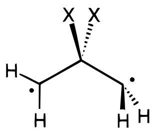
Hoffmann's 1968 extended Hückel calculations predicted a large preference for ring opening of cyclopropane (**1a**) to the (0,0)-trimethylene diradical (**2a**) by conrotation of two methylene groups.[1] However, subsequent ab initio calculations found that the preference for conrotation over both disrotatory ring opening to **2a** and rotation of just one methylene group to give the (0,90)-diradical (**3a**) amounts to only 1−2 kcal/mol.[2,3] Moreover, alkyl substituents are calculated to reduce significantly the already small preference predicted for conrotatory ring opening and ring closure.[2a] These computational findings explain the failure of experiments on substituted cyclopropanes to detect any significant preference for stereomutation via coupled conrotation.[4]



1a, X = H
b, X = F
c, X = SiH$_3$



2a, X = H
b, X = F
c, X = SiH$_3$



3a, X = H
b, X = F
c, X = SiH$_3$

Transition-state theory predicts that disrotatory ring opening of **1a** to **2a** should be followed, preferentially, by conrotatory closure of **2a**, because the conrotatory transition state is the lower energy of these two transition states for ring closure to **1a**.[2b] Since disrotatory ring opening, followed by conrotatory ring closure, has the same net effect as passage across the transition state for rotation of a single methylene group,[2a,5] transition-state theory, when applied to the ab initio potential energy surface computed for stereomutation of **1a**, predicts nearly equal rate constants for double rotation and net single rotation.[2b] This prediction is in accord with the experimental results of Baldwin and co-workers on the stereomutation of cyclopropane-*1,2,3*-d_3-*1*-^{13}C.[6]

More recently, calculations that have simulated the reaction dynamics on the ab initio potential energy surfaces have predicted a 3−5-fold preference for double rotation.[7] These calculations find that conservation of angular momentum tends to result in molecules of **2a**, formed from **1a** via disrotation, reclosing to **1a** by this same mode of coupled rotation. Thus, molecules which pass over the disrotatory transition state for ring opening are found largely to undergo stereomutation by coupled rotation, rather than by net single rotation, as predicted by transition-state theory. The predictions of the dynamics calculations are in accord with the experimental results of Berson and co-workers on the stereomutation of cyclopropane-*1,2*-d_2.[8−10]

The calculated preference for conrotatory ring opening and

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

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(3) Reference 2a contains a complete list of calculations performed prior to 1992.

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S0002-7863(98)00720-3 CCC: $15.00

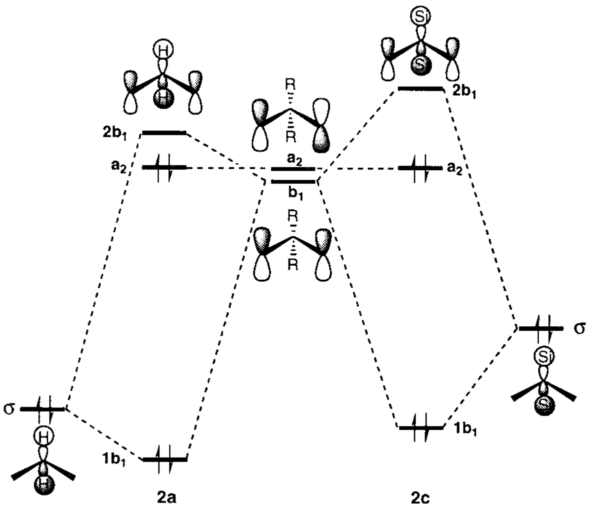

Figure 1. Schematic orbital interaction diagram, depicting the effect of hyperconjugative electron donation from the C(2)−R bonds to the p-π AOs at C(1) and C(3) in **2a** (R = H) and **2c** (R = SiH_3).

reclosure of cyclopropane (**1a**) was traced by Hoffmann to interaction of the p-π AOs at C(1) and C(3) with the σ and σ^* orbitals of the C−H bonds at C(2) in the (0,0) geometry of trimethylene diradical (**2a**).[1] As shown on the left-hand side of Figure 1, electron donation from the b_1 combination of filled C−H bonding σ orbitals at C(2) to the in-phase (b_1) combination of p-π AOs at C(1) and C(3) stabilizes the resulting $1b_1$ MO but raises the energy of the $2b_1$ MO. On the other hand, because the out-of-phase (a_2) combination of the p-π AOs has a node at C(2), a_2 is not destabilized by mixing with the C−H bonds at this carbon. Consequently, occupancy of the a_2, rather than the $2b_1$, MO is favored in **2a**, and this leads to the predicted preference for conrotatory ring opening and ring closure.

Qualitative arguments, similar to those employed by Hoffmann, have been used to predict that replacement of the weakly electron-donating C−H bonds in **2a** by the strongly electron-accepting C−F bonds in **2b** should lead to **1b** undergoing stereomutation with a large preference for *disrotation*. This conclusion has been supported by the results of ab initio calculations,[11a,b] and experiments have recently confirmed the computational predictions that disrotation is preferred to conrotation, monorotation, and cleavage of a ring bond to the fluorinated carbon in the stereomutation of a 2,3-dialkyl derivative of **1b**.[12] The additional prediction—that the strong electron donation from the b_1 combination of p-π AOs into the low-lying C−F σ^* orbitals in **2b** should result in stabilization of the lowest singlet state of this diradical, relative to both the triplet and **1b**[11]—has also been supported by the results of recent experiments.[13]

Replacement of the C−H bonds at C(2) of **2a** with bonds that are stronger, hyperconjugative, electron donors than C−H should also stabilize the lowest singlet state of the resulting diradical. For example, since C−Si bonds are known to provide more hyperconjugative stabilization than C−H bonds for carbocations,[14] the C−Si bonds in **2c** should donate electrons into the b_1 combination of p-π AOs at C(1) and C(3) more strongly than the C−H bonds in **2a**. As shown schematically in Figure 1, the stronger hyperconjugative electron donation expected in **2c** than in **2a** should result in the $1b_1$ MO being more stabilized and the $2b_1$ MO more destabilized in 2,2-disilyltrimethylene than in the hydrocarbon diradical. Therefore, conrotatory opening and closure should be more favored, relative to disrotation and monorotation, in the stereomutation of 1,1-disilylcyclopropane (**1c**) than in the stereomutation of cyclopropane (**1a**). In addition, the lowest singlet state of **2c** should be thermodynamically stabilized, not only relative to the triplet state of this diradical, but also toward ring closure to **1c**.

Calculations provide a convenient method of testing these qualitative predictions, prior to attempting to verify them experimentally. We have performed ab initio calculations to locate and compute the energies of the intermediates and transition states on the potential surface for stereomutation of **1c**, and we have also calculated the singlet−triplet splitting in diradical **2c**. Herein we report the results of these calculations and compare them to the results of similar calculations of the potential surfaces for stereomutation of **1a** and **1b** and on the singlet−triplet splittings in diradicals **2a** and **2b**.

Computational Methodology

The 6-31G* basis set was used throughout this work.[15] Optimization of the geometry of 1,1-disilylcyclopropane (**1c**) was carried out at the RHF level of theory. The geometries of singlet diradicals were optimized with (2/2)CASSCF wave functions, and the geometries of monoradicals and triplet diradicals were optimized at the ROHF level. Vibrational analyses on optimized geometries were performed at the same levels of theory, and the vibrational frequencies computed were used, without scaling, to compute zero-point energy corrections. The RHF, (2/2)CASSCF, and ROHF calculations were carried out using the Gaussian 94 package of programs.[16]

To assess the effects of including dynamic correlation,[17] single-point CASPT2N[18] calculations were carried out at each stationary point. Since CASPT2N uses second-order perturbation theory, the CASPT2N calculation on **1c** is equivalent to MP2, the CASPT2N calculations on radicals and triplet diradicals to ROMP2, and those on singlet diradicals to (2/2)CASPT2N. Except for the MP2 calculation on **1c**, the

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(9) Experimental results on the stereomutation of cyclopropane-d_2, very similar to those of Berson and co-workers,[8] have been reported by Cianciosi, S. J.; Ragunathan, N.; Freedman, T. R.; Nafie, L. A.; Baldwin, J. E. *J. Am. Chem. Soc.* **1990**, *112*, 8204. More recently, however, a statistical analysis has led Baldwin to conclude that one of the rate constants, measured by him and co-workers, contains too large an uncertainty to warrant any definitive conclusion being drawn about the ratio of double to single methylene rotations in the stereomutation of cyclopropane-d_2. See: Baldwin, J. E. In *The Chemistry of the Cyclopropyl Group*; Rappoport, Z., Ed.; Wiley: New York, 1995; Vol. 2, Chapter 9.

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Table 1. Energies (kcal/mol) of the Stationary Points on the Potential Surface for Ring Opening of 1,1-Disilylcyclopropane (**1c**), Relative to the Energy of **1c**[a]

			2-electron/2-orbital active space			10-electron/10-orbital active space	
structure	state	symmetry	$\Delta E_{\mathrm{CASSCF}}$	$\Delta E_{\mathrm{CASPT2N}}$	ΔZPE	$\Delta E_{\mathrm{CASSCF}}$	$\Delta E_{\mathrm{CASPT2N}}$
1c	$^1A_1$	C_{2v}	−697.216120[a]	−697.804070[a]	75.4	−697.323399[a]	−697.809634[a]
2c[b]	$^1A_1$	C_{2v}	40.8	50.9	−5.2	54.0	51.4
2c[c]	$^3B_2$	C_{2v}	47.0	62.8	−5.2	60.5	62.5
3c[d]	$^1A''$	C_s	49.6	67.0	−6.4	63.6	66.6
2,3-Con TS[e]	^1A	C_2	42.4	57.1	−4.6	60.8	57.2
2,3-Dis MT[d]	$^1A'$	C_s	50.5	68.1	−7.0	64.4	67.6
2,3-Mono TS[e]	^1A	C_1	49.5	67.3	−5.8	63.6	66.9
1,2-Con TS[f]	^1A	C_1	40.1	62.4	−4.1	60.8	63.0
1,2-Mono TS[f]	^1A	C_1	40.1	62.9	−4.1	60.7	63.6

[a] Absolute energy in hartrees. [b] Reaction intermediate. [c] Mountain top at (2/2)CASSCF, but see ref 27. [d] Mountain top, accessed by cleavage of the C(2)−C(3) bond. [e] Transition state, accessed by cleavage of the C(2)−C(3) bond. [f] Transition state, accessed by cleavage of the C(1)−C(2) bond. [g] Geometries were optimized at the (2/2)CASSCF/6-31G* level of theory.

MOLCAS suite of ab initio programs was used for all the CASPT2N calculations.[19]

It has been found that similar CASPT2N calculations on the opening of other three-membered rings give results that are comparable to CASPT2N calculations, performed with much larger CASSCF active spaces.[20] Nevertheless, at each stationary point on the potential surface for stereomutation of **1c**, we also carried out (10/10)CASSCF and (10/10)CASPT2N calculations, in which the electrons in all the C−C and C−Si bonds were correlated.

Results and Discussion

The geometries of all the stationary points on the potential surface for the stereomutation of **1c** are available as Supporting Information. The CASSCF and CASPT2N energies of these geometries, computed with both (2/2) and (10/10) active spaces, are given in Table 1.

Although there are large differences between the (2/2)- and (10/10)CASSCF relative energies, the (2/2)- and (10/10)-CASPT2N relative energies differ by less than 1 kcal/mol. Since the CASPT2N calculations with the larger active space should be the more accurate, unless otherwise noted, the discussion of the potential surface for stereomutation of **1c** uses the (10/10)-CASPT2N energies.

Comparison of the (10/10)CASSCF and (10/10)CASPT2N results in Table 1 shows that inclusion of dynamic electron correlation stabilizes both the (0,0) diradical (**2c**) and the conrotatory transition state leading to it by ca. 6 kcal/mol, relative to all of the other diradical species. Inclusion of dynamic electron correlation is generally found to provide selective stabilization for the most highly delocalized structures.[17,21]

Calculations at the (0,0) Geometry (2c). The optimized C_{2v} geometry of the lowest singlet state of 2,2-disilyltrimethylene (**2c**) was found to be a minimum, with an energy 50.9 kcal/mol above that of 1,1-disilylcyclopropane (**1c**) at the (2/2)CASPT2N-MP2 level of theory. In contrast, the lowest singlet state of the parent (0,0)-trimethylene (**2a**) has been found to have two imaginary frequencies and, thus, to be a mountain top on the C_3H_6 potential energy surface.[2] Additionally, the (2/2)CASPT2N energy of **2a** was found to be higher than the MP2 energy of **1a** by 63.9 kcal/mol,[7b] so the presence of the geminal silyl groups at C(2) of **2c** lowers the energy of the ring-opened (0,0) diradical by 13.0 kcal/mol. Both these findings indicate that the C−Si bonds in **2c** provide greater electronic stabilization for this diradical than the C−H bonds at C(2) in **2a** provide for the parent trimethylene.

Further evidence for electronic stabilization of **2c** by the geminal silyl groups comes from comparison of the geometry of **2c** with that of **2a**. The C−C bond lengths of **2c** are 1.468 Å, which is 0.032 Å shorter than the C−C bond lengths of **2a**.[2a] Also, the C−C−C bond angle of 120.4° in **2c** is 5.1° larger than that in **2a**. This latter difference between the geometries of these two (0,0)-trimethylene diradicals can be traced to an important difference between the wave functions for them, which also reflects the stabilization of **2c** by the silyl groups.

The configuration in which the a_2 nonbonding (NB)MO is doubly occupied constitutes 54% of the (2/2)CASSCF wave function for **2a**.[2a] As pointed out by Hoffmann,[1] and as illustrated in Figure 1, occupancy of the a_2 combination of p-π AOs at C(1) and C(3) is favored, because the $2b_1$ combination is destabilized by hyperconjugative electron donation from the b_1 combination of C−H bonds at C(2). Leaving the destabilized $2b_1$ MO empty allows hyperconjugative stabilization of the $1b_1$ MO to provide the maximum amount of energy lowering for **2a**.

The greater electron-donating ability of the C−Si bonds in **2c**, relative to the C−H bonds in **2a**, results in the configuration in which the a_2 NBMO is doubly occupied constituting 75% of the (2/2)CASSCF wave function for **2c**. Since, as shown in Figure 1, the through space interaction between the p-π AOs on C(1) and C(3) is antibonding in the a_2 NBMO, the larger occupancy of the a_2 NBMO in **2c** than in **2a** results in a larger C(1)−C(2)-C(3) bond angle in the former than in the latter diradical. Thus, the 5.1° larger C(1)−C(2)−C(3) bond angle in **2c** than in **2a** can be attributed to the greater hyperconjugative electron-donating ability of the C(2)−Si bonds in **2c**, compared to the C(2)−H bonds in **2a**.

Stabilization Energy of 2c and Ring Strain in 1c. It is tempting to identify the 13.0 kcal/mol smaller energy difference between **1c** and **2c** than between **1a** and **2a** as the thermodynamic stabilization energy of **2c** that is provided by replacing the hydrogens at C(2) in **2a** by the *gem*-disilyl groups in **2c**. However, to do so would ignore possible effects that the two silyl groups might have on the ring strain in **1c**. The contribution of the latter factor can be assessed by computing the energy of the isodesmic reaction in eq 1, which is calculated to be exothermic by 7.2 kcal/mol at the MP2/6-31G* level.

$$\mathbf{1a} + \text{2,2-disilylpropane} \rightarrow \mathbf{1c} + \text{propane} \qquad (1)$$

The pair of silyl groups in **1c** makes the reaction in eq 1 energetically favorable, because there is greater carbon 2s

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

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character in the bonds to the electropositive silicons in **1c** than in the C−H bonds in **1a**.[22] This difference, in turn, makes the 2p character of the cyclopropane C−C bonds larger in **1c** than in **1a**. Since high 2p character is favorable for the strained C−C bonds of a cyclopropane ring, the silyl groups reduce the ring strain in **1c**, relative to that in **1a**.[23]

If the C−Si bonds in **1c** make it 7.2 kcal/mol less strained than **1a**, ring opening of **1c** to **2c** must require this much more energy than ring opening of **1a** to **2a**. Therefore, the stabilization energy of diradical **2c**, relative to **2a**, must amount to a total of 13.0 + 7.2 = 20.2 kcal/mol. Indeed, the isodesmic reaction in eq 2, is computed to be energetically favorable by 20.2 kcal/mol.

$$\mathbf{2a} + \text{2,2-disilylpropane} \rightarrow \mathbf{2c} + \text{propane} \qquad (2)$$

The energy of the reaction in eq 2 is not really a pure measure of the greater hyperconjugative stabilization of **2c**, relative to **2a**, because it contains a contribution from the effect that the silicons have on weakening the strengths of the individual C−H bonds in 2,2-disilylpropane.[24] An isodesmic reaction that provides an estimate of this effect is given in eq 3.

$$\text{propane} + \text{2,2-disilyl-1-propyl}\cdot \rightarrow \text{1-propyl}\cdot + \text{2,2-disilylpropane} \qquad (3)$$

This reaction is calculated to be endothermic by 4.7 kcal/mol at the R(O)MP2 level of theory. If the energy of 20.2 kcal/mol for the reaction in eq 2 is corrected by twice the difference between the C−H BDEs of propane and 2,2-disilylpropane from the reaction in eq 3, 10.8 kcal/mol is obtained as the electronic stabilization energy of **2c**, relative to **2a**.

A more direct way to assess the electronic stabilization of **2c** via isodesmic reactions is to compare the C−H BDE of 2,2-disilylpropane in forming 2,2-disilyl-1-propyl radical with the C−H BDE of this radical in forming the lowest singlet state of **2c**. Were there no interaction between the radical centers in **2c**, the two C−H BDEs of 2,2-disilylpropane in forming the singlet state of this diradical would be identical. The difference between the first and second BDEs is given by eq 4, where X = SiH_3 for 2,2-disilylpropane.

$$2H_3CCX_2CH_2\cdot \rightarrow H_3CCX_2CH_3 + \cdot H_2CCX_2CH_2\cdot \qquad (4)$$

We have previously used the energy calculated for the isodesmic reaction in eq 4 to show that the interaction of the p-π AOs on C(1) and C(3) with the b_1 combination of C−X bonds at C(2) is competitive in **2a** (X = H), but cooperative in **2b** (X = F).[11b] More specifically, for X = H the R(O)MP2-(2/2)CASPT2N energy[25] for the reaction in eq 4 is unfavorable by 0.7 kcal/mol, showing that interaction of two primary radical centers with different CH_2 groups in two 1-propyl radicals is more stabilizing than interaction of both radical centers with the same CH_2 group in **2a**. In contrast, for X = F the R(O)-MP2-(2/2)CASPT2N energy[25] for the reaction in eq 4 is favorable by 3.8 kcal/mol, showing that interaction of two primary radical centers with the same CF_2 group, as in **2b**, is *more* stabilizing than their interaction with different CF_2 groups in two 2,2-difluoro-1-propyl radicals.

For X = SiH_3 the reaction in eq 4 is computed to be favorable by 10.1 kcal/mol at the R(O)MP2/(2/2)CASPT2N level, a much larger exothermicity than that computed for X = F. The hyperconjugative electron donation in **2c** of the electron pair in the b_1 combination of C−Si bonds at C(2) into the in-phase combination of the p-π AOs on C(1) and C(3) is clearly a *highly* cooperative, stabilizing interaction. It is 6.3 kcal/mol more stabilizing than the hyperconjugative interaction in **2b** and 10.8 kcal/mol more stabilizing than that in **2a**.[26]

Singlet−Triplet Energy Separation in 2c. A different measure of the stabilization provided for the lowest singlet state of **2c** by the geminal silyl groups is the energy difference between the singlet and triplet states of this diradical. In the lowest triplet one electron occupies each of the NBMOs, and the Pauli principle prevents these two electrons from appearing simultaneously in the same region of space. Consequently, the Coulombic repulsion between the electrons in the NBMOs is minimized in the triplet state.

On the other hand, in the lowest singlet state, the NBMO of lower energy (a_2 in both **2a**[1] and **2c** and $2b_1$ in **2b**[11]) can have an electron occupation number that is greater than one. The larger the energy difference between the a_2 and b_1 NBMOs, the larger the occupation number of the lower energy NBMO will be, and the more likely it is that the singlet will fall below the triplet in energy. Therefore, the relative sizes of the singlet−triplet splittings, computed at the optimized (0,0) geometries[27] of **2a**−**c**, reflect the amount of hyperconjugative stabilization of the singlet diradicals. With inclusion of dynamic electron correlation at the (2/2)CASPT2N level, the triplet is calculated to be the ground state of **2a** by 0.7 kcal/mol; however, in **2b** the singlet is computed to be the ground state by 4.8 kcal/mol. In **2c** the singlet is also predicted to be the ground state, but by 11.9 kcal/mol at the (2/2)CASPT2N level and 11.1 kcal/mol with (10/10)CASPT2N. The singlet−triplet energy gaps in **2a**−**c** are close to the energies of the isodesmic reaction in eq 4 for these three diradicals.

Calculations at the (0,90) Geometry (3c). The size of the electronic stabilization in the (0,0) geometry of singlet 2,2-disilyltrimethylene diradical (**2c**) can also be assessed by comparison of its energy with that of the (0,90) singlet geometry (**3c**), in which the nonbonding AO at C(3) interacts with a combination of C−Si bonds at C(2) that has σ rather than π symmetry. As shown in Table 1, **3c** is calculated to be 16.1 kcal/mol higher in energy than **2c** at the (2/2)CASPT2N level of theory. The energy difference between the (0,0) and (0,90) geometries, **2a** and **3a**, in the hydrocarbon diradical is only 1.7 kcal/mol at the same level of theory.[7b] Thus, the energy

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[22] Bent, H. A. *Chem. Rev.* **1961**, *61*, 275.

[23] The same type of argument can be used to explain why the fluorines in **1b** cause it to have more ring strain than **1a**.[11a,b]

[24] Auner, N.; Walsh, R.; Westrup, J. *J. Chem. Soc., Chem. Commun.* **1986**, 207. (b) Davidson, I. M. T.; Barton, T. J.; Hughes, K. J.; Ijadi-Maghsoodi, S.; Revis, A.; Paul, G. C. *Organometallics* **1987**, *6*, 644.

[25] Since dynamic electron correlation selectively stabilizes the most delocalized species in eq 4 (i.e., the diradical),[17,21] the reaction in this equation is calculated to be energetically more favorable by CASPT2N calculations than by the R(O)HF/(2/2)CASSCF calculations that were used in ref 11b.

[26] The difference between the values of +10.1 and −0.7 kcal/mol for the hyperconjugative stabilization energies of, respectively, **2c** and **2a** from the reaction in eq 4 is equal to the value of 10.8 kcal/mol that is obtained from the reaction in eq 2 after correcting it for twice the difference between the C−H BDEs of propane and 2,2-disilylpropane from the reaction in eq 3.

[27] Vibrational analyses at the (2/2)CASSCF level, which for a triplet is equivalent to ROHF, revealed two imaginary frequencies for the $^3B_2$ state of **2c**. Minima of C_s and C_2 symmetry, 0.6 kcal/mol lower in energy than the C_{2v} geometry, were found at this level of theory. However, inclusion of dynamic electron correlation resulted in the (2/2)CASPT2N energy of the (0,0) geometry being found to be 0.5 kcal/mol lower than that of either the C_s or C_2 minima; thus, we believe that the lowest triplet state of **2c** really does prefer a C_{2v} geometry. Unfortunately, the two imaginary frequencies found for this geometry at the ROHF level make its zero point vibrational energy artificially low (ΔZPE = −6.7 kcal/mol). Therefore, we have used the ROHF zero point energy of the C_2 minimum, rather than that of the C_{2v} mountain top, for $^3B_2$ in Table 1.

difference between **2c** and **3c** is 14.4 kcal/mol larger than that between **2a** and **3a**, which provides another measure of the greater stabilization energy of diradical **2c**, compared to diradical **2a**.

The differences between the geometries of **2c** and **3c** also reflect the fact that hyperconjugative stabilization is much greater in the (0,0) geometry (**2c**) of the 2,2-disilyltrimethylene diradical than in the (0,90) geometry (**3c**). Of particular note is the finding that, on rotating C(3) by 90° to form **3c** from **2c**, *both* C−C bond lengths increase significantly, C(1)−C(2) by 0.040 Å and C(2)−C(3) by 0.051 Å. At the same time the C(1)−C(2)−(3) bond angle decreases by 8.6°,[28] and the C−Si bond lengths shorten by 0.004 Å.

In contrast, on going from **2a** to **3a**, the lengths of the C(1)−C(2) and C(2)−C(3) bonds only increase by, respectively, 0.003 and 0.007 Å. In addition, the decrease of 1.3° in the C−C−C bond angle on going from **2a** to **3a** is 7.3° less than the decrease on going from **2c** to **3c**.

Bent's rule[22] predicts that the electropositive silyl groups should result in a smaller C(1)−C(2)−C(3) bond angle in **3c** than in **3a**. The C(1)−C(2)−C(3) bond angle of 111.8° in **3c** is, in fact, 2.2° smaller than that in **3a**. Therefore, the 5.1° *larger* C(1)−C(2)−C(3) bond angle in **2c** than in **2a** cannot be caused by an inductive effect of the silicons. It results instead from a greater antibonding interaction between the p-π AOs on C(1) and C(3) in **2c** than in **2a**.

Potential Surface for Stereomutation of 1c. The much lower energy of the (0,0) geometry (**2c**), relative to that of the (0,90) geometry (**3c**), strongly suggests that coupled methylene rotation should be preferred to rotation of a single methylene group in the stereomutation of **1c**. However, vibrational analyses find that **2c** has all real frequencies and that **3c** has two imaginary frequencies. Therefore, **2c** is an intermediate, not a transition state, on the pathway for stereomutation by coupled methylene rotation in **1c**, and **3c** does not even lie on the pathway for rotation of a single methylene group.

In order to make quantitative predictions about the stereomutation of **1c**, we performed (2/2)CASSCF calculations to locate the transition states for con-, dis-, and monorotation. As noted above, the geometries of these transition states are available as Supporting Information, and the CASSCF and CASPT2N energies that are computed at these geometries are given in Table 1.

There are, in principle, two concerted pathways by which **1c** can open to **2c**. One is the "allowed" conrotatory pathway, which passes over a C_2 transition state whose (10/10)CASPT2N energy is 5.8 kcal/mol above that of **2c**. After inclusion of the corrections for the differences between the zero point energies (ΔZPE) of **1c** and the transition state,[29] a barrier height of 52.6 kcal/mol is predicted for conrotatory ring opening of **1c** to **2c** via a C_2 transition state, whose energy is computed to be 6.4 kcal/mol greater than that of **2c**.

The other possible concerted mode of opening of **1c** to **2c** is disrotation. Because the a_2 NBMO has a much higher electron occupation number than the $2b_1$ NBMO in **2c**, ring opening of **1c** by a disrotatory pathway is "forbidden" by orbital symmetry.[1] In fact, there is apparently no truly disrotatory reaction pathway that connects **1c** to **2c**, because the stationary point found along the lowest energy C_s pathway has two imaginary frequencies, one for disrotation of the methylene groups and the other for a rotation of the CH_2 groups that breaks C_s symmetry. The C_s stationary point is therefore a mountain top on the global potential energy surface, so there must be pathways of lower energy which connect **1c** to two mirror-image transition states that lack this plane of symmetry.

We did, in fact, find a C_1 transition state, which was lower in energy than the C_s disrotatory mountain top by ca. 1 kcal/mol. The geometry of this transition state resembles that of the (0,90) structure (**3c**). Table 1 shows that the (2/2)CASSCF energy of the C_1 transition state is 0.1 kcal/mol lower than that of **3c**, but at the (2/2)CASPT2N level these energies are reversed. Since analytical energy derivatives for CASPT2N wave functions are not available in MOLCAS 3, we cannot say for certain whether **3c**, or a geometry very close to it, is a transition state on the CASPT2N energy surface.

The reaction coordinate at the C_1 transition state on the (2/2)CASSCF energy surface is for rotation of the methylene group that in **3c** has already rotated 90° from its orientation in **1c** and, hence, lies in the plane of the three carbon atoms. Whatever the precise geometry of the transition state that lies in this region of the (2/2)CASPT2N potential energy surface, it too must be the transition state for rotation of just one methylene group.

Table 1 shows that, after the ΔZPE correction, the CASPT2N energy of the transition state for rotation of just one methylene group is 8.5 kcal/mol higher than that of the C_2, conrotatory transition state. Consequently, were **1c**-*trans-2,3-d*$_2$ to be prepared in optically active form and pyrolyzed at 400 °C, racemization, via coupled conrotation of the CHD groups, should be several hundred times faster than epimerization by cleavage of the bond between C(2) and C(3) and rotation of just one CHD group.

However, it is also possible that, upon pyrolysis of **1c**, one of the ring bonds to C(1) might break,[30] and cleavage of a ring bond to C(1) can only result in epimerization. Since the two silyl groups at C(1) should make a ring bond to this carbon intrinsically weaker than the ring bond between C(2) and C(3),[31] epimerization of **1c**-*trans-2,3-d*$_2$ via this pathway might compete with racemization of this cyclopropane by coupled conrotation of C(2) and C(3). Therefore, we searched for a C_1 transition state for methylene rotation upon cleavage of a C−C ring bond to C(1).

After considerable effort, we were able to locate two such C_1 transition states, one for coupled conrotation of a CH_2 and the $C(SiH_3)_2$ group and the other for rotation of just a CH_2 group.[32] As shown in Table 1, at the (10/10)CASSCF level

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[28] Since the hybridization of C(2) should affect the lengths of the bonds to this carbon, the large (8.6°) decrease in the C(1)−C(2)−C(3) bond angle on going from **2c** to **3c** could be responsible, at least in part, for the increase in the lengths of both the C(1)−C(2) and C(2)−C(3) bonds. In fact, on reoptimizing the geometry of **3c** with the C(1)−C(2)−C(3) bond angle constrained to 120.4°, the same bond angle as in **2c**, the C−C bonds in **3c** do both shorten, but only by about 0.005 Å. Therefore, most of the order of magnitude larger increase in both C−C bond lengths on going from **2c** to **3c** must be due to the interaction of the p-π AOs on C(1) and C(3) with the b_1 combination of C−Si bonds at C(2) being highly cooperative in **2c**.

[29] The ΔZPE corrections in Table 1 are based on RHF frequencies for **1c** and (2/2)CASSCF frequencies for all the other stationary points.

[30] Another possible reaction of **1c** on pyrolysis, cleavage of a C−Si bond, is computed to be endothermic by 88.9 kcal/mol at the (10/10)-CASPT2N level, so this process should not compete with any of the reactions that involve breaking C−C bonds in the three-membered ring. Cleavage of a C−Si bond in intermediate **2c** is also computed to be endothermic at the (10/10)CASPT2N level, in this case by 18.6 kcal/mol.

[31] (a) Doncaster, A. M., Walsh, R. *J. Chem. Soc., Faraday Trans. 1* **1976**, *72*, 1212. (b) Walsh, R. *Acc. Chem. Res.* **1981**, *14*, 246. (c) Coolidge, M. B.; Borden, W. T. *J. Am. Chem. Soc*. **1988**, *110*, 2298.

[32] At the (2/2)CASSCF level a (0,0), C_s geometry was found to have two imaginary frequencies and an energy that was only 0.1 kcal/mol higher than either transition state. However, upon inclusion of dynamic electron correlation at the (10/10)CASPT2N level, the energy of the (0,0) geometry was calculated to be 0.8 kcal/mol lower than that of the conrotatory transition state and 1.4 kcal/mol lower than that of the monorotatory transition state.

both of these transition states are computed to have about the same energy as the conrotatory (C_2) transition state leading to **2c**. Although we did not locate the C_1 transition state for disrotation of a CH_2 and the $C(SiH_3)_2$ group, it seems safe to conjecture that the energy of this transition state is not very different from the energies of the two C_1 transition states that we did find for cleaving a ring bond to C(1).

As shown in Table 1, inclusion of dynamic electron correlation at the CASPT2N level has a dramatic effect on the energies of these two transition states for cleavage of a ring bond to C(1), relative to the energy of the transition state for conrotation of C(2) and C(3) to form **2c**. As expected,[17,21] the most highly delocalized transition state is stabilized the most. After correction for ΔZPE, the CASPT2N energy of the transition state for ring opening by conrotation of C(2) and C(3) is computed to be 6−7 kcal/mol below both transition states that involve cleavage of a ring bond to C(1). At 400° a difference in transition-state energies of this size corresponds to about 2 orders of magnitude in rate.

Although stereomutation of **1c** by coupled conrotation of C(2) and C(3) is favored energetically, statistical factors favor single methylene rotation, by cleavage of a ring bond to C(1). Not only are there at least two and probably three different C_1 transition states of nearly the same energy for cleavage of a bond to C(1), but each of these transition states can be formed by cleavage of two equivalent ring bonds.[33] Nevertheless, at 400° the statistical factor that favors cleavage of a ring bond to C(1) and rotation of either C(2) or C(3) should be overwhelmed by the large energetic preference for coupled conrotation of C(2) and C(3). Our calculations lead us to predict that at this temperature racemization of optically active **1c**-*trans-2,3-*d_2 should be at least an order of magnitude faster than its epimerization to the cis isomer.

Conclusions

Our CASPT2N calculations find that the geminal silyl groups in **2c** are even better than geminal fluorines in **2b**[11a,b] at stabilizing the lowest singlet state of the (0,0)-trimethylene diradical. This is evident from the comparison of the energies computed for the isodesmic reaction in eq 4 for $X = SiH_3$ and $X = F$ and from the larger amount of energy by which the singlet is calculated to be the ground state in **2c** than in **2b**.

Unlike **2b**, which is the transition state for disrotatory ring opening of **1b**,[11] **2c** is an intermediate on the potential surface for stereomutation of **1c**, 6.4 kcal/mol lower in energy than the conrotatory transition state that connects **1c** to **2c**. The transition state for conrotation of C(2) and C(3) is calculated to be 8.5 kcal/mol lower in energy than the transition state for cleavage of the C(2)−C(3) bond and rotation of just one of these methylene groups.

The silyl substituents at C(1) of **1c** not only stabilize **2c** and the conrotatory transition state that connects **1c** to this diradical intermediate, they also weaken the ring bonds to C(1). However, the CASPT2N energies of the transition states for cleavage of one of these bonds to C(1) and rotation of a methylene group are all >6 kcal/mol higher than the transition state for coupled conrotation of C(2) and C(3). Therefore, we predict that in the pyrolysis of optically active **1c**-*trans-2,3-*d_2 the rate of racemization should be found to be at least an order of magnitude faster than the rate of epimerization.

There would be both synthetic and analytical advantages to using substituents, other than deuteria, as stereochemical markers in **1c**. Moreover, with the proper choice of substituents at C(2) and C(3), it should be possible to distinguish between con- and disrotation by comparing the rates of racemization of the optically active cis and trans isomers of a derivative of **1c**.[12] Finally, an experimental test of the prediction that the ground state of **2c** is a singlet is likely to require a cyclic derivative of this diradical.[13] Therefore, investigation of substituent effects on both the stereomutation of **1c** and the singlet−triplet splitting in **2c** would seem to be a worthwhile focus for future calculations and subsequent experiments.[34]

Acknowledgment. We thank the National Science Foundation for support of this research and Professor Barry Carpenter for helpful discussions. A.S. thanks the Norwegian Research Council for the financial support that made her stay at the University of Washington possible.

Supporting Information Available: Optimized geometries for all the species whose energies are given in Table 1 (10 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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[33] In transition-state theory the symmetry numbers of $\sigma = 2$ for the C_2 transition state for conrotation of C(2) and C(3) and $\sigma = 1$ for each of the three C_1 transition states for single methylene rotation by cleavage of a ring bond to C(1) account correctly for the fact that the latter three transition states can each be accessed by cleavage of one of two equivalent bonds. However, simply counting the number of distinct transition states for cleavage of a ring bond to C(1) is probably, at best, only qualitatively correct in predicting the effect on the rate of this reaction of the very flat potential surface for $C(SiH_3)_2$ rotation in the diradical formed by rotation of a methylene group in **1c**. On such a potential surface, dynamical effects are likely to be important, so the predictions made by transition-state theory are likely to be quantitatively incorrect.[7]

[34] Experiments would not be performed with silyl groups at C(1) but would, instead, probably employ trimethylsilyl substituents at this carbon. The electronic effects of SiH_3 and $Si(CH_3)_3$ groups should be at least qualitatively similar, but steric interactions between bulky trimethylsilyl groups at C(1) and substituents at C(2) and C(3) could be significant and thus might have an effect on the ratio of coupled to single rotation of the latter two carbons.