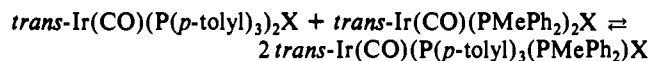


Thus, even at $-70\text{ }^{\circ}\text{C}$, the phosphines are fully exchanged. As the temperature is increased, the rate of exchange becomes competitive on the NMR time scale and broadened resonances are observed.



Very similar exchanges are observed between complexes with different X groups. Reaction between $\text{trans-Ir}(\text{CO})(\text{Me})(\text{P}(p\text{-tolyl})_3)_2$ and $\text{trans-Ir}(\text{CO})(\text{Cl})(\text{PMePh}_2)_2$ results in a statistical mixture of $\text{trans-Ir}(\text{CO})(\text{Cl})(\text{PMePh}_2)_2$, $\text{trans-Ir}(\text{CO})(\text{Me})(\text{PMePh}_2)_2$, $\text{trans-Ir}(\text{CO})(\text{Cl})(\text{P}(p\text{-tolyl})_3)_2$, $\text{trans-Ir}(\text{CO})(\text{Me})(\text{P}(p\text{-tolyl})_3)_2$, $\text{trans-Ir}(\text{CO})(\text{Cl})(\text{PMePh}_2)(\text{P}(p\text{-tolyl})_3)$, and $\text{trans-Ir}(\text{CO})(\text{Me})(\text{PMePh}_2)(\text{P}(p\text{-tolyl})_3)$ at $-70\text{ }^{\circ}\text{C}$. In this reaction the spectra remain sharp at room temperature. Reaction of $\text{trans-Ir}(\text{CO})(\text{OMe})(\text{P}(p\text{-tolyl})_3)_2$ with $\text{trans-Ir}(\text{CO})(\text{Cl})(\text{PMePh}_2)_2$ also leads to the full range of exchanged products. In this reaction, by $-30\text{ }^{\circ}\text{C}$ all of the resonances broaden.

The reactions described above show a surprisingly facile intermolecular exchange process. Formation of the mixed phosphine product requires that the phosphine is the group transferred. Square-planar complexes are known to undergo facile associative substitution.¹ Although a phosphine bridging two metals is not common, an association with bridging X groups leading to phosphine exchange would be possible. However, a dependence on the bridging group X might be expected. For X = Me, OMe, or Cl, the exchange has been completed by $-70\text{ }^{\circ}\text{C}$. An alternate possibility would be phosphine dissociation from a square-planar complex producing $\text{Ir}(\text{CO})\text{LX}$ and L.⁹⁻¹¹ The L could then exchange with other iridium complexes leading to effective L transfer. Dissociation of PPh_3 from $\text{Rh}(\text{Cl})(\text{PPh}_3)_3$ was shown to occur with a rate constant of 0.71 s^{-1} ,¹⁰ although the equilibrium constant for PPh_3 dissociation is $\sim 10^{-7}\text{ M}$.⁹ A very small equilibrium constant would be consistent with our inability to observe free L in our reactions. Other examples of phosphine dissociation from square-planar complexes have not been reported. When excess PMePh_2 is added to $\text{trans-Ir}(\text{CO})(\text{Cl})(\text{P}(p\text{-tolyl})_3)_2$ at $-70\text{ }^{\circ}\text{C}$, the spectrum is invariant as one warms the sample to room temperature, with free $\text{P}(\text{tolyl})_3$ and a broad resonance at -16.2 ppm that is probably due to the five-coordinate complex $\text{Ir}(\text{CO})(\text{Cl})(\text{PMePh}_2)_3$. The same species is formed by addition of PMePh_2 to $\text{trans-Ir}(\text{CO})(\text{Cl})(\text{PMePh}_2)_2$. Addition of $\text{P}(p\text{-tolyl})_3$ to $\text{trans-Ir}(\text{CO})(\text{Cl})(\text{P}(p\text{-tolyl})_3)_2$ at a 0.1 molar ratio shows ³¹P resonances for free $\text{P}(p\text{-tolyl})_3$ and $\text{trans-Ir}(\text{CO})(\text{Cl})(\text{P}(p\text{-tolyl})_3)_2$ at $-70\text{ }^{\circ}\text{C}$, but both are broadened significantly.

We cannot completely exclude exchange caused by reaction of the square-planar complexes with traces of free phosphine. The samples used are recrystallized, show no trace of free phosphine in the ³¹P spectrum, and show no time- or temperature-dependent NMR spectra. Thus it is unlikely that free phosphine is responsible for these reactions.

On the basis of the similarity in the rates to those observed for addition of free phosphine and the known phosphine dissociation from $\text{Rh}(\text{Cl})(\text{PPh}_3)_3$, it is probable that the rapid phosphine exchange observed between square-planar iridium complexes occurs through dissociation of phosphine from an iridium and subsequent associative reactions of the free phosphine with square-planar complexes.

Acknowledgment. We are grateful for support from the National Science Foundation (CHE-9015897) for this research. The Varian VXR-400 NMR instrument was purchased through a grant from the Department of Education (2-2-01011).

(8) $\text{trans-Ir}(\text{CO})(\text{Cl})(\text{PMePh}_2)(\text{P}(p\text{-tolyl})_3)$: ³¹P NMR 10.1 (d), 29.0 (d), $J_{\text{P-P}} = 300\text{ Hz}$. $\text{trans-Ir}(\text{CO})(\text{Me})(\text{PMePh}_2)(\text{P}(p\text{-tolyl})_3)$: ³¹P NMR 9.9 (d), 23.0 (d), $J_{\text{P-P}} = 340\text{ Hz}$. $\text{trans-Ir}(\text{CO})(\text{OMe})(\text{PMePh}_2)(\text{P}(p\text{-tolyl})_3)$: ³¹P NMR 9.8 (d), 25.6 (d), $J_{\text{P-P}} = 370\text{ Hz}$.

(9) Wink, D. A.; Ford, P. C. *J. Am. Chem. Soc.* **1987**, *109*, 436.

(10) Halpern, J. A.; Wong, C. S. *J. Chem. Soc., Chem. Commun.* **1973**, 629.

(11) (a) Faraone, G.; Ricevuto, V.; Romeo, R.; Trozzi, M. *J. Chem. Soc. A* **1971**, 1877. (b) Romeo, R. *Comments Inorg. Chem.* **1990**, *11*, 21.

Solvent Effects on a Diels-Alder Reaction from Computer Simulations

James F. Blake and William L. Jorgensen*

Department of Chemistry, Yale University
New Haven, Connecticut 06511-8118

Received June 3, 1991

The traditional notion that the rates of Diels-Alder reactions are insensitive to solvent effects¹ is certainly false in aqueous media.²⁻⁶ For example, rate accelerations of 741 and 6805 have been obtained in water for the reactions of cyclopentadiene (CP) with methyl vinyl ketone (MVK)^{2a} and a quinone.⁶ Suggested origins of the effects are hydrophobic association,^{2,4,6} micellar catalysis,^{3a,b} high internal solvent pressure,^{3c} solvent polarity,⁵ and hydrogen bonding.⁷ In order to probe this phenomenon further, we have carried out Monte Carlo simulations to compute the changes in free energy of solvation (ΔG_{sol}) during the reaction of CP and MVK in liquid propane, methanol, and water.

The approach is an updated version of our efforts on $\text{S}_{\text{N}}2$, addition, and association reactions.⁸ To begin, ab initio molecular orbital calculations were used to determine the minimum energy reaction path (MERP) in the gas phase. Houk and co-workers previously found only minor variations in transition-state (TS) structure for the reaction of 1,3-butadiene and acrolein when optimized at the 3-21G, 6-31G(d), and MP2/6-31G(d) levels.⁹ Accordingly, we located the four transition states for CP plus MVK corresponding to MVK being s-cis or s-trans and the approach being exo or endo with the 3-21G basis set, and 6-31G(d)//3-21G calculations were subsequently performed.¹⁰ Consistent with the acrolein precedent,⁹ the endo-cis TS was found to be lowest in energy. This TS provided a starting point for the reaction path following procedure in GAUSSIAN 90 that traces the MERP from TS to reactants and product.^{11,12} Essentially, a movie containing 65 frames was obtained covering reaction coordinate (r_c , defined as the average of the lengths of the two forming C-C bonds) values from 1.5 to 8.2 Å. Four frames are condensed in Figure 1.

The next issue is the intermolecular potential functions for the fluid simulations. Well-proven potentials for the solvents are available; the TIP4P model was adopted for water along with the OPLS potentials for propane and methanol.¹³ The latter employ

(1) Sauer, J.; Sustmann, R. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 779.

(2) (a) Rideout, D. C.; Breslow, R. *J. Am. Chem. Soc.* **1980**, *102*, 7816.

(b) Breslow, R.; Maitra, U.; Rideout, D. *Tetrahedron Lett.* **1983**, *24*, 1901.

(c) Breslow, R.; Maitra, U. *Tetrahedron Lett.* **1984**, *25*, 1239. (d) Breslow, R.; Guo, T. *J. Am. Chem. Soc.* **1988**, *110*, 5613. (e) Breslow, R.; Rizzo, C. *J. J. Am. Chem. Soc.* **1991**, *113*, 4340. (f) Breslow, R. *Acc. Chem. Res.* **1991**, *24*, 159.

(3) (a) Grieco, P. A.; Garner, P.; He, Z. *Tetrahedron Lett.* **1983**, *24*, 1897.

(b) Grieco, P. A.; Yoshida, K.; Garner, P. *J. Org. Chem.* **1983**, *48*, 3137. (c) Grieco, P. A.; Nunes, J. J.; Gaul, M. D. *J. Am. Chem. Soc.* **1990**, *112*, 4595.

(4) (a) Schneider, H.-J.; Sangwan, N. K. *J. Chem. Soc., Chem. Commun.* **1986**, 1787. (b) Sangwan, N. K.; Schneider, H.-J. *J. Chem. Soc., Perkin Trans. 2*, **1989**, 1223.

(5) Cativiela, C.; Garcia, J. I.; Mayoral, J. A.; Avenoza, A.; Peregrina, J. M.; Roy, M. A. *J. Phys. Org. Chem.* **1991**, *4*, 48.

(6) Blokzijl, W.; Blandamer, M. J.; Engberts, J. B. F. *N. J. Am. Chem. Soc.* **1991**, *113*, 4241.

(7) Rodgman, A.; Wright, G. F. *J. Org. Chem.* **1953**, *18*, 465. Kelly, T. R.; Meghani, P.; Ekkundi, V. S. *Tetrahedron Lett.* **1990**, *31*, 3381.

(8) For reviews, see: (a) Jorgensen, W. L. *Adv. Chem. Phys., Part II* **1988**, *70*, 469. (b) Jorgensen, W. L. *Acc. Chem. Res.* **1989**, *22*, 184.

(9) Birney, D. M.; Houk, K. N. *J. Am. Chem. Soc.* **1990**, *112*, 4127.

(10) Storer, J. W.; Raimondi, L.; Houk, K. N., to be published.

(11) The ab initio calculations were performed with GAUSSIAN 90, Revision F: Frisch, M. J.; Head-Gordon, M.; Trucks, G. W.; Foresman, J. B.; Schlegel, H. B.; Raghavachari, K.; Robb, M.; Binkley, J. S.; Gonzalez, C.; Defrees, D. J.; Fox, D. J.; Whiteside, R. A.; Seeger, R.; Melius, C. F.; Baker, J.; Martin, R. L.; Kahn, L. R.; Stewart, J. J. P.; Topiol, S.; Pople, J. A., Gaussian, Inc., Pittsburgh PA, 1990.

(12) Gonzalez, C.; Schlegel, H. B. *J. Phys. Chem.* **1990**, *94*, 5523.

(13) Fukui, K. *Acc. Chem. Res.* **1981**, *14*, 363.

(14) (a) Jorgensen, W. L.; Chandrasekhar, J.; Madura, J. D.; Impey, R. W.; Klein, M. L. *J. Chem. Phys.* **1983**, *79*, 926. (b) Jorgensen, W. L.; Madura, J. D.; Swenson, C. S. *J. Am. Chem. Soc.* **1984**, *106*, 6638. (c) Jorgensen, W. L. *J. Phys. Chem.* **1986**, *90*, 1276.

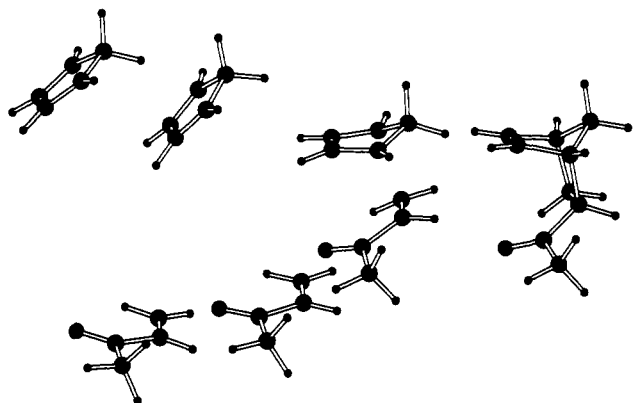


Figure 1. Structures along the MERP at $r_c = 8.2, 6.8, 2.2,$ and 1.6 \AA .

united-atom CH_2 and CH_3 groups; however, an all-atom representation was used for the solutes. The intermolecular potential energy consists of Coulombic and Lennard-Jones (12-6) interactions.¹³ The Lennard-Jones parameters, σ and ϵ , are relatively transferable,¹⁴ and standard values for hydrocarbons and carbonyl groups were used;¹⁵ they were scaled linearly between reactants and product. Previously, we fit the atomic charges to reproduce ab initio results on complexes of the reacting system with a water molecule.⁸ In view of the size of the present system and the modest anticipated charge shifts, simpler alternatives were considered, namely, Mulliken charges or charges fit to electrostatic potential surfaces (EPS).¹⁶ Though EPS charges are in vogue,¹⁷ a better correlation ($r = 0.99$) exists between 6-31G(d) Mulliken charges and the OPLS charges for neutral molecules with first-row atoms than for 6-31G(d) EPS charges ($r = 0.93$).¹⁸ Smaller basis sets give poorer fits. Since the OPLS charges have been chosen to reproduce properties of liquids,¹³⁻¹⁵ 6-31G(d) Mulliken charges were used for the reacting system. They were obtained from 6-31G(d)/3-21G calculations on the 65 frames. The charge shifts are small; e.g., the carbonyl O and C progress from -0.56 and 0.53 for the reactants to -0.61 and 0.56 for the TS and to -0.54 and 0.55 for the product. The 6-31G(d) dipole moments for MVK, the TS, and product are 3.06, 3.44, and 2.89 D.

Finally, the Monte Carlo simulations were executed in the NPT ensemble at $25 \text{ }^\circ\text{C}$ and 1 atm with Metropolis sampling and periodic boundary conditions. The cubic cells contained 500 water, 260 propane, or 260 methanol molecules plus the reacting system. Forty-three of the 65 frames were used, spaced roughly 0.15 \AA apart. The BOSS program¹⁹ perturbed the system between adjacent frames and computed the change in ΔG_{sol} via statistical perturbation theory.^{8b,20} Double-wide sampling was used,²¹ though many free energy increments were calculated in both directions. Each simulation involved 10^6 configurations of equilibration and 4×10^6 configurations of averaging. A solute-solvent molecule interaction was included if any solute atom was within 9, 10, and 12 \AA of the central atom in water, methanol, and propane.

The key results are in Figure 2, which shows the variation in ΔG_{sol} along the reaction path. Solvent effects are negligible in propane. However, in water there is strong stabilization ($-4.2 \pm 0.4 \text{ kcal/mol}$) of the TS, which occurs at the minimum at 2.22 \AA . Perturbations to 6-31G(d) EPS charges yielded an increased

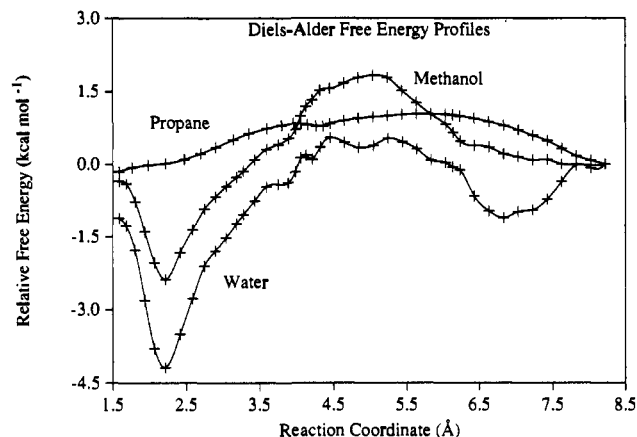


Figure 2. Computed changes in free energies of solvation.

effect of $-5.4 \pm 0.5 \text{ kcal/mol}$. The minimum is followed by a 3.1 kcal/mol uptick to bring the product to $-1.1 \pm 0.4 \text{ kcal/mol}$. The gas-phase energy profile for the reaction is flat to 3.3 \AA , so the minimum at 6.8 \AA in Figure 2 predicts a solvent-separated intermediate. A water molecule is found between the reactants, with a hydrogen often pointing toward the center of the CP ring.^{15b,22} The predicted stabilization of the TS in water relative to propane of 4.2 kcal/mol compares well with the observed rate data, which give a 3.8 kcal/mol lowering of the free energy of activation in water relative to isooctane.^{2a} The situation in methanol is intermediate; the predicted stabilization of the TS is $2.4 \pm 0.3 \text{ kcal/mol}$, while the rate data indicate a 1.5 kcal/mol shift.^{2a} These comparisons assume a lack of solvent dynamical effects on the barrier crossing.²³

Efforts were made to unravel the origin of the acceleration in water. Clearly, micelles are not required. To try to gauge electrostatic effects, the charges for the TS were perturbed to the reactant and product values while the TS geometry was maintained. In going to the product charges, ΔG_{hyd} increases by $2.7 \pm 0.1 \text{ kcal/mol}$, which accounts for most of the 3.1 kcal/mol uptick. The increase is smaller ($0.8 \pm 0.1 \text{ kcal/mol}$) in going to the reactant charges, though the significant geometrical change is a complication. Further analysis found that although the number of hydrogen bonds to the carbonyl O remains at 2-2.5 during the reaction, the strength of each bond is 1-2 kcal/mol greater at the TS. This reflects the sensitivity of hydrogen bonding to small charge variations.²¹ The contribution of hydrophobic effects was approached by computing a full free energy profile with all the partial charges set to 0 for the reacting system. ΔG_{hyd} declines smoothly from reactants to product by $4.4 \pm 0.4 \text{ kcal/mol}$. This could account for the rate acceleration; however, the chargeless model undoubtedly overestimates the hydrophobic component. An overlooked experimental estimate of this comes from solubility data. The changes in ΔG_{hyd} for the reactions of 1,3-butadiene + ethylene \rightarrow cyclohexene and isoprene + ethylene \rightarrow 1-methylcyclohexene are -1.5 and -1.3 kcal/mol .²⁴ These values agree well with the overall change of -1.1 kcal/mol in Figure 2. The TS and product are close in geometry; a significant difference in hydrophobicity seems unlikely. Consequently, the present results support the idea that the aqueous acceleration for the CP + MVK reaction contains a significant nonhydrophobic component stemming from enhanced polarization of the TS that leads to stronger hydrogen bonds at the carbonyl oxygen. The variations for the accelerations of aqueous Diels-Alder reactions with cyclopentadiene^{2,6} can then be ascribed to variations in the polarization of the dienophile at the TS with the hydrophobic component contributing about a factor of 10 to the rates.

(14) Jorgensen, W. L.; Tirado-Rives, J. *J. Am. Chem. Soc.* **1988**, *110*, 1657.

(15) (a) Jorgensen, W. L.; Briggs, J. M.; Contreras, M. L. *J. Phys. Chem.* **1990**, *94*, 1683. (b) Jorgensen, W. L.; Severance, D. L. *J. Am. Chem. Soc.* **1990**, *112*, 4768.

(16) Cox, S. R.; Williams, D. E. *J. Comput. Chem.* **1981**, *2*, 304. Williams, D. E.; Yan, J. M. *Adv. At. Mol. Phys.* **1988**, *23*, 87.

(17) Besler, B. H.; Merz, K. M., Jr.; Kollman, P. A. *J. Comput. Chem.* **1990**, *11*, 431.

(18) Nguyen, T. B.; Jorgensen, W. L., unpublished results.

(19) Jorgensen, W. L. *BOSS, Version 2.9*; Yale University: New Haven, CT, 1990.

(20) Zwanzig, R. W. *J. Chem. Phys.* **1954**, *22*, 1420.

(21) Jorgensen, W. L.; Ravimohan, C. *J. Chem. Phys.* **1985**, *83*, 3050.

(22) Atwood, J. L.; Hamada, F.; Robinson, K. D.; Orr, G. W.; Vincent, R. L. *Nature* **1991**, *349*, 683.

(23) (a) Truhlar, D. G.; Hase, W. L.; Hynes, J. T. *J. Phys. Chem.* **1983**, *87*, 2664. (b) Gertner, B. J.; Wilson, K. R.; Hynes, J. T. *J. Chem. Phys.* **1989**, *90*, 3537.

(24) Hine, J.; Mookerjee, P. K. *J. Org. Chem.* **1975**, *40*, 292.

Acknowledgment. This work was supported by the National Science Foundation, CHE-9014941.

Supplementary Material Available: Complete specifications of the geometries of the reactants, TS, and product from the 3-21G optimizations in Z-matrix format and the potential function parameters (3 pages). Ordering information is given on any current masthead page.

Evidence for a Dominant Suprafacial-Inversion Pathway in the Thermal Unimolecular Vinylcyclopropane to Cyclopentene 1,3-Sigmatropic Shift

Joseph J. Gajewski* and Leif P. Olson

Department of Chemistry, Indiana University
Bloomington, Indiana 47405

Received May 31, 1991

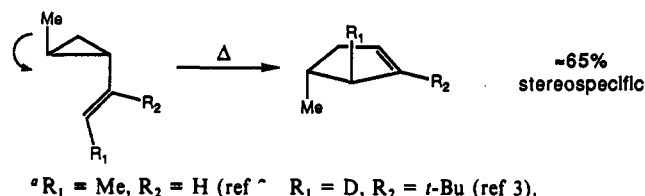
All previous studies of the thermal, unimolecular isomerization of vinylcyclopropane to cyclopentene¹ demonstrated dominant suprafacial-inversion stereochemistry in this 1,3-sigmatropic shift, but relied on *trans*-2-methyl substitution at the migrating carbon to reveal the pathway^{2,3} (Scheme I).

Concern that steric effects may be responsible for the stereoselectivity by forcing outward rotation of the *trans*-methyl group as the C-1,C-2 bond breaks, which might present the back side of the migrating carbon to the end of the allylic moiety for a least motion closure,⁴ prompted examination of the pyrolysis of *r*-1,*t*-2,*t*-3-2,3-dideuterio-1-[(*Z*)-1'-*tert*-butyl-2'-deuteriovinyl]-cyclopropane (**1**). A complication is the geometric isomerization of starting vinylcyclopropane, which in the parent case occurs ca. 20 times faster than the 1,3-shift^{1,2} and gives a nearly statistical distribution of diastereomers at all three ring centers.⁵

Vinylcyclopropane **1** was chosen for study in the anticipation that the *tert*-butyl group would retard formation upon pyrolysis of a *trans*oid allylic species which could only reclose to starting material and compromise its stereochemistry. Indeed, it was found that, upon pyrolysis at 290 °C, **1** (for synthesis, see supplementary material) undergoes formation of a random mixture of cyclopropane ring diastereomers⁵ only 4.5 times faster than 1,3-shift.

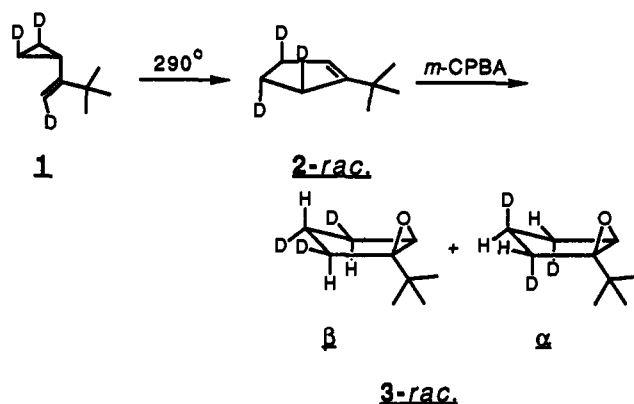
Fortunately, all of the ring protons of the epoxide of protio 1-*tert*-butylcyclopentene were found to be separately visible in the 500-MHz ¹H NMR spectrum and are assignable on the basis of a low-energy boat conformation.⁶ Molecular mechanics found the same low-energy conformation of the product epoxide,⁷ and the coupling constant calculation protocol of Haasnoot⁸ produced coupling constants similar to those observed. Of particular note is that there are two *trans* coupling systems on the ring, with one (α) having $J_{trans} = 0$ Hz, which corresponds to the endo C-2 and endo C-4 protons interacting with the exo C-3 proton, and the other (β) corresponding to exo C-2 and exo C-4 protons interacting with the endo C-3 proton with $J_{trans} = 9$ Hz. The *cis* coupling

Scheme I^a



constants are not inconsequential ($J_{cis} = 8-9$ Hz) and lead to doubling of the C-2 and C-4 protons and tripling of the C-3 protons, all in addition to the doubling by geminal coupling ($J_{gem} = 12-14$ Hz).

Observation of the ¹H NMR spectra (500 MHz; unlocked, deuterium decoupled) of the epoxidized, GC-purified cyclopentene product resulting from the rearrangement of **1** over varying pyrolysis times showed that the rearrangement is not random. Samples of **1** (90% C-2 and C-3 deuterium incorporation *trans* to C-1 substituent; >98% deuterium incorporation *cis* to *tert*-butyl) were pyrolyzed to 60%, 6.4%, and 4.5% conversion to **2**. The



shorter the pyrolysis time, the more closely the ¹H NMR spectrum of the product epoxide resembles that predicted for a purely suprafacial inversion process, and the less it resembles that predicted for a random mixture. In particular, the multiplets associated with the exo C-2 and C-4 and endo C-3 protons from the *sr*, *ar*, and *ai* components in the mixture decrease in intensity, leaving the singlets predicted for α , which is the *si* product.⁹

It is not possible to calculate the stereospecificity in the 1,3-shift to high accuracy, but it appears to be in excess of 85%. Regardless of the exact value, it is clear that the 55-80% suprafacial-inversion stereochemistry observed with 2-*trans*-alkyl-substituted vinylcyclopropanes is not a result of steric effects.

Demonstration of suprafacial-inversion stereochemistry is consistent with concert in the rearrangement with a competing, entropically more favorable, biradical pathway which randomizes the stereochemistry of starting material. The stereochemistry is also consistent with disrotatory ring opening followed by rapid (relative to bond rotation) closure of the biradical resulting from inward rotation of the vinyl group; the biradical resulting from outward rotation of the vinyl group might be responsible for the loss of stereointegrity of the starting material. The origin of the disrotatory ring opening stereomode is not obvious. The observation of a substantial *normal* deuterium kinetic isotope effect at the exomethylene carbon in the rearrangement of vinylcyclopropane itself¹⁰ and of 2-methyl-1-vinylcyclopropanes,³ which is

(1) (a) Neureiter, N. P. *J. Org. Chem.* **1959**, *24*, 2044. (b) Marshall, D. C.; Frey, H. M. *J. Chem. Soc.* **1962**, 3981.

(2) Andrews, G. D.; Baldwin, J. E. *J. Am. Chem. Soc.* **1976**, *98*, 6705. **Note Added in Proof:** Baldwin and Ghatlia (Baldwin, J. E.; Ghatlia, N. D. *J. Am. Chem. Soc.* **1991**, *113*, 6273) found similar behavior for the case with R₁ = D and R₂ = H.

(3) Gajewski, J. J.; Squicciarini, M. P. *J. Am. Chem. Soc.* **1989**, *111*, 6717.

(4) W. von E. Doering, suggestion made at the 1988 Reaction Mechanisms Conference, University of Pittsburgh.

(5) Willcott, M. R., III; Cargle, V. H. *J. Am. Chem. Soc.* **1969**, *91*, 4310. A doublet superimposed on a doublet of doublets is observed for anti ¹H(s); this spectrum does not change with pyrolysis time.

(6) (a) Lafferty, W. J. *J. Mol. Spectrosc.* **1970**, *36*, 84. (b) Steyn, R.; Sable, H. *Z. Tetrahedron* **1971**, *27*, 4429.

(7) Gajewski, J. J.; Gilbert, K. E.; McKelvey, J. In *Advances in Molecular Modeling*; Liotta, D., Ed.; JAI Press: Greenwich, CT, 1990; Vol. 2.

(8) Haasnoot, C. A. G.; deLeeuw, F. A. A. M.; Altona, C. *Tetrahedron* **1980**, *36*, 2783.

(9) One epoxide of the suprafacial-inversion product from **1** should have only endo C-2 and endo C-4 protons with an exo C-3 proton for the α coupling system ($J_{trans} = 0$ Hz), and since there should be no *cis* protons in the *si* product (and no J_{gem} regardless of stereochemistry), only three ring singlets should be observed for this epoxide. The other epoxide has protons only at exo C-2, exo C-4, and endo C-3, so the β system doublet-doublet-triplet pattern, respectively, is expected.

(10) Chickos, J. *Abstracts of Papers*, 187th National Meeting of the American Chemical Society, St. Louis, MO; American Chemical Society: Washington, DC, 1984; ORGN 228.