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# Articles

## Computational Explorations of Vinylcyclopropane−Cyclopentene Rearrangements and Competing Diradical Stereoisomerizations

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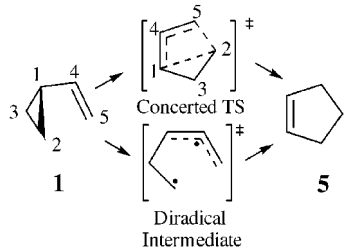
The rearrangements and stereoisomerizations of four systems, vinylcyclopropane, 4-*tert*-butylvinylcyclopropane, 5-methylvinylcyclopropane, and 2,5-dimethylvinylcyclopropane, as well as a variety of deuterated derivatives and 1- and 2-methyl-, methoxy-, difluoro-, and amino-substituted species, were studied by density functional theory calculations using the B3LYP functional and the 6-31G* basis set. Energies were evaluated with CASSCF(4,4)/6-31G* single point calculations. The major product is obtained by the *si* pathway. Structures on this path are essentially pure diradical in character. Higher energy diradical species and intermediates are responsible for the scrambling of the stereochemistry. The stereoselectivity of the reaction is increased by substituents which increase the relative energy of the species involved in competing stereoselectivities. The computed secondary kinetic isotope effects reproduce the experimental values reported in the literature.

### Introduction

The rearrangement of vinylcyclopropane to cyclopentene (Scheme 1) was discovered by Neureiter and Vogel independently in 1959.[1] Since then it has been widely applied in organic synthesis.[2] The reaction is an example of mechanistically ambiguous hydrocarbon rearrangements thought to involve diradical intermediates, but with characteristics of concerted reactions.[3,4] For example, other 1,3-shifts and 1,5-shifts exhibit a multiplicity of products, but a stereoselectivity which is incompatible with fully equilibrated diradical intermediates. The origin of stereoselectivity in such reactions has been the focus of attention of several generations of mecha-

**Scheme 1. The Vinylcyclopropane−Cyclopentene Rearrangement with the Potential Concerted Transition State and Diradical Intermediate**

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(1) Neureiter, N. P. *J. Org. Chem.* **1959**, *24*, 2044; Vogel, E. *Angew. Chem.* **1960**, *72*, 4−26. See footnote 162.

(2) For a recent review: (a) Baldwin, J. E. *J. Comput. Chem.* **1998**, *19*, 222. Other examples include: (b) Klärner, F.-G.; Yaslak, S.; Wette, M. *Chem. Ber.* **1979**, *112*, 1168. (c) Saicic, R. N.; Matovic, R.; Cekovic, Z. *Gazz. Chim. Ital.* **1991**, 121. (d) Feldman, K. S.; Berven, H. M.; Romanelli, A. L. *J. Org. Chem.* **1993**, *58*, 6851. (e) Hudlický, T.; Kutchan, T. M.; Naqvi, S. M. *Org. React. (N.Y.)* **1985**, *33*, 247.

(3) Carpenter, B. K. *J. Am. Chem. Soc.* **1996**, *118*, 10329, and references therein.

(4) Klärner, F.-G. *Topics Stereochem.* **1984**, *15*, 1, and references therein.

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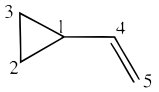
**Table 1. Product Distribution of the Vinylcyclopropane Rearrangement**

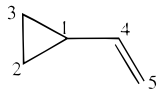


| system | product distribution *si* | *ar* | *sr* | *ai* | refs |
|---|---|---|---|---|---|
| 2,3,5-$d_3$ | 40 | 13 | 23 | 24 | 7 |
| 2-*d*, 5-Me | 55 | 15 | 18 | 13 | 9c |
| 2-Me, 5-Me | 65 | 8 | 22 | 5 | 9d−f |
| 2-Ph, 5-Me | 44 | 20 | 25 | 11 | 9b |
| 2-Me, 5-Ph | 60 | 10 | 19 | 11 | 9g |
| 2-Ph, 5-Ph | 67 | 12 | 17 | 4 | 9h−i |
| 2,3-$d_2$, 4-*tert*-but | >90 | | | | 17a |
| 2-Me, 4-*tert*-but, 5-*d* | 86 (*trans*) | | 14 (*syn*) | | 17b |

nistic chemists. Hoffmann's *twixtyl*[5] and Doering's *continuous diradical*[6] are concepts which suggest species characterized by flat potential surfaces and unselective rotations about single bonds. Carpenter recently proposed *dynamic matching* to explain how selectivity can be induced by inertial effects.[3]

The vinylcyclopropane rearrangement exhibits characteristics of both stepwise and concerted mechanisms. A stepwise mechanism involving diradical intermediates is suggested by the formation of all four possible stereoisomeric products. Deuterium labeling experiments reveal that the *si*:*ar*:*sr*:*ai* product ratio is 40:13:23:24 in the unsubstituted case.[7] The *si* and *ar* products are Woodward−Hoffmann allowed, while the *sr* and *ai* are Woodward−Hoffmann forbidden.[8] Substitution at the 2 and 5 positions, either by a methyl or a phenyl group, changes this ratio, in favor of the *si* product (Table 1).[9] Cyclic derivatives give similar results.[9j,k] Further evidence for a diradical process is the measured activation energy of 51.7 ± 0.5 kcal/mol for the rearrangement of the unsubstituted vinylcyclopropane.[10] This value corresponds to the estimated energy to form the diradical intermediate in Scheme 1.[11] The parent reaction has nearly random stereochemistry, but a concerted mechanism—competing with minor stepwise pathway—is consistent with the Woodward−Hoffmann allowed stereochemistry when the vinyl group is substituted by a *tert*-butyl group at C4. In addition, the large normal secondary kinetic isotope effects indicate that the vinyl terminus is involved in the rate-determining step (Table 2), suggesting a concerted mechanism,[12,13] although a vinyl to allyl radical transformation might also account for this. Density functional theory (DFT) calculations, reported in a preliminary account of this work, showed that the rearrangement is energetically concerted, although its transition structure is essentially a pure diradical, and many other diradical species are only slightly higher in energy.[14] This was also confirmed by a CASSCF study.[15]

**Table 2. Secondary Kinetic Deuterium Isotope Effects. The Computed Values Were Obtained with the UB3LYP/6-31G* Transition Structures, 2 and 2-*t*-But**



| substituents | experimental *T*/(°C) | $k_H/k_D$ | computed $k_H/k_D$ unsubst | *tert*-Bu |
|---|---|---|---|---|
| 2-$d_2$ | 338 | 1.14 ± 0.02[a] | 1.16 | |
| *tert*-Bu 2-*d*,3-*d* | 312 | 1.14 ± 0.02[b] | | 1.12 |
| 5-cis-*d* | 341 | 1.08 ± 0.05[c] | 1.08 | |
| 5-trans-*d* | 341 | 1.15 ± 0.03[c] | 1.09 | |
| 5-$d_2$ | 338 | 1.17 ± 0.02[a] | 1.17 | |
| | 341 | 1.21 ± 0.03[c] | 1.17 | |
| *tert*-Bu 5-$d_2$ | 280 | 1.17 ± 0.02[d] | | 1.17 |

[a] Reference 13. [b] Reference 17a. [c] Reference 12. [d] Reference 17b.

Experimental studies of the rearrangement have been complicated by the fact that stereoisomerization of the cyclopropane moiety competes with the rearrangement. Depending on the substitution pattern, the barrier to this stereoisomerization is 2.6−3.4 kcal/mol lower than that to rearrangement.[7,9a,b,16,17] This is true even in systems with bulky substituents, such as a *tert*-butyl group on C4.

We report the results of computations on the rearrangement and stereoisomerization of the parent vinylcyclopropane and of three substituted systems using CASSCF and DFT calculations of the potential energy surface and isotope effects. We have found that (1) the major pathway is energetically concerted in all four cases, although it involves a diradical transition state, (2) electronic factors control motions of diradicals and influence stereoselectivity, (3) stereochemical scrambling involves species which stray from the concerted pathway, but all species eventually pass through the same transition state leading to the products, and (4) substituents can induce stereoselectivity by preventing deviations from the concerted pathway. In addition, we studied substituent effects on the reactant and transition structure of the rearrangement. This allowed dissection of substituent effects into stabilization of the reactant (vinylcyclopropane) and stabilization of the radical site in the transition structure.

(5) Hoffmann, R.; Swaminathan, S.; Odell, B. G.; Gleiter, R. *J. Am. Chem. Soc.* **1970**, *92*, 7091.
(6) Doering, W. v. E.; Sachdev, K. *J. Am. Chem. Soc.* **1974**, *96*, 1168.
(7) Baldwin, J. E.; Villarica, K. A.; Freedberg, D. I.; Anet, F. A. L. *J. Am. Chem. Soc.* **1994**, *116*, 10845.
(8) The letters *s* and *a* stand for suprafacial and *a*ntarafacial on the allyl fragment C1−C5, while *i* and *r* refer to *i*nversion and *r*etention of the geometry.
(9) (a) Baldwin, J. E.; Bonacorsi, S., Jr. *J. Am. Chem. Soc.* **1996**, *118*, 8258. (b) Baldwin, J. E.; Bonacorsi, S., Jr. *J. Org. Chem.* **1994**, *59*, 7401. (c) Baldwin, J. E.; Ghatlia, N. D. *J. Am. Chem. Soc.* **1991**, *113*, 6273. (d) Schmidt, T. Ph.D. Dissertation, University of the Ruhr, Bochum, 1972. (e) Andrews, G. D.; Baldwin, J. E. *J. Am. Chem. Soc.* **1976**, *98*, 6705. (f) Mazzocchi, P. H.; Tamburin, H. J. *J. Am. Chem. Soc.* **1970**, *92*, 7220. (g) Baldwin, J. E.; Bonacorsi, S., Jr. *J. Am. Chem. Soc.* **1993**, *115*, 10621. (h) Asuncion, L. A.; Baldwin, J. E. *J. Org. Chem.* **1995**, *60*, 5778. (i) Asuncion, L. A.; Baldwin, J. E. *J. Am. Chem. Soc.* **1995**, *117*, 10672. (j) Baldwin, J. E.; Bonacorsi, S. J.; Burrell, R. C. *J. Org. Chem.* **1998**, *63*, 4721. (k) Baldwin, J. E.; Burrell, R. C. *J. Org. Chem.* **1999**, *64*, 3567.
(10) Lewis, D. K.; Charney, D. J.; Kalra, B. L.; Plate, A.-M.; Woodard, M. H.; Cianciosi, S. J.; Baldwin, J. E. *J. Chem. Phys. A* **1997**, *101*, 4097.
(11) The energy barrier for cyclopropane stereomutation is 60.5 kcal/mol: (a) Setzer, D. W.; Rabinovitch, B. S. *J. Am. Chem. Soc.* **1964**, *86*, 564. (b) Rabinovitch, B. S.; Schlag, E. W.; Wiberg, K. B. *J. Chem. Phys.* **1958**, *28*, 504. The stabilization by an allyl radical is 12.6 kcal/mol: (c) Benson, S. W.; Bose, A. N.; Nangia, P. *J. Am. Chem. Soc.* **1963**, *85*, 1388.
(12) Baldwin, J. E.; Villarica, K. A. *Tetrahedron Lett.* **1994**, 7905.
(13) Chickos, J. *Abstracts of Papers*, 187th National Meeting of the American Chemical Society, St. Louis, MO, April 8−13, 1984; American Chemical Society: Washington, DC, 1984; ORGN 228.
(14) Houk, K. N.; Nendel, M.; Wiest, O.; Storer, J. W. *J. Am. Chem. Soc.* **1997**, *119*, 10545.
(15) Davidson, E. R.; Gajewski, J. J. *J. Am. Chem. Soc.* **1997**, *119*, 10543.
(16) Gajewski, J. J. *Hydrocarbons Thermal Isomerizations*; Academic: New York, 1980; pp 81−87, and references therein.
(17) (a) Gajewski, J. J.; Olson, L. P.; Willcott, M. R., III. *J. Am. Chem. Soc.* **1996**, *118*, 299. (b) Gajewski, J. J.; Squicciarini, M. P. *J. Am. Chem. Soc.* **1989**, *111*, 6717.

Geometry optimizations using UB3LYP/6-31G* calculations were followed by CASSCF(4,4)/6-31G* single point calculations. MRCI calculations on the unsubstituted system and dynamics calculations based on the MRCI energies and B3LYP structures give good agreement with the experiment.[18]

## Computational Methodology

Calculations were carried out using GAUSSIAN94.[19] Geometries were optimized by density functional calculations using the (U)B3LYP functional and the 6-31G* basis set. Reactants and products were computed with closed-shell wave functions, while open-shell wave functions were used for all other structures.[20] The DFT energies were corrected for unscaled zero point energies; they are labeled $E_1$. Energies were further evaluated by CASSCF(4,4)/6-31G* single point calculations on the DFT geometries; these are not corrected for the zero point energy and they are labeled $E_2$. CASSCF(4,4)/6-31G*//(U)B3LYP/6-31G* energies which are corrected by the (U)B3LYP zero point energy are labeled $E_{2,ZPE}$.

Although the use of spin annihilation with DFT has met with mixed reviews,[21] a spin correction procedure as shown in eq 1−3, developed by Yamaguchi et al.,[22] was used to correct the open-shell singlet DFT energies. These energies are labeled $E_{SC}$.

$$\Psi_U = c_s^1\Phi + c_T^3\Phi \quad (1)$$

$$E_{SC} = {}^1E_{UB} + f_{SC}[{}^1E_{UB} - {}^3E_{UB}] \quad (2)$$

$$f_{SC} = \frac{{}^1\langle S^2\rangle}{{}^3\langle S^2\rangle - {}^1\langle S^2\rangle} \quad (3)$$

$E_{SC}$ is the spin corrected energy of the singlet, ${}^1E_{UB}$ is the energy of the spin-contaminated UB3LYP singlet wave function of the optimized structure, and ${}^3E_{UB}$ is the energy of the triplet at the same geometry, and $f_{SC}$ is the fraction of triplet state mixed into the pure singlet state to give the spin contaminated wave function $\Psi_u$.

In the general discussion we will mostly refer to the $E_2$ energies, since they proved to be closest to the relative energies expected by the experiments. The DFT energies will be discussed in detail in a separate section. The isodesmic reactions used in the study of substituent effects were solely computed by (U)B3LYP/6-31G*.

Kinetic isotope effects (KIE) were calculated using the Bigeleisen equation,[23] implemented in the program QUIVER.[24]

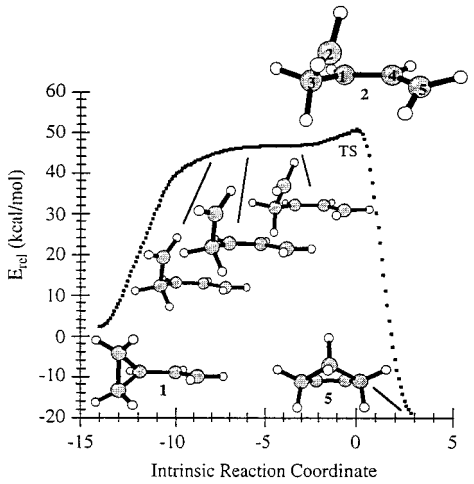



**Figure 1.** UB3LYP/6-31G* IRC of the *si* transition structure of the rearrangement (179 points in total). $E_{rel}$ is relative to *s-trans* vinylcyclopropane and is not corrected by zero point energies. The distances in **2** are C1−C2 = 2.489 Å, C2−C5 = 2.681 Å, C1−C4 = 1.369 Å, and C4−C5 = 1.413 Å.

The DFT force constants were scaled by 0.963 in these computations.[25]

## Results and Discussion

**The Rearrangement of the Parent System.** Only one transition structure for the rearrangement was found: that for the concerted *si* sigmatropic shift, **2** (Figure 1).[15] The transition structure has a considerable diradical character, the $\langle S^2\rangle$ value is 0.85 with UB3LYP. An intrinsic reaction coordinate (IRC) was mapped (Figure 1). It connects the reactant with the product without involving any intermediate. The reaction path involves breaking of the C1−C2 bond with partial rotation about the C1−C3 bond. A broad flat plateau leads to the diradical transition state, **2**, 46.9 kcal/mol ($E_1$) above *s-trans* vinylcyclopropane[26] and about 2.5 kcal/mol ($E_2$) above the plateau. The C1−C4 and C4−C5 bond lengths of **2** are almost equal, as expected for an allyl radical, and the C1−C2 and C2−C5 distances (2.489 and 2.681 Å) are too long for significant bonding.

The major pathway passes through **2**, and provides the *si* product. Figure 2 is a plot of the IRC as a function of the breaking C1−C2 and forming C2−C5 bond lengths. By extensive systematic variations of the C1−2 and C2−C5 bond lengths, it was possible to locate only two additional transition structures on the UB3LYP surface. In terms of their C1−C2 and C2−C5 bonds, they are both close to the main reaction IRC, so that they can be reached by motions deviating from the minimal energy pathway. Both structures can lead to the loss of stereoselectivity. The *cis* $C_s$ (0, 0) structure, **3**, lies 1.6 (1.1) kcal/mol ($E_2$ ($E_{2,ZPE}$)) above the *si* transition structure of the rearrangement.[27a] A return from **3** to the concerted path produces either of the four possible products. A second structure, *cis* $C_s$ (0, 90), **4**, with the terminal $CH_2$ rotated almost 90°, lies 0.3 (−0.1) kcal/mol ($E_2$ ($E_{2,ZPE}$)) above the

(18) Doubleday, C., Jr.; Nendel, M.; Houk, K. N.; Thweatt, D.; Page, M. *J. Am. Chem. Soc.* **1999**, *121*, 4720.

(19) Gaussian 94 (Revision B.1), Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T. A.; Peterson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, 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.; Pople, J. A., Gaussian, Inc., Pittsburgh, PA, 1995.

(20) Transition structures initially obtained by a closed-shell wave function, proved to be UHF unstable. Upon release of the spin restriction constraint, they collapsed to the UB3LYP geometries.

(21) Spin correction does not properly reproduce the correct shape for the potential energy curve of bond dissociations: (a) Wittbrodt, J. M.; Schlegel, H. B. *J. Chem. Phys.* **1996**, *105*, 6577. (b) Goldstein, E.; Beno, B.; Houk, K. N. *J. Am. Chem. Soc.* **1996**, *117*, 6036. The procedure has been used successfully for computations of singlet−triplet gaps: (c) Cramer, C. J.; Dulles, F. J.; Giessen, D. J.; Almlöf, J. *Chem. Phys. Lett.* **1995**, *245*, 165.

(22) (a) Yamaguchi, K.; Jensen, F.; Dorigo, A.; Houk, K. N. *Chem. Phys. Lett.* **1988**, *149*, 537. (b) Yamakami, S.; Kawakami, T.; Nagao, H.; Yamaguchi, K. *Chem. Phys. Lett.* **1994**, *231*, 25.

(23) Bigeleisen, J.; Maier, M. G. *J. Chem. Phys.* **1947**, *15*, 261.

(24) Saunders, M.; Laidig, K. E.; Wolfsberg, M. *J. Am. Chem. Soc.* **1989**, *111*, 8989.

(25) Rauhut, G.; Pulay, P. *J. Phys. Chem.* **1995**, *99*, 3093.

(26) In the unsubstituted case, the *s-trans* conformer is 1.7 kcal/mol below the gauche conformer using B3LYP/6-31G*. The gauche conformer is more stable by 4.8 kcal/mol in the case of 4-*tert*-butylvinylcyclopropane and the barrier is relative to the gauche conformer in this case.

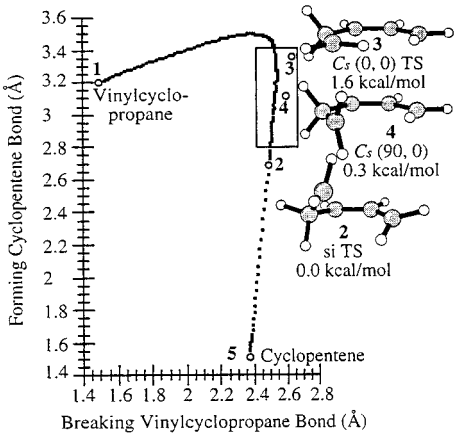



**Figure 2.** IRC of the concerted *si* shift, plotted as a function of forming cyclopentene and breaking vinylcyclopropane C−C bond lengths (in Å). Structure **2** is the transition state for the *si* shift and **3** and **4** are higher energy transition structures involved in *ar* (**3**), *sr* (**4**), and *ai* (**3** + **4**) pathways.

*si* transition structure, and returns to the concerted path to yield all four products as well.[18] Due to the flatness of the surface, the IRC mapping was unsuccessful for **3** and **4**, but the imaginary mode characterizes both as transition structures for the C2−$H_2$ rotation.

The rotation about the terminal C2−$H_2$ unit, leading to the *ai* product, could also occur readily in the plateau region of the *si* IRC. This motion requires only about 0.8 kcal/mol,[28] and dynamic effects are thus likely to play a significant role in the preference for the *si* pathway.[18] The surface shows similarities to that of the cyclopropane isomerization, insofar as the molecule can adopt a number of stationary points without a significant change in energy.[27a] The free energy surface in this plateau region is likely to contain a local minimum because of the favorable entropy in this region of the potential energy surface.

The preference for the *si* product is also observed in the [1,3] sigmatropic shift of norbornene where the experimentally observed product mixture can be explained by diradical structures close to (but not located on) the lowest energy pathway of the reaction.[29] Thus the preference for *si* products of 1,3-shifts involving diradical structures on the potential energy surface is a general phenomenon.

The vinylcyclopropane−cyclopentene rearrangement has been studied independently by Davidson and Gajewski using CASSCF(4/4)/6-31G* calculations.[15] Although both studies agree in that there is no intermediate on the reaction pathway, there are notable differences in the hypersurfaces. The reaction pathway obtained by UB3LYP/6-31G* shows only one transition structure, **2**, which is reached through a very flat plateau. The CASSCF(4,4)/6-31G* **TS13** is equivalent to our transition

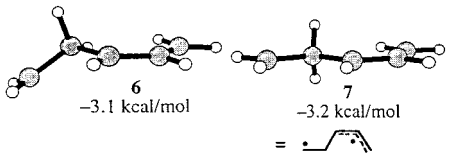



**Figure 3.** Transition structures **6** and **7** for the stereoisomerization of gauche vinylcyclopropane. The energies are relative to **2** ($E_2$, kcal/mol).

structure of rearrangement, **2**, and it reproduces the experimental secondary kinetic isotope effects. **TSG** is the transition structure for stereoisomerization at C2, and a *nonminimum* energy path can be found which connects **TSG** to **TS13** without involving a minimum.[30] The UB3LYP/6-31G* calculations provide no stationary point analogous to **TSG**. However, there are structures on the stereoisomerization path of our **7** which have H−C2−C3−C1 dihedral angles similar to that of **TSG**, indicating that **TSG** is a transition structure on the minimum energy path from vinylcyclopropane to our **3**. The third CASSCF(4,4)/6-31G* transition structure, **TS-cs**, corresponds to our **4**. It is the transition structure for stereoisomerization at C2, and it is responsible for passage from *s* to *a* stereochemistry. At the CASSCF level, it is 0.3 kcal/mol higher in energy than **TS13**, this is similar to the difference between **2** and **4** (0.3 $E_2$, −0.1 $E_{2,ZPE}$).

The CASSCF calculations predict an isomerization at C2 at the stage of **TSG**, which is 2.9 kcal/mol lower in energy than the transition structure for rearrangement, and 3.2 kcal/mol lower than **TS-cs**. These results predict an equal distribution of the four possible isomers, potentially with small deviations due to dynamical effects. According to the B3LYP calculations, the minor isomers *ai*, *ar*, and *sr* are formed through the structures **3** and **4**, which are themselves not part of the reaction pathway. Any isomerization product needs therefore to return to the main reaction pathway before conversion to the product occurs.

Single point MRCI calculations on the fully optimized CASSCF(4,4) structures have been performed using the 6-31G* and cc-pVDZ basis sets.[18] These energies agree in general well with the fully optimized CASSCF(4,4)/6-31G* and the CASSCF(4,4)/6-31G*//(U)B3LYP/6-31G* energies, although there are some differences: for example, the energy of **4** is 0.9 kcal/mol above that of the transition state of rearrangement, **2** (compared to 0.2 and 0.3 for the other methods). There is also a basis set dependence on this level, accounting for differences in the relative energies up to 1 kcal/mol. The MRCI calculations also reproduce the experimental barrier of the rearrangement more closely than the (U)B3LYP and CASSCF calculations. Doubleday et al. parametrized the AM1 potential to closely reproduce the energies obtained from the MRCI calculations and to reproduce the UB3LYP IRC. Quasiclassical trajectory calculations starting from the saddle points found in our work (**2**, **3**, and **4**) gave predictions of the stereochemistry in close agreement with experiment.[18]

**The Stereoisomerization of the Parent System.** The rearrangement competes with the stereoisomeriza-

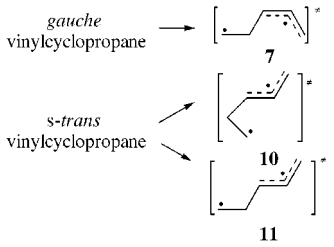
(27) The (0,0) notation corresponds to that reported in (a) Getty, S. J.; Davidson, E. R.; Borden, W. T. *J. Am. Chem. Soc.* **1992**, *114*, 2085. Other recent reports about the cyclopropane isomerization are found in (b) Baldwin, J. E.; Yamaguchi, Y.; Schaefer, H. F., III. *J. Phys. Chem.* **1994**, *98*, 7513. (c) Yamaguchi, Y.; Schaefer, H. F., III.; Baldwin, J. E. *Chem. Phys. Lett.* **1994**, *185*, 143. (d) Doubleday, C., Jr. *J. Phys. Chem.* **1996**, *100*, 3520.

(28) This barrier was computed by single point calculations on a structure at a reaction coordinate of −5.3. This structure has the same forming bond length as **4**.

(29) Beno, B. R.; Wilsey, S.; Houk, K. N. *J. Am. Chem. Soc.* **1999**, *121*, 4816.

(30) However, a real frequency in **TSG** becomes negative along the reaction coordinate for the [1,3]-methyl shift, and it connects **TSG** to the second transition structure, **TS13**, without involving another minimum.

**Scheme 2. Types of Transition Structures Possible for the Stereoisomerization of Vinylcyclopropane.**




tion of vinylcyclopropane in all compounds studied experimentally. Four stereoisomerization pathways are possible, depending on the conformation of the reacting vinylcyclopropane and the direction of rotation of the terminal $CH_2$ group during the bond breaking. One of them is the closure of the cyclopropane bond of **3**. Three other pathways are involved in the stereoisomerization (Scheme 2); these do not lead to rearrangement. The three pathways are all diradical in nature but have different numbers of transition structures and intermediates located on them. Structures **10** and **11** can only rearrange by rotation about the Cl−C4 bond of the allyl radical moiety with a barrier of about 15 kcal/mol.[31]

If the terminal methylene unit C2−$H_2$ of gauche vinylcyclopropane rotates in the direction opposite to that required to form **3** and gives **7** instead, only stereoisomerization will occur. There are two transition structures related to **7** (Figure 3). Structure **6**, obtained directly from vinylcyclopropane, is located 3.1 (3.7) kcal/mol ($E_2$ ($E_{2,ZPE}$)) below the transition structure for the rearrangement, **2**. The conformation about the C2−C3 bond resembles that of **2**; the main distinction between the two structures is the dihedral angle about the C1−C3 bond (the dihedral angle about this bond is 138° for **6** and 40° for **2**). The H−C2−C3−C1 dihedral angles are very similar to those of Gajewski's and Davidson's structure **TSG**: 35° and −153° compared to 38° and −167°, further indicating that their **TSG** is part of the stereoisomerization surface of our **3**. The second transition structure, **7**, is $C_s$ symmetric. It is 3.2 (4.0) kcal/mol ($E_2$ ($E_{2,ZPE}$)) lower in energy than **2**, and it corresponds to the $C_s$ *cis* (0, 0) structure, **3**.[32]

Two pathways for stereoisomerization are open to *s-trans* vinylcyclopropane, differing in the dihedral angle about C3−C1: one is *trans* and the other *cis* (Scheme 2). The first path contains two transition structures and one minimum on the UB3LYP/6-31G* level (Figure 4). However, CASSCF(4,4) single point calculations increase the energy of the intermediate relative to the transition structures (independently of inclusion of the zero point energy), and the local minimum found by DFT disappears with CASSCF. Therefore the intermediate might be an artifact of the DFT calculations. The first DFT transition structure on this path, **8**, is located 4.3 (4.8) kcal/mol ($E_2$ ($E_{2,ZPE}$)) below the transition structure for the rearrangement, **2**. IRC mapping links **8** to a local minimum, **9**, 0.2 kcal/mol below **8** ($E_1$, 0.3 (0.4) kcal/mol *above* **8** by $E_2$ ($E_{2,ZPE}$)). This intermediate is also connected to the *trans* $C_s$ (0, 0) transition structure, **10**, 2.7 (3.4) kcal/mol ($E_2$ ($E_{2,ZPE}$)) below **2**.

(31) Computed by UB3LYP/6-31G* single point calculations.

(32) Due to the flatness of the potential energy surface, no intermediate could be located, and the IRC mapping failed.

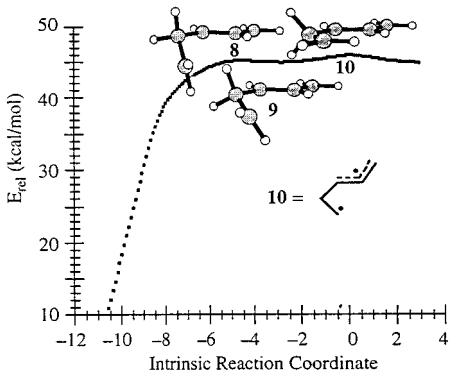



**Figure 4.** UB3LYP/6-31G* IRC of a stereoisomerization path of *s-trans* vinylcyclopropane. $E_{rel}$ is relative to *s-trans* vinylcyclopropane and is not corrected by zero point energies. **8** and **10** are transition structures, **9** is an intermediate.

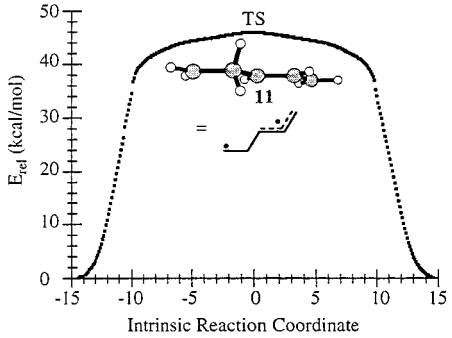



**Figure 5.** UB3LYP/6-31G* IRC of the second stereoisomerization path of *s-trans* vinylcyclopropane. $E_{rel}$ is relative to *s-trans* vinylcyclopropane and is not corrected by zero point energies. **11** is a transition structure.

Only one transition structure was located on the second *s-trans* stereoisomerization pathway (Scheme 2 and Figure 5). The $C_s$ symmetric **11**, is located 3.5 (4.4) kcal/mol below **2** ($E_2$ ($E_{2,ZPE}$)). This is the lowest energy path of stereoisomerization. An IRC connects **11** directly to *s-trans* vinylcyclopropane without involving any intermediates (Figure 5). The experimentally measured energy difference between rearrangement and stereoisomerization is about 2.7−3.4 kcal/mol. This is reproduced by $E_2$ and is 4.4−3.4 kcal/mol by $E_{2,ZPE}$ (= CASSCF(4,4)/6-31G*//(U)B3LYP/6-31G* + (U)B3LYP/6-31G* ZPE)). All three barriers of stereoisomerization are close in energy, ranging from 2.7 to 3.4 kcal/mol below the barrier of rearrangement.[33]

**The Rearrangement of 4-*tert*-Butylvinylcyclopropane.** The rearrangement of 4-*tert*-butylvinylcyclopropane is stereospecific.[17] The relative yield of the *si* product is above 90%, although the experimental SKIEs are close to those of the unsubstituted compound implying a transition structure closely resembling that of the parent reaction (Table 2). According to our B3LYP calculations (Table 3), the reactant (**1-*t*-Bu**) rearranges via the transition structure, **2-*t*-Bu** (Figure 6). As expected by the SKIEs, **2-*t*-Bu** is similar to the parent transition structure **2**; these are superimposed in Figure 9. The

(33) The structure corresponding to the $C_s$ transition structures is a secondary stationary point in the case of the stereoisomerization of cyclopropane. In the case of vinylcyclopropane, the stereoisomerization is monorotatory due to increased inertia of the vinyl-substituted carbon compared to the methylene group. No other pathways were found on the UB3LYP/6-31G* surface.

**Table 3. The Relative Energies of the Transition Structures Involved in the Rearrangement and Stereoisomerization of Vinylcyclopropane, 4-*tert*-Butylvinylcyclopropane, 5-Methylvinylcyclopropane, and 2,5-Dimethylvinylcyclopropane. $E_1$ Is the (U)B3LYP/6-31G* Energy, $E_{SC}$ Is the Spin-Corrected (U)B3LYP/6-31G* Energy and $E_2$ Is the CASSCF(4,4)/6-31G*// (U)B3LYP/6-31G* Energy. All Energies Are in kcal/mol, and—except for $E_2$—They Are Corrected by the Zero Point Energy**

| | parent | | | | 4-*tert*-butyl | | | | 5-methyl | | | | 2,5-dimethyl | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $E_1$ | $E_{SC}$ | $E_2$ | $E_2$+ZPE | $E_1$ | $E_{SC}$ | $E_2$ | $E_2$+ZPE | $E_1$ | $E_{SC}$ | $E_2$ | $E_2$+ZPE | $E_1$ | $E_{SC}$ | $E_2$ | $E_2$+ZPE |
| Structures Involved in the Rearrangement | | | | | | | | | | | | | | | | |
| *t* **1** | −46.9 | −42.8 | – | – | −41.2 | −37.2 | – | – | −46.5 | −42.3 | – | – | −44.2[a] | −39.8[a] | – | – |
| *g* **1** | −45.2 | −41.1 | – | – | −45.9 | −42.0 | – | – | −44.9 | −40.7 | – | – | −42.7[a] | −38.3[a] | – | – |
| **5** | −67.7 | −63.6 | – | – | −71.4 | −67.4 | – | – | −64.8 | −60.6 | – | – | −61.2[b] | −56.8[b] | – | – |
| **2** | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| | | | | | | | | | | | | | (0.5)[c] | (0.8)[c] | (0.7)[c] | (0.7)[c] |
| **3** | −1.6 | 1.2 | 1.6 | 1.1 | 0.5 | 2.8 | 4.1 | 3.4 | −1.5 | 1.4 | 1.9 | 1.3 | −0.6 | 3.5 | 2.0 | 1.6 |
| **4** | −2.6 | 2.2 | 0.3 | −0.1 | −0.9 | 4.0 | 2.5 | 2.2 | −2.7 | 2.3 | 0.6 | 0.2 | −1.8 | 3.2 | 1.4 | 1.1 |
| Stereoisomerization of *gauche* Vinylcyclopropane | | | | | | | | | | | | | | | | |
| **6** | −5.0 | −0.4 | −3.1 | −3.7 | | | | | | | | | | | | |
| **7** | −5.4 | −0.9 | −3.2 | −4.0 | −4.7 | −0.3 | −2.6 | −3.4 | −5.5 | −0.9 | −3.1 | −3.9 | −5.0 | −0.2 | −2.5 | −3.3 |
| Stereoisomerization of *s-trans* Vinylcyclopropane | | | | | | | | | | | | | | | | |
| **8** | −5.9 | −2.8 | −4.3 | −4.8 | | | | | | | | | | | | |
| **9** | −6.1 | −3.3 | −4.0 | −4.4 | | | | | | | | | | | | |
| **10** | −5.4 | −1.5 | −2.6 | −3.4 | 5.5 | 8.3 | 9.8 | 9.5 | −5.5 | −1.4 | −2.6 | −3.3 | −5.5 | −1.0 | −3.4 | −3.6 |
| **11** | −5.9 | −1.7 | −3.5 | −4.4 | −0.8 | 3.4 | 2.3 | 1.5 | −5.9 | 1.5 | −3.3 | −4.3 | −5.2 | −0.4 | −3.0 | −3.8 |

[a] Lowest energy conformer. [b] This is the lowest energy conformation: (3*R*,4*S*)-3,4-dimethylcyclopentene. (3*S*,4*R*)-3,4-dimethylcyclopentene is 0.7 kcal/mol higher in energy, and (3*S*,4*R*)-3,4-dimethylcyclopentene is 2.3 kcal/mol higher in energy. [c] Relative energy of **12**.

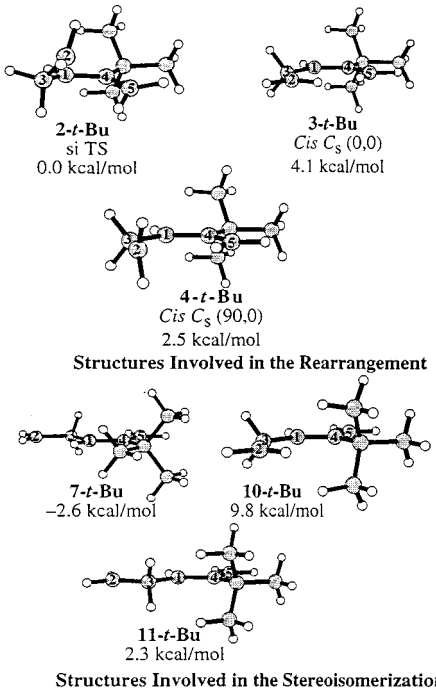



**Figure 6.** Structures involved in the rearrangement and stereoisomerization of 4-*tert*-butylvinylcyclopropane. The relative energies with respect to *2-t-Bu* are in kcal/mol ($E_2$).

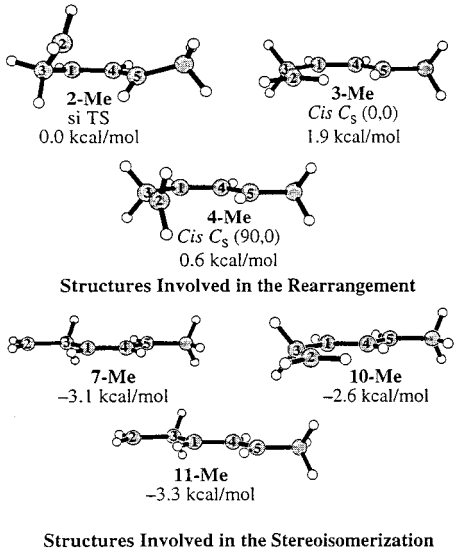



**Figure 7.** Structures involved in the rearrangement and stereoisomerization of 5-methylvinylcyclopropane. The relative energies with respect to *2*-Me are in kcal/mol ($E_2$).

activation barrier is 45.9 kcal/mol ($E_1$);[26] compared to 46.9 kcal/mol ($E_1$) in the parent system; the *tert*-butyl group has little influence on the activation energy of the major path. However, the stereochemical scrambling pathways are significantly *destabilized* by this group. Both *cis* $C_s$ structures, **3-*t*-Bu** and **4-*t*-Bu**, are higher in energy than **2-*t*-Bu**: **3-*t*-Bu** and **4-*t*-Bu** are located 4.1 (3.4) and 2.5 (2.2) kcal/mol (both $E_2$ ($E_{2,ZPE}$)) above **2-*t*-Bu** due to the crowding of C1−$H_2$ and C5−$H_2$ by the buttressing effect of the *tert*-butyl group. The C1−C4−C5 angle is decreased by 5° in the case of **2-*t*-Bu**, and by 7° in the case of both, **3-*t*-Bu** and **4-*t*-Bu**. This angle decrease triggers a shortening of the C2−C5 distance while the C1−C2 distance remains unchanged.[34] The absence of stereochemical scrambling in the *tert*-butyl case results from significant destabilization of minor pathways which scramble the stereochemistry. This is consistent with the suggestion by Baldwin[9k] and described in our Communication.[14]

**The Stereoisomerization of 4-*tert*-Butylvinylcyclopropane.** As in the unsubstituted system, the stereoisomerization of 4-*tert*-butylvinylcyclopropane is faster than the rearrangement. The experimental energy difference is about 2.7 kcal/mol.[17a] Because the $C_s$ structures are the maxima along the parent stereoisomerization pathways, only the analogues, **7-*t*-Bu**, **10-*t*-But** and **11-*t*-Bu**, but none of the intermediates nor the other transition structures, were investigated. Only **7-*t*-Bu** is

(34) In the case of **2-*t*-Bu**, **3-*t*-Bu**, and **4-*t*-Bu**, the C2−C5 distances are shortened by 0.01, 0.05, and 0.05 Å, respectively.

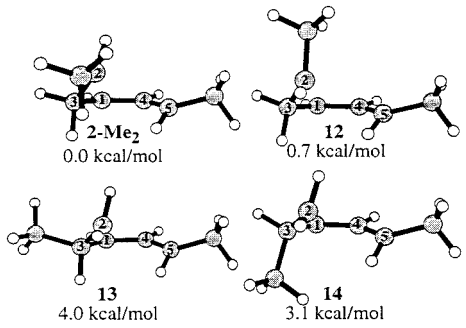



**Figure 8.** Transition structures for the rearrangement of 2,5-dimethylvinylcyclopropane and 3,5-dimethylvinylcyclopropane. **2-Me$_2$** is the lowest energy conformer. The relative energies with respect to *2*-Me-2 are in kcal/mol ($E_2$).

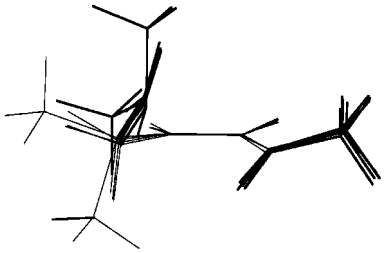


**Figure 9.** Overlay of the structures shown in Figure 8.

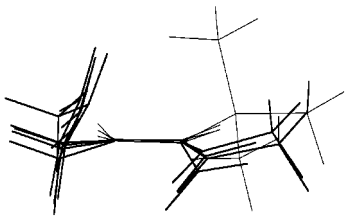


**Figure 10.** Overlay of **2**, **2-*t*-But**, **2-Me**, and **2-Me$_2$**.

a transition structure (Figure 6); it is lower in energy (by 2.6 (3.4) kcal/mol ($E_2$ ($E_{2,ZPE}$))) than the transition structure of the rearrangement, **2-*t*-Bu**. This energy difference is smaller than in the parent case, as found experimentally.[17a]

Both *trans* structures, **10-*t*-Bu** and **11-*t*-Bu**, are higher in energy than **2-*t*-Bu**. Both are second-order saddle points and are located 9.8 (9.5) kcal/mol ($E_2$) and 2.3 (1.5) kcal/mol ($E_2$ ($E_{2,ZPE}$)), respectively, above **2-*t*-Bu**.

**The Rearrangement and Stereoisomerization of 5-Methylvinylcyclopropane.** Experiments show that the reaction of 5-methylvinylcyclopropane is more stereoselective than that of the unsubstituted compound, but much less stereoselective than that of 4-*tert*-butylvinylcyclopropane. The *si*:*ar*:*sr*:*ai* ratio is 55:15:18:13 compared to 40:13:23:24 in the unsubstituted case.[9c] As for the two other systems, only one transition structure for the rearrangement, **2-Me**, was found on the potential energy hypersurface (Figure 7). The barrier of 46.5 kcal/mol[35] is only 0.5 kcal/mol lower than that of the unsubstituted rearrangement. Again, the barrier height, the geometrical features, and the spin contamination are similar to the parent system (Figure 10). The *cis* $C_s$ structures involved in the scrambling of the stereochemistry are destabilized relative to the parent **3** and **4**, although they are relatively more stable than **3-*t*-But** and **4-*t*-But**. Structure **3-Me** is 1.9 (1.3) kcal/mol ($E_2$) above **2-Me**, while **4-Me** is located 0.6 (0.2) kcal/mol ($E_2$ ($E_{2,ZPE}$)) above **2-Me**. This compares to 1.6 (1.1) and 0.3 (−0.1) kcal/mol in the parent case and to 4.1 (3.4) and 2.5 (2.2) kcal/mol in the 4-*tert*-butyl system. Both, **3-Me** and **4-Me** are transition structures for the C2−H$_2$ rotation.

Experimental data for the barrier of the stereoisomerization are not available, but our calculations predict that **7-Me**, **10-Me**, and **11-Me** are 3.1 (3.9), 2.6 (3.3), and 3.3 (4.3) kcal/mol ($E_2$ ($E_{2,ZPE}$)) below the transition structure of the rearrangement, **2-Me**. In all cases, the structures are similar to the corresponding unsubstituted ones, and the methyl group on C5 is *trans* relative to cyclopropyl (Figure 7).

**The Rearrangement and Stereoisomerization of 2,5-Dimethylvinylcyclopropane.** The experimental stereoselectivity of the 2,5-dimethylvinylcyclopropane rearrangement is increased compared to 5-methylvinylcyclopropane (and thus to the unsubstituted vinylcyclopropane), but the reaction is not nearly as stereospecific as that of 4-*tert*-butylvinylcyclopropane. The *si*:*ar*:*sr*:*ai* ratio is 65:8:22:5 compared to 40:13:23:24 in the unsubstituted case[9d−f] and to a relative yield of the *si* product of above 90% in the 4-*tert*-butyl case.[17] Since the cyclopropane moiety is expected to isomerize rapidly, either C2 or C3 can be substituted by the methyl group. There are thus four *si* transition structures (two with the methyl group on C2 and two with the methyl group on C3), while three structures equivalent to the $C_s$ symmetric **3** and two structures equivalent to **4** exist. Because the structure equivalent to **3** in which the methyl group is on the inside of C2 (pointing toward C5) is expected to be highly strained, only two structures are considered for **3**.

The barrier for the *si* rearrangement is 44.2 kcal/mol ($E_1$), 2.7 kcal/mol lower than in the parent case.[36] In the transition structure, **2-Me$_2$**, the methyl group is at C2, and it is *trans* relative to the vinyl group (Figure 8). The isomeric transition structure, **12**, in which the methyl group on C2 is *cis* to the vinyl group is 0.7 (0.7) kcal/mol ($E_2$ ($E_{2,ZPE}$)) higher in energy, while the C3-substituted structures, **13** and **14**, are 4.0 and 3.1 kcal/mol above **2-Me$_2$**. The carbon backbone is similar in all four structures as can be seen in the overlay of these in Figure 9. The energy difference between **12** and **2-Me$_2$** is comparable to that between the *si* transition structure and the structures scrambling the stereochemistry in the parent case. Thus **12** should be accessible to the molecule. Dimethylvinylcyclopropanes can therefore easily rearrange through *trans* or *cis* 2-substituted transition structures.

As expected by the observed higher stereoselectivity (65% of the *si* product in the product mixture compared to 40% in the unsubstituted and 55% in the 5-methyl case), the analogues to the *cis* $C_s$ (0, 0) and *cis* $C_s$ (0, 90) structures are destabilized compared to the unsubstituted and the 5-methyl-substituted case. The lowest energy structure corresponding to the unsubstituted *cis* $C_s$ (0,0)

(35) Relative to *trans* 5-methylvinylcyclopropane. The *s-trans* conformer of 5-methylvinylcyclopropane is 1.6 kcal/mol lower in energy than the gauche structure.

(36) This barrier is relative to the *s-trans* conformer of 2,5-dimethylvinylcyclopropane in which the C2 methyl group is *trans* to the vinyl group. The other *s-trans* conformer is 1.3 kcal/mol ($E_1$) higher in energy, while the four gauche conformers are located at 1.5 (C2, *trans*; $E_1$), 1.7 (C2, *cis*; $E_1$), 2.3 (C3, *trans*; $E_1$) and 3.7 kcal/mol (C3, *cis*; $E_1$).

**Table 4. The Relative Energies of the C2- and C3-Substituted Structures Analogous to 2, 3, and 4 in kcal/mol**

| | methyl on | $E_1$ | $E_{SC}$ | $E_2$ | $E_{2,ZPE}$ |
|---|---|---|---|---|---|
| **2-Me$_2$** | C2 | 0.0 | 0.0 | 0.0 | 0.0 |
| **12** | C2 | 0.5 | 0.8 | 0.7 | 0.7 |
| **13** | C3 | 4.9 | 5.2 | 4.0 | 3.8 |
| **14** | C3 | 4.0 | 4.4 | 3.1 | 2.8 |
| **3-Me$_2$** | C2 | −0.6 | 3.5 | 2.1 | 1.6 |
| | C3 | 3.6 | 7.5 | 5.3 | 4.7 |
| **4-Me$_2$** | C2 | −1.8 | 3.2 | 1.4 | 1.1 |
| | C3 | 1.9 | 7.0 | 3.9 | 3.4 |

**3** is 2.0 (1.6) kcal/mol ($E_2$ ($E_{2,ZPE}$), methyl group on C2)[37] above the transition structure for the *si* rearrangement, **2-Me$_2$**, while the analogue to *cis* $C_s$ (0, 90) **4** is 1.4 (1.1) kcal/mol ($E_2$ ($E_{2,ZPE}$)) above **2-Me$_2$**.[37] The relative energies of the C2- and C3-substituted structures are found in Table 4.

For the stereoisomerization, only the C2-substituted transition structures were considered. As in the monomethylated case, there are no experimental data on the difference in barrier heights between the rearrangement and stereoisomerization for this system. The structures corresponding to **7** and **11** are transition states. They are located 2.5 (3.3) and 3.0 (3.8) kcal/mol ($E_2$ ($E_{2,ZPE}$)), respectively, below **2-Me$_2$**. The structure corresponding to **10** is a local minimum, 3.4 (3.6) kcal/mol ($E_2$) lower in energy than **2-Me$_2$**. The computed energy difference between the rearrangement and the stereoisomerization of 2.5−3.0 (3.3−3.8) kcal/mol ($E_2$ ($E_{2,ZPE}$) is similar to the unsubstituted case.

**Secondary Kinetic Isotope Effects.** Experimental secondary kinetic isotope effects (SKIE) are only available for vinylcyclopropane and 4-*tert*-butylvinylcyclopropane. Calculations of secondary kinetic isotope effects using transition structure **2** and **2-*t*-But** reproduce these SKIEs within the experimental error (Table 2).

We have also calculated the SKIEs for the methylated systems. The SKIEs are similar for the four systems, and they are independent of the substitution pattern. This is reflected in the fact that the substitution does not change the geometry of the transition structure significantly as can be seen in an overlay of the transition structures in Figure 10. Because the carbon backbone of the transition structure is not planar, small angle changes, such as experienced by the *tert*-butyl substitution, do not result in significant steric crowding. As a result, the carbon backbone and the H−C2−C3−C1 dihedral angles are maintained in all of the transition structures, and the position of the transition state does not shift along the reaction coordinate (Figure 10).

The large normal SKIE on C2 is due to the fact that the bond between C1 and C2 is broken in **2**, and the orbitals which were bonding in vinylcyclopropane are nearly orthogonal. At the same time, the force constants at C5 are decreased relative to those in vinylcyclopropane due to the allyl radical character of **2** and the partial rotation about the C4−C5 bond,[38] leading to a large normal SKIE. The agreement of experimental and predicted isotope effects, as well as the close similarity between the experimental values of the *tert*-butyl and parent cases, provide strong evidence for the rate-determining transition state.

**Energies.** The uncorrected UB3LYP/6-31G*, the spin-corrected values, and the CASSCF(4,4)/6-31G* single point energies are summarized in Table 3. With the exception of the barrier heights, the energies reported in this account have been $E_2$ energies (=CASSCF(4,4)/6-31G*//UB3LYP/6-31G*), because they reproduced the experimental energy difference between stereoisomerization and rearrangement very closely.

The UB3LYP/6-31G* energies predict too large a difference between the rearrangement and the stereoisomerization pathways (e.g., 5.0−5.4 kcal/mol compared to 2.6−3.4 kcal/mol experimentally in the unsubstituted case). However, the trend of the increasing stereoselectivity from the unsubstituted to the 5-methyl to the 2,5-dimethyl and finally to the 4-*tert*-butyl-substituted system is reproduced. The relative energies of **3** and **4** and their analogues increase relative to the transition structure of the rearrangement. On the other hand, the energies of **3** and **4** are below the transition structure **2** in the parent case.

In all four cases, spin correction decreases the barrier to rearrangement significantly. The corrections are between 4.0 and 5.4 kcal/mol for the transition structures of the rearrangement. Because the singlet and triplet are degenerate, the relative energies of the closed-shell and pure diradical species, such as the *cis* $C_s$ structures **3** and **4**, are not changed by spin projection. Thus the structures involved in the stereoisomerization experience only a slight correction in energy upon spin projection (the corrections are between −1.2 and +0.4 kcal/mol). The energy difference between the rearrangement and the stereoisomerization is now predicted to be smaller than in the experiments. The spin-corrected prediction is 0.9−1.7 kcal/mol in the parent case and 0.2 kcal/mol for the 4-*tert*-butyl system, compared to 3.4 and 2.7 kcal/mol experimentally. In the uncorrected case, it is about 4.5 kcal/mol. Both methods deviate by the same order of magnitude, but in opposite directions. The spin corrected relative energies occupy a narrower range than the uncorrected UB3LYP/6-31G* energies.

CASSCF(4,4) single point calculations (without the inclusion of the zero point energy) predict the *si* transition structure **2** to be lower in energy than the *cis* $C_s$ structures **3** and **4** in all four systems. Depending on the pathway, the barrier for stereoisomerization is 2.7−3.4 kcal/mol lower in energy than the rearrangement in the parent case, and it is 2.6 kcal/mol lower in the 4-*tert*-butyl system. This corresponds to the experimental values of 3.4 kcal/mol and 2.7 kcal/mol, respectively. These energies provide the closest prediction to the experimentally measured values.

If the (U)B3LYP/6-31G* zero point energy is included in the relative energies of the CASSCF(4,4) single point calculations, the difference between the stereoisomerization and the rearrangement is 4.4−3.4 kcal/mol in the parent case and 3.4 kcal/mol in the 4-*tert*-butyl case. Both times the calculations predict a slightly larger difference than experimentally observed. However, the energies of the structures analogous to **3** and **4** still increase mirroring the increase of the experimentally observed stereoselectivity.

**Substituent Effects on the Barrier Height of the Rearrangement.** The transition structure of the rearrangement, **2**, is a diradicaloid structure. Electronically

(37) The *cis* $C_s$ (0, 0) structure with the methyl group at C3 is 5.3 kcal/mol ($E_2$), the *cis* $C_s$ (90, 0) with the methyl group on C3 is 3.9 kcal/mol ($E_2$) above the transition structure of the rearrangement.

(38) Olson, L. P.; Niwayama, S.; Yoo, H.-Y.; Houk, K. N.; Harris, N. J.; Gajewski, J. J. *J. Am. Chem. Soc.* **1996**, *118*, 886.

**Table 5. Comparison of Experimental ($E_{exp}$) and Computed ($E_1$, $E_2$, and $E_{SC}$) Activation Energies of the Rearrangement of Vinylcyclopropane in kcal/mol, as Well as Stabilization of Vinylcyclopropane ((4), $E_{VCP}$) and Stabilization of the Radical ((5), $E_{Rad}$)**

| substituent | position | $E_{exp}$ | $E_1$ | $E_{SC}$ | $E_2$ | $E_{VCP}$ | $E_{Rad}$ |
|---|---|---|---|---|---|---|---|
| H | | 51.7 ± 0.5[a] | 46.9 | 42.8 | 45.7 | 0.0 | 0.0 |
| Me | 1 | 49.4 ± 0.5[b] | 43.7 | 39.8 | 45.0 | 3.6 | |
| | 2 | 48.6 ± (>0.5)[c] | 44.5 | 40.3 | 43.2 | 4.2 | 4.8 |
| OMe | 1 | 45.7 ± 0.6[d] | 39.7 | 35.9 | 42.8 | 7.4 | |
| | 2 | 38.7 ± 0.2[e] | 37.5 | 33.2 | 39.4 | 6.8 | 9.7 |
| $F_2$ | 2 | 41.5 ± 0.4[f] | 38.2 | 33.5 | 36.9 | 8.6 | 6.8 |
| | 3 | 37.9 ± 0.4[f] | 37.9 | 32.7 | 36.5 | 8.6 | |
| $NH_2$ | 2 | 31.2 ± 1.0[g] | 35.2 | 30.7 | 40.5 | 6.1 | 13.2 |
| | | | 34.5 | 34.9 | 39.0 | | |

[a] Reference 10. [b] Reference 40. [c] Reference 39a. [d] Reference 41b. [e] Reference 41a. [f] Reference 43. [g] Reference 42.

innocuous substituents, such as methyl groups, do not change structural features of **2** significantly, although they lower the barrier height slightly. Other substituents might be expected to lower the barrier more dramatically. We studied the influence of substitution on C2 and C1, the atoms of the cyclopropane bond broken in the transition structure. The computed results are compared to available experimental data in Table 5.

Experimentally, a simple methyl substitution on C2 lowers the barrier of rearrangement by about 3 kcal/mol compared to the unsubstituted case,[39] and a methyl at C1 lowers the barrier by about 2 kcal/mol (Table 5).[40] Electron-donating groups at C2 lower the barrier significantly: 2-methoxyvinylcyclopropane has an experimentally measured barrier to rearrangement which is 13 kcal/mol lower than that of the unsubstituted vinylcyclopropane.[41a] The substitution of C1 by a methoxy group lowers the barrier as well, albeit by a lesser amount (6 kcal/mol).[41b] The substitution by a dimethylamino group lowers the activation energy even more. The barrier to rearrangement of 2-dimethylaminovinylcyclopropane is about 20 kcal/mol lower than that of the parent rearrangement.[42] In all the cases mentioned so far, the substituted bond of the cyclopropane moiety is more easily broken than the unsubstituted one. The 2,2-difluoro system is an exception. The activation barrier is 37.9 kcal/mol for 3,3-difluorovinylcyclopropane, and 41.5 kcal/mol for 2,2-difluorovinylcyclopropane.[43]

(U)B3LYP/6-31G* calculations reproduce the general trend in the barrier heights correctly (Table 5, Figure 11). The relative order of the two methyl-substituted systems is exchanged, as is the relative barrier height of the 3,3-difluoro and the 2-methoxy systems. In both cases, the experimental barriers are less than 1.0 kcal/mol of each other and within the experimental error.

(39) There are two different barriers for the rearrangement of 2-methylvinylcyclopropane in the literature: (a) 48.6 ± (>0.5) kcal/mol: Ellis, R. J.; Frey, H. M. *J. Chem. Soc.* **1964**, 5578. (b) 44.6 ± 0.6 kcal/mol: Roth, W. R.; König, J. *Justus Liebigs Ann.* **1965**, *688*, 28.

(40) Ellis, R. J.; Frey, H. M. *J. Chem. Soc.* **1964**, 959.

(41) Again, there are two barriers for the rearrangment of 1-methoxyvinylcyclopropane, but only one for that of 2-methoxyvinylcyclopropane: (a) 44.7 ± 1.2 kcal/mol (1-methoxyvinylcyclopropane), 38.7 ± 0.2 kcal/mol (2-methoxyvinylcyclopropane): Simpson, J. M.; Richey, H. G., Jr. *Tetrahedron Lett.* **1973**, 2545. (b) 45.7 ± 0.7 kcal/mol (1-methoxyvinylcyclopropane): McGaffin, G.; de Meijere, A.; Walsh, R. *Chem. Ber.* **1991**, *124*, 939.

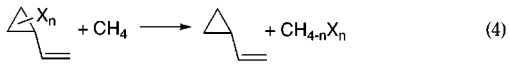
(42) Shull, D. W.; Richey, H. G., Jr. *Tetrahedron Lett.* **1976**, 575.

(43) Roth, W. R.; Kirmse, W.; Hoffmann, W.; Lennarts, H.-W. *Chem. Ber.* **1982**, *115*, 2508.

However, the difference between computed and experimental barrier heights is significant. In all but one case, the barrier height is underestimated by as much as 6.0 kcal/mol ($E_1$). The error is larger in the case of C1 substitution than that of C2, and it is largest in the case of methyl substituents. The result is similar in the CASSCF(4,4)/6-31G* single point calculations on the (U)-B3LYP/6-31G* structures. Both methods underestimate the barrier height in almost all cases and have similar quantitative errors. Spin correction increases this error; the barrier height is underestimated in all systems.

The substituted transition structures are very similar to the parent **2**, although their C2−C1 and C2−C5 distances vary from **2**. While the maximum deviation of the C2−C1 distance is only +0.02 Å, it is up to +0.11 Å for the C2−C5 bond (both values are for the 2-amino-substituted structure which has also the lowest barrier). In agreement with the Hammond postulate, lowering the barrier increases the forming bond length in the transition structure. The transition state shifts to an earlier position on the potential energy hypersurface.

To lower the barrier of reaction, the transition structure must be stabilized relative to reactants. To distinguish how a specific substituent stabilizes vinylcyclopropane and the radical site of the transition structure, two isodesmic reactions were examined. The stabilization of the vinylcyclopropanes is reflected in eq 4, while radical stabilization is mimicked by eq 5.



(4)

$$CH_3^{\bullet} + CH_{4-n}X_n \rightarrow CH_{3-n}X_n^{\bullet} + CH_4 \qquad (5)$$

The stabilization of vinylcyclopropane is largest in the difluoro case, while the amino-substituted system has the lowest activation barrier (computationally and experimentally) due to large stabilization of the transition state. The amino group stabilizes vinylcyclopropane less than the difluoro or the methoxy substitution, while the methyl substitution has the smallest influence on the stability of vinylcyclopropane. Except in the case of the methylated systems, the stabilization of the reactant is much smaller than the lowering of the barrier height might suggest (Table 5).

The radical site is more sensitive to stabilization than vinylcyclopropane. The amino group stabilizes the radical site by 13.2 kcal/mol relative to the unsubstituted system. Methoxy (9.7 kcal/mol), difluoro (6.8 kcal/mol), and methyl (4.8 kcal/mol) substitutions have smaller effects. The calculations reproduce the relative order of the barrier heights of the 2-substituted systems. The relative order also follows the polarizability of the substituents. Related calculations on hydroxy- and cyano-substituted vinylcyclopropanes have been reported.[44, 45]

## Conclusions

The concerted pathway is diradical in nature with no cyclic conjugation. Nevertheless, some vestiges of the

(44) Sperling, D.; Fabian, F. *Eur. J. Org. Chem.* **1936**, *1*, 215.

(45) Quirante, J. J.; Enriquez, F.; Hernando, J. M. *J. Mol. Struct. (THEOCHEM)* **1990**, *204*, 193.

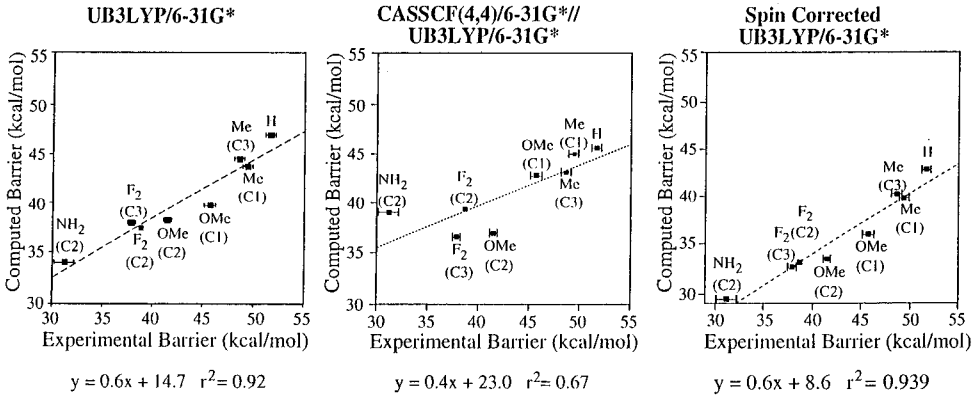



**Figure 11.** Graphs of the experimental versus the computed barriers of rearrangement of various substituted vinylcyclopropanes. The experimental values are from references 10, 39a, and 40−43.

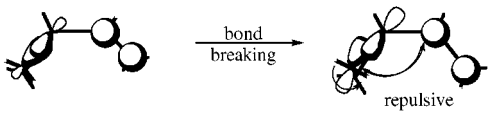



**Figure 12.** Top view of breaking cyclopropane bond and vinyl group p orbitals. Upon bond breaking, repulsive interactions cause rotation.

Woodward−Hoffmann allowed *si* stereochemistry are observed. As shown in Figure 12, as the cyclopropane bond stretches, an anti-aromatic interaction develops involving the breaking bond orbital and the occupied $\pi$ orbital. This promotes rotation about the C2−C3 bond to minimize cyclic conjugation, lowering the repulsive HOMO−HOMO interaction and maximizing the HOMO−LUMO interaction (not shown). These are the same orbital interactions which cause the phenomenon of "torquoselectivity."[46] Other studies of VCP have been reported.[46] Related rotational preferences have been discovered in theoretical studies of cyclopropane[27] and cyclobutane[47] reactions. Orbital interactions govern the most favored motions upon bond-breaking, while dynamic effects determine how much the pathways involving stereochemical scrambling will compete with the electronically favored stereochemistries.[18]

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**Supporting Information Available:** Cartesian coordinates, energies, zero-point energies, and imaginary frequencies (for transition structures) of structures reported in the paper. This material is available free of charge via the Internet at http://pubs.acs.org.

JO991026F

(46) Dolbier, W. R., Jr.; Koroniak, H.; Houk, K. N.; Sheu, C. *Acc. Chem. Res.* **1996**, *29*, 471.

(47) (a) Doubleday, C., Jr. *J. Am. Chem. Soc.* **1993**, *115*, 11968. (b) Bernardi, F.; Bottoni, A.; Olivucci, M.; Venturini, A.; Robb, M. A. *J. Chem. Soc., Faraday Trans.* **1994**, *90*, 1617.