# The Vinylcyclopropane−Cyclopentene Rearrangement: A Prototype Thermal Rearrangement Involving Competing Diradical Concerted and Stepwise Mechanisms

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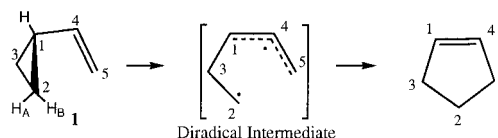*University of Notre Dame, Notre Dame, Indiana 46556*

The vinylcyclopropane rearrangement (Scheme 1) exhibits characteristics of both stepwise and concerted mechanisms. A stepwise mechanism is suggested by the formation of all four possible stereoisomeric products. Deuterium-labeling experiments determine that the *si*:*ar*:*ai*:*sr* product ratio is 40:13:23:24 in the unsubstituted case.[1] The ratio changes upon substitution, but the *si* product remains the major product in all cases.[2] The measured activation energy (51.7 kcal/mol)[3] corresponds closely to the estimated energy of the formation of the diradical intermediate in Scheme 1.[4] The rearrangement competes with the stereoisomerization of the cyclopropane moiety of the molecule, which occurs via a diradical mechanism having a barrier 2.6−3.4 kcal/mol lower than the barrier to rearrangement.[1,2,5,6] The major product, *si*, is that predicted by the Woodward−Hoffmann rules for an allowed concerted reaction and is formed with >95% stereoselectivity when the vinyl group is substituted at C-4 by the electronically innocuous *tert*-butyl group.[6] Secondary kinetic isotope effects indicate that the vinyl terminus is involved in the rate determining step ($k_H/k_{D_2} = 1.14 \pm 0.02$ at C2, $k_H/k_{D_2} = 1.17-1.21 \pm 0.02$ at C5), consistent with a concerted mechanism.[6−8]

The reaction is a prototype of mechanistically ambiguous hydrocarbon rearrangements thought to involve diradical intermediates, but having characteristics of concerted reactions.[9,10] For example, other 1,3-shifts and 1,5-shifts exhibit a multiplicity of products, but a stereoselectivity incompatible with equilibrated diradical intermediates. The origin of stereoselectivity in such reactions has perplexed several generations of chemists. Hoffmann's "twixtyl"[11] and Doering's "continuous diradical"[12] suggest species characterized by flat potential surfaces and

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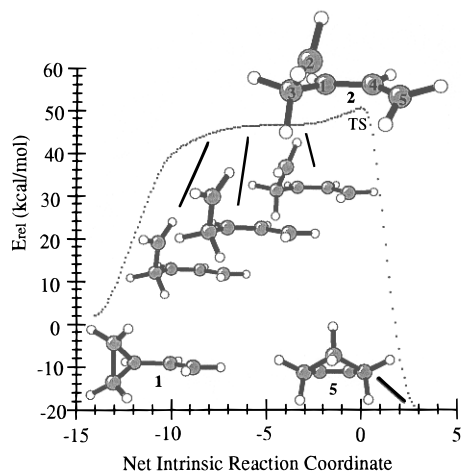(7) Baldwin, J. E.; Villarica, K. A. *Tetrahedron Lett.* **1994**, 7905.
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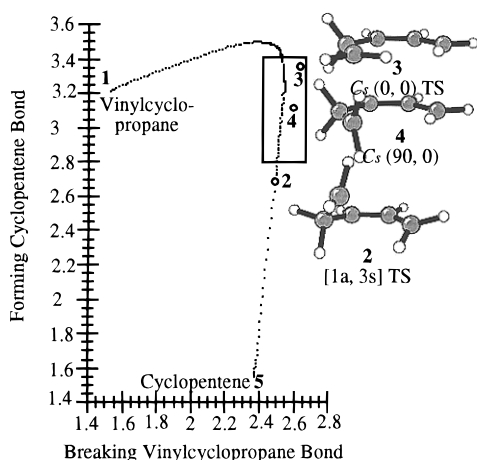(9) Carpenter, B. K. *J. Am. Chem. Soc.* **1996**, *118*, 10329.
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**Scheme 1.** The Vinylcyclopropane−Cyclopentene Rearrangement



unselective rotations about single bonds. Carpenter recently proposed the concept of dynamic matching to explain how selectivity can be induced by inertial effects.[9]

We report preliminary results on the vinylcyclopropane rearrangements of the parent and 4-*tert*-butyl-substituted compounds using CASSCF and density functional theory (DFT) calculations of the potential energy surface and isotope effects.[13] We have found that (1) the major pathway involves a single diradicaloid transition state, (2) electronic factors influence preferred motions of diradicals and combine with dynamic factors to control stereochemical outcomes, (3) stereochemical scrambling involves species which deviate from the concerted pathway with minor energetic consequences, but all species eventually pass through the same transition state leading to cyclopentenes, and (4) substituents can induce overall stereoselectivity by destabilizing species which afford stereochemical scrambling. Similar results have been obtained by Davidson and Gajewski with CASSCF/6-31G* calculations.[14]

The transition structure (**2**) for the concerted *si* sigmatropic shift connecting vinylcyclopropane and cyclopentene is shown in Figure 1.[14] An intrinsic reaction coordinate (IRC) was mapped and includes no 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 structure, **2**, 46.9 kcal/mol ($E_1$) above *s-trans*-vinylcyclopropane[15] 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.

Calculations of secondary kinetic isotope effects (KIEs) with transition structure **2** reproduce the experimental KIEs measured for this reaction ($k_H/k_{D_2} = 1.16$ for C2; $k_H/k_{D_2} = 1.17$ for C5). The bond to C2 is broken in **2**, and the orbitals which were bonding in vinylcyclopropane are nearly orthogonal. This leads to a large normal KIE at C2. 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.[16]

The major pathway passes through **2**, and provides the *si* product. Figure 2 is a plot of the concerted IRC as a function of the breaking C1−C2 and forming C2−C5 bond lengths. Two additional transition structures which are involved in the loss of stereochemical integrity have been located. The *cis* $C_s$ (0,0)

(13) Calculations were carried out using Gaussian94.[13a] Geometries were optimized by density functional calculations using the (U)B3LYP functional and the 6-31G* basis set. The DFT energies corrected by unscaled zero-point energies are labeled $E_1$. Energies were also determined by CASSCF-(4,4)/6-31G* single-point calculations on the DFT geometries; these are labeled $E_2$. Kinetic isotope effects (KIE) were calculated using the Bigeleisen equation,[13b] implemented in the program QUIVER,[13c] using DFT force constants scaled by 0.963.[13d] (a) Gaussian 94 (Revision B.1); Frisch, M. J.; et al.; Gaussian, Inc.: Pittsburgh PA, 1995. (b) Bigeleisen, J.; Maier, M. G. *J. Chem. Phys.* **1947**, *15*, 261. (c) Saunders, M.; Laidig, K. E.; Wolfsberg, M. *J. Am. Chem. Soc.* **1989**, *111*, 8989. (d) Rauhut, G.; Pulay, P. *J. Phys. Chem.* **1995**, *99*, 3093.
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(15) In the unsubstituted case, the *s-trans* conformer is 1.7 kcal/mol below the *gauche* conformer using B3LYP/6-31G*, while the *gauche* conformer is more stable by 4.8 kcal/mol for 4-*tert*-butylvinylcyclopropane.
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**Figure 1.** UBecke3LYP/6-31G* IRC of the *si* transition structure of the rearrangement. $E_{rel}$ is not ZPE corrected. The CC distances in **2** are the following: C1−C2 = 2.489 Å, C2−C5 = 2.681 Å, C1−C4 = 1.369 Å, and C4−C5 = 1.413 Å.



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

structure, **3**, lies 1.6 kcal/mol ($E_2$) above the *si* transition structure of the rearrangement. From **3** a return to the concerted path produces either the *si* or the *ar* products. A second structure, *cis* $C_s$ (0,90), **4**, with the terminal CH$_2$ rotated 90°, lies 0.6 kcal/mol ($E_2$) above the *si* transition structure and returns to the concerted path to lead to *si* or *ai* products.

In addition, the rotation about the terminal C2−H$_2$ unit, which leads to the *sr* product, can occur readily in the plateau region of the *si* IRC. Although this rotation only requires about 0.8 kcal/mol,[18] dynamic effects are likely to cause the preference for the *si* pathway. 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.[17]

The competing stereoisomerization of vinylcyclopropane can occur via a variety of pathways, depending on the starting geometry of vinylcyclopropane and the direction of rotation of the terminal CH$_2$ group during the bond breaking. Figure 3
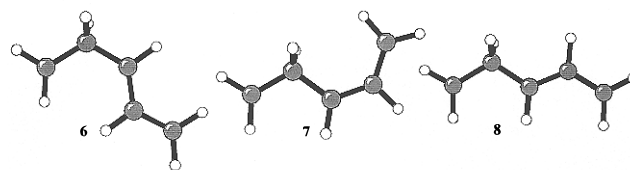


**Figure 3.** Transition structures for stereoisomerization of vinylcyclopropane rearrangement to cyclopentene. The $E_2$ energies are the following: **6**, −2.7 kcal/mol (**6-*t*-But** 9.8); **7** −3.2 kcal/mol (**7-*t*-But** −2.6); **8** −3.4 kcal/mol (**8-*t*-But** 2.3).
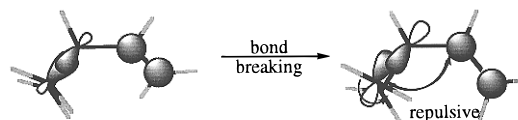


**Figure 4.** Top view of breaking cyclopropane bond and vinyl group π orbitals. Upon bond breaking, repulsive interactions between orbitals at C2 and C4 are relieved by counterclockwise rotation about the C2−C3 bond.

shows three transition structures which can result in scrambling of the cyclopropane stereochemistry, but are not involved in the rearrangement to cyclopentene. The calculated $E_2$ energies reproduce the experimental energy difference of 2.6−3.4 kcal/mol between the isomerization and rearrangement pathways.[3,4] Details will be provided in a full paper.

The rearrangement of 4-*tert*-butylvinylcyclopropane occurs with high stereospecificity, but the KIEs imply a transition state which is nearly the same as that of the parent system ($k^H/k^D_2$ = 1.14 ± 0.02 for 2-D,3-D (calculated 1.12); $k^H/k^D_2$ = 1.17 ± 0.02 (calculated 1.17)).[6] Indeed, **1-*t*-But** is predicted to rearrange via the transition structure, **2-*t*-But**, which is essentially identical to the parent transition structure **2**. The activation barrier is 45.9 kcal/mol ($E_1$), which is similar to the parent system.[15] However, the stereochemical scrambling pathways are significantly destabilized by the *tert*-butyl group and essentially shut off. Both *cis* $C_s$ structures are higher in energy than **2-*t*-But**. The structures **3-*t*-But** and **4-*t*-But** are 4.1 and 2.6 kcal/mol, respectively (both $E_2$), higher due to the crowding of C1−H$_2$ and C5−H$_2$ by the butressing effect of the *t*-butyl group. This is consistent with the observed stereospecificity of the rearrangement.

The concerted vinylcyclopropane rearrangement pathway is diradical in nature with no cyclic conjugation, but the Woodward−Hoffmann allowed *si* stereochemistry is nevertheless preferred. As shown in Figure 4, orbital interactions cause rotation about the C2−C3 bond. These are the same orbital interactions which cause the phenomenon of "torquoselectivity",[19] and rotational preferences in cyclopropane[17] and cyclobutane[20] reactions. The energetic landscape described here is determined by electronic effects, but the full understanding of stereochemistry will require dynamic considerations.[9]

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