Calculational Evidence for Lack of Intermediates in the Thermal Unimolecular Vinylcyclopropane to Cyclopentene 1,3-Sigmatropic Shift

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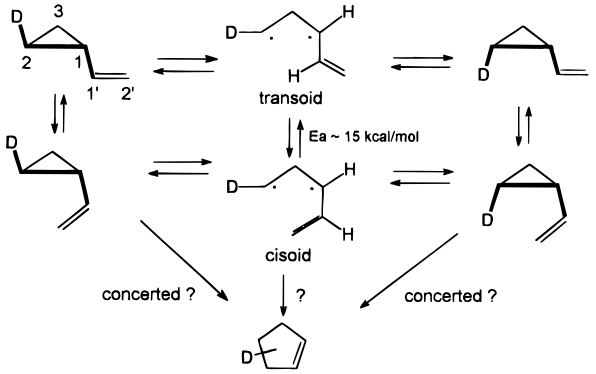
Upon pyrolysis, vinylcyclopropane undergoes a rearrangement to cyclopentene[1a] which has been characterized as a first-order reaction in the gas phase. Frey determined that $\log k\ (s^{-1}) = (13.5 - 49\,600)/2.303RT$ for loss of vinylcyclopropane,[1b] and Wellington reported $\log k\ (s^{-1}) = (13.6 - 49\,700)/2.303RT$ for formation of cyclopentene.[1c] Numerous studies reveal that geometric isomerization of starting material occurs 5−40 times faster than allylic rearrangement.[2] In the simplest case, the Arrhenius parameters for the interconversion of *cis*- and *trans*-2-deuteriovinylcyclopropane are $\log k\ (s^{-1}) = (14.02 - 47\,100/2.3RT$.[2b] The mechanism of the geometric isomerization has been generally attributed to reversible formation of a biradical in which rotation around non-allylic bonds occurs faster than ring closure back to starting material. Because of the orbital overlap in the allylic moiety it is generally expected that both *transoid* and *cisoid* species are possible. These biradicals, however, would not be expected to interconvert, since allyl radical resonance energy of 10−15 kcal/mol would be lost. This constitutes a barrier which would be expected to be substantially larger than the barrier to ring closure. Therefore, the only fate of the *transoid* species would be reclosure to the geometric isomers of starting material. The *cisoid* biradical species, however, might be responsible for both geometric isomerization and allylic rearrangement (Scheme 1). Alternatively, a concerted 1,3-sigmatropic shift might be responsible for the ring-expanding rearrangement so that the geometric isomerization could therefore occur *via* biradicals or some process separate from the 1,3-shift.

In principle, four stereochemical outcomes can be envisioned for the rearrangement of the parent compound as a result of breaking either the C1−C2 bond (or the C1−C3 bond), since the methylene (CH_2) carbon can migrate with retention or inversion and the allylic unit can be used either suprafacially or antarafacially. Baldwin and Andrews found that the 1,3-shift proceeded via all four possible pathways in the pyrolysis of optically active *trans*-2-methyl-1-(*trans*-1′-propenyl)cyclopropane, but the Woodward−Hoffmann "allowed" suprafacial inversion pathway constituted 65% of the total reaction.[3]

Concern that the methyl group at the migration terminus might influence the direction of rotation provoked studies on materials having a deuterium label on C2′,[4] and these indicated dominant (ca. 55−70%) suprafacial inversion stereochemistry in the 1,3-sigmatropic shift. Concern that the alkyl substitution at the migrating carbon might have an effect led to the study in our laboratory of 2,3,2′-trideuterio-1′-*tert*-butylvinylcyclopropane, which rearranged with at least 70% suprafacial inversion stereochemistry, and a more detailed examination suggested at least 90% stereospecificity in an *si* sense after correction for the geometric isomerization of starting material.[5] However, with the parent system involving deuterium labeling at C2, C3, and C2′, Baldwin et al. found that the ratio of *si*, *ar*, *sr*, and *ai* products is 40:13:23:24, respectively, when isotope effects are ignored.[6]

Scheme 1. Observed Thermally Induced Isomerizations of 2-Deuteriovinylcyclopropane via Hypothetical *Cisoid* and *Transoid* Biradical Intermediates



Theoretical work on the vinylcyclopropane rearrangement using density functional theory and unrestricted Hartree−Fock calculations has been reported by the Houk group,[7] but we felt it was appropriate to use a complete active space self-consistent field (CASSCF) method (4-orbital/4-electron) with a 6-31G* basis set since biradical-like species were most likely involved.[8] Exploration of the vinylcyclopropane energy surface focused only on those structures whose allyl moiety has a geometry that can give rise to cyclopentene; the only exception was the global minimum for vinylcyclopropane, namely, the *anti* form. No symmetry restrictions were imposed on the calculations, and the vibrational frequencies of all species were calculated in order to exclude those with more than one imaginary frequency.

Contrary to the mechanistic hypothesis of Scheme 1, CASSCF calculations reveal the presence of only four minima on the energy surface for the vinylcyclopropane to cyclopentene thermal rearrangement in the all-protio case. These are three conformations of vinylcyclopropane (the two enantiomers of a *gauche* conformation, **VCP-g**, and the *anti* conformation, **VCP-a**) and cyclopentene, **CP**. *No biradical intermediates could be found.* However, four transition states were located. These are a transition state for geometric isomerization by single rotation about the C2−C3 bond, **TSG**; a C_s transition state for single rotation about the C1−C3 bond, **TS-ca** (*cisoid* allyl with *anti* substitution), a transition state for the 1,3-shift, **TS13**; and a C_s transition state for enantiomerization of the suprafacial inversion transition state, **TS-cs** (*cisoid* allyl with *syn* substitution). The minima (except for **VCP-a**) and saddle points are depicted on an energy surface starting with 2′,2-dideuteriovinylcyclopropane (Scheme 2) in which the C2−C3−C1−C1′ dihedral angle is plotted against the *trans*-C2D−D−C3−C2−C1 dihedral angle. The use of two deuteriums provides a minimally labeled

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(7) Wiest, O.; Storer, J.; Fennen, J.; Nendel, M.; Houk, K. N. *Book of Abstracts*, 210th National Meeting of the American Chemical Society, Chicago, IL, Fall 1995; American Chemical Society: Washington, DC, 1995; ORGN 33.

(8) See Davidson, E. R.; Gajewski, J. J.; Shook, C. A.; Cohen, T. *J. Am. Chem. Soc.* **1995**, *117*, 8495.

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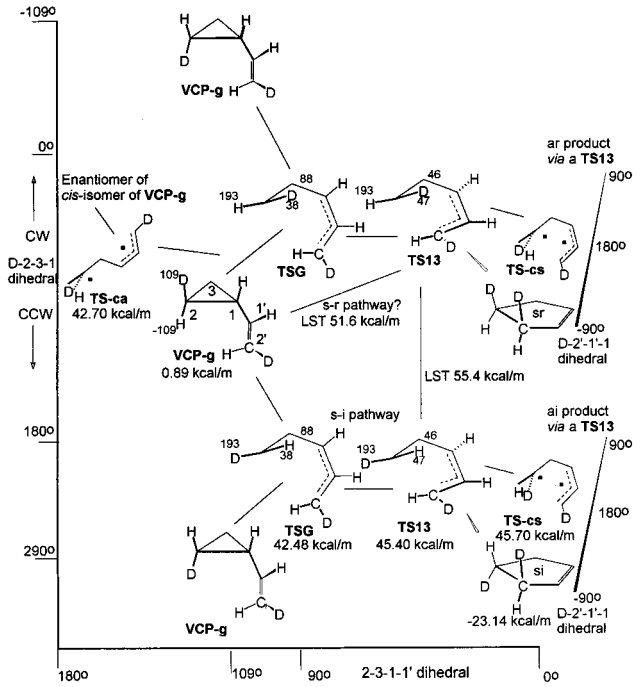
Scheme 2. Potential Energy Surface from a CASSCF(4o/4e)/6-31G* Calculation Where the Geometries Are Restricted to *Cisoid*-Allylic Species (Energies Are Relative to **VCP-a**)



system for analysis of the reaction pathways. Thus, there are *trans* and *cis* isomers of **VCP-g** and two geometric isomers of **TSG** and **TS13**. Scheme 2 also includes a coordinate for the D−C2′−C1′−C1 dihedral angle where it is relevant, namely, for the formation of **CP** from **TS13**, for the conversion of **TS13** to **TS-cs**, and for the formation of a **CP** with antarafacial use of the allylic moiety *via* a **TS13** from **TS-cs**. Scheme 2 also includes the potential energies of all species relative to **VCP-t**.

While no minima corresponding to biradical intermediates were found, **TSG** not only serves to interconvert **VCP-g** with its geometric isomer but branches uphill to **TS13,** and **TS13** branches to **TS-cs** which serves only to interconvert **TS13** with its enantiomer (in the absence of labels).

The transition states for C2 rotation, **TSG**, and for the 1,3-shift, **TS13**, were similar geometrically except for the C2−C3−C1−C1′ torsion angle which is 88° and 46°, respectively, and an allylic unit deformed in the direction of bond formation between C2′ and C2 in the latter case. The C2−C2′ distance in **TS13** was calculated to be 2.772 Å. Vibrational frequencies were calculated to determine that the secondary deuterium kinetic isotope effect at C2′ (k_{H_2}/k_{D_2} = 1.15−1.18 at 290−330 °C)[9] could be reproduced by the transition state **TS13**. An intrinsic reaction coordinate (IRC) calculation revealed that **TS13** is formed from the transition state for C2 rotation, **TSG**. However, **TSG** can be obtained by two different rotational directions of C2 from a particular *gauche* conformation of vinylcyclopropane. Thus, the transition state **TS13** from each of the transition states for C2 rotation can give rise to two different cyclopentenes: one is the product derived by the suprafacial-inversion stereochemical pathway and the other is derived by the suprafacial-retention stereopathway.

A direct, least-motion, Woodward−Hoffmann "forbidden" suprafacial-retention transition state could not be located but a linear synchronous transit calculation (LST) connecting ***VCP-g*** *and* ***TS13*** *via the sr pathway suggests that if it exists, it would be 6.2 kcal/mol higher in energy than the transition state,* ***TS13***. **TS13** would appear to be the Woodward−Hoffmann "allowed" transition state which could be formed directly from **VCP-g**, but **TSG** intervenes. While conservation of orbital symmetry factors appear to dominate the ring opening, all four stereoisomers of the cyclopentene product can be formed since the 1,3-sigmatropic shift transition states can be formed by two equal energy pathways, and each can interconvert with their enantiomers *via* an appropropriate **TS-cs** (Scheme 2), which is only 0.3 kcal/mol higher in potential energy than **TS13**. This should give nearly equal amounts of the four possible stereoisomeric cyclopentenes from appropriately labeled vinylcyclopropane.[10]

While inclusion of zero-point energy and entropy corrections lowers the apparent free energy of **TS-cs** relative to that of **TS13** by ca. 1.6 kcal/mol, it should be recognized that the harmonic approximation used for these calculations is of dubious value with low-frequency vibrations which contribute the most to the entropy. Further, the free energy of a particular structure is a *non sequitur*. Nonetheless despite apparent orbital symmetry control in the ring opening, the Woodward−Hoffmann "allowed" *si* transition state is not highly stabilized with respect to the biradical-like transition state species **TS-cs**, possibly because of steric impediment of overlap in **TS13**. Inclusion of electron correlation at the MP2 level increased the energy gap between the lowest energy transition state for geometric isomerization, **TSG**, and 1,3-shift via **TS13** to 6.7 kcal/mol.

These results are not consistent with the observation of >90% stereospecific formation of suprafacial-inversion product in the 1,3-shift of deuterium-labeled 1′-*tert*-butylvinylcyclopropane. It may be possible that the *tert*-butyl group stabilizes **TS13** by increasing the overlap as a result of steric effects and destabilizes the other transition states for steric reasons as well. The latter expectation is supported by DFT calculations performed by Houk et al.[11]

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Supporting Information Available: A list of the cartesian coordinates for all maxima and saddle points and their energies (5 pages). See any current masthead page for ordering and Internet access information.

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(10) Scheme 2 reveals that the pathways for formation of the **TS13** to form the *si* and the *sr* products are not identical. To form the **TS13** that gives the *sr* product C2 must rotate in one direction (clockwise) then in the other direction (counterclockwise), but to form the **TS13** that gives the *si* product, C2 rotates continuously in one direction. It might be argued that the dominance of *si* and *ai* products over *sr* and *ar* products (64:36)[6] represents a preference for the less torturous path consistent with dynamical considerations, see: Carpenter, B. K. *Acc. Chem. Res.* **1992**, *25*, 520.

(11) Houk, K. N.; Nendel, M.; Wiest, O.; Storer, J. W. *J. Am. Chem. Soc.* **1997**, *119*, 10545.