for a pronounced shortening of the C_1–OCH_3 bond. This shortening is increased by Coulomb effects involving the strongly positively charged C_1 atom and the three adjacent O atoms. Electrostatic effects between methyl hydrogens and the O atoms of the ring also play a role since they add to the stability of the endo form.

Acknowledgment. This work was supported by Grants CHE-8303615 and CHE-8603834 from the National Science Foundation. Support at the Universität Köln was provided by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie. Helpful discussions on various aspects of this research with Dr. Kurt W. Hillig II are gratefully acknowledged. We thank Professor H. D. Rudolph and Dr. V. Typke of Ulm University for the program ZFAP6 which was invaluable throughout this entire project.

Supplementary Material Available: Tables S1–S17 listing transition frequencies and centrifugal distortion constants for the ground vibrational states of the normal and isotopic species and observed and calculated Stark coefficients (18 pages). Ordering information is given on any current masthead page.

Transition Structures for Homodienyl 1,5-Sigmatropic Hydrogen Shifts: Origin of the High Endo Stereoselectivity

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Abstract: The endo and exo transition structures for the homodienyl hydrogen shift of 1-methyl-2-vinylcyclopropane have been obtained with ab initio quantum mechanical calculations. The difference in energy between the endo and exo transition states is estimated to be 17 kcal/mol, favoring the endo mode of reaction, as compared to Berson's estimate of at least 12 kcal/mol made on the basis of experimental data. The transition structures are compared to that obtained earlier for the simplest ene reaction of propene with ethylene. Orbital overlap factors, which lead to the endo preference, are discussed.

The best understood stereoelectronic imperative is that developed by Woodward and Hoffmann, differentiating thermally allowed and forbidden reactions.[1] Among the thermally allowed pericyclic reactions, there are stereoisomeric variants that have activation energy differences as large as those between allowed and forbidden reactions.[2] These are understood in a few cases, but general rules have not yet emerged. We have been investigating such reactions theoretically, and here we describe theoretical studies of an especially well-documented spectacular reaction of this type.

Scheme I

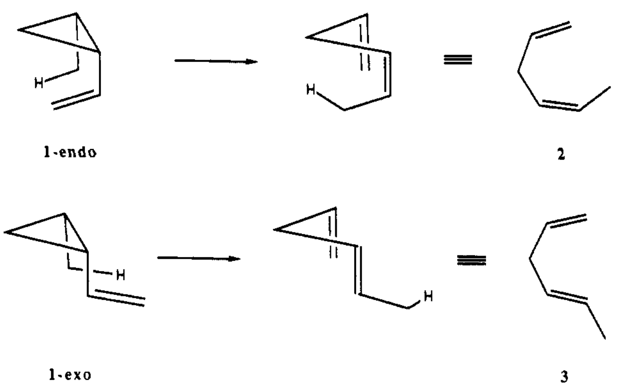
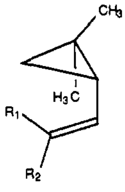


Table I. Energetics of the Retro-Ene Reactions of *cis*-1-Methyl-2-vinylcyclopropane (Theoretical Results Are Obtained with the 3-21G Basis Set)[a]

adduct	E_a	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	ΔH_{rxn}	T, K
endo	48.8	45.3	−6.4	−11.0	
exo	65.9	62.0	−6.1	−12.7	
exptl I[b]	31.3			−5.2[c]	543
exptl II[d]	31.2 ± 0.7		−4.7		439–493
exptl III[e]	31.1	30.2 ± 0.6	−3.7		443–463

[a] Absolute energies (au) of the reactant, endo transition structure, exo transition structure, cis product, and trans product are −231.675 44, −231.596 70, −231.570 47, −231.693 02, and −231.695 72, respectively. [b] Reference 4. [c] Reference 10. [d] Reference 8c,d. [e] Reference 8b.



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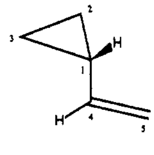

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In connection with our study of the ene reaction,[3] we have undertaken a study of the intramolecular retro-ene reaction of *cis*-1-methyl-2-vinylcyclopropane (**1**). This transformation is also known as the homodienyl 1,5-hydrogen shift. It can occur in two stereochemically distinct modes, endo or exo, both of which are thermally allowed. The endo transition state gives *cis*-1,4-hexadiene (**2**) while the exo transition state gives *trans*-1,4-hexadiene (**3**), as shown in Scheme I. Daub and Berson[4] estimated that the endo transition state is at least 12 kcal/mol lower in energy than the exo transition state. This free energy difference was estimated from experiments on substituted derivatives. Activation energies were measured for compounds having *tert*-butyl substitution at the terminal vinyl position of 1,1-dimethyl-2-vinylcyclopropane (**4**). The trans-substituted system (**4**, R_2 = *t*-Bu) leads to a 7.0 kcal/mol lower activation energy than the *cis-tert*-butyl system (**4**, R_1 = *t*-Bu), which corresponds to a $\Delta\Delta G^{\ddagger}$ of 6.5 kcal/mol; and the *cis-tert*-butyl system gives a cis to trans product ratio of 99.4:0.6, which corresponds to a $\Delta\Delta G^{\ddagger}$ of 5.5 kcal/mol. Thus, the formation of the cis product occurs with a rate that is over 5 orders of magnitude faster than the rate of formation of the trans product. Berson, following an earlier suggestion by Winstein,[5] proposed that this rate difference "is

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(1) Woodward, R. B.; Hoffmann, R. *The Conservation of Orbital Symmetry*, Academic: New York, **1970**.

(2) See, for example: (a) Rondan, N. G.; Houk, K. N. *J. Am. Chem. Soc.* **1985**, *107*, 2099. (b) Kirmse, W.; Rondan, N. G.; Houk, K. N. *J. Am. Chem. Soc.* **1984**, *106*, 7989.

(3) Loncharich, R. J.; Houk, K. N. *J. Am. Chem. Soc.* **1987**, *109*, 6947.

(4) Daub, J. P.; Berson, J. A. *Tetrahedron Lett.* **1984**, *25*, 4463.

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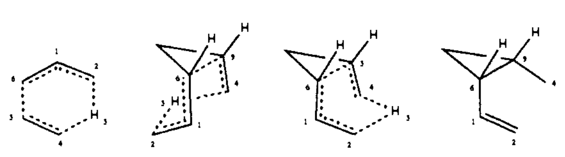
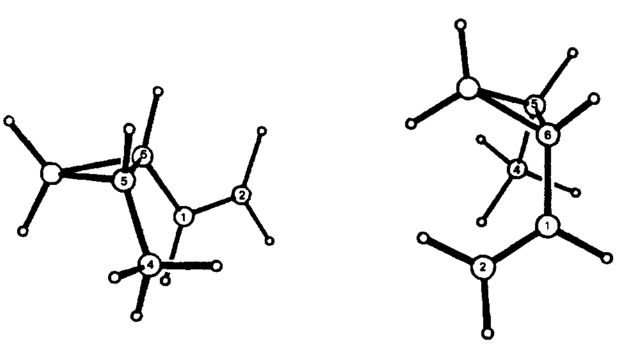


	5	TS-endo	TS-exo	exo-1
$C_4C_5C_6C_1$	-37.8	-13.6	-8.5	-1.5
$H_3C_2C_1H_6$	-59.4	-55.4	-65.6	
$H_3C_4C_5H_6$	11.2	5.8	-23.7	
$C_1C_2C_3$	96.2	95.3	91.0	
$C_2H_3C_4$	156.6	147.1	149.4	
$H_3C_4C_5$	103.2	103.6	104.6	111.9
$C_4C_5C_6$	110.6	114.9	109 7	121.8
$C_5C_6C_1$	100.6	107.0	104.7	121.1
$C_6C_1C_2$	119.3	124.2	120.1	124.6
C_1C_2	1 402	1.392	1.398	1.318
C_1C_6	1.374	1.373	1.374	1.478
C_2H_3	1.349	1.480	1.453	
H_3C_4	1.447	1.351	1.446	
C_4C_5	1.397	1.401	1.395	1 516
C_5C_6	2.110	2.006	1.987	1.523

Figure 1. 3-21G geometries of the reactant, endo and exo transition structures of the homodienyl 1,5-hydrogen shift of *cis*-1-methyl-2-vinylcyclopropane. For comparison, the geometry of the prototype ene reaction of propene with ethylene is also shown.



exo-1 endo-1

Figure 2. 3-21G conformations of *cis*-1-methyl-2-vinylcyclopropane, *exo*-1 and *endo*-1.

plausibly associated with orbital overlap factors". We have located the transition structures for these homodienyl hydrogen shifts with ab initio molecular orbital theory and have identified in detail the overlap factors that lead to the endo stereoselectivity of this reaction. We note particularly the distortions that occur in an unfavorable transition state and how the molecule adapts to the poor overlap with which it is confronted.

The homodienyl hydrogen shift of *cis*-1-methyl-2-vinylcyclopropane (**1**) was studied with the GAUSSIAN 82 series of programs,[6] with the 3-21G basis set.[7] All structures were optimized with analytical gradient methods, and the stationary points on the potential surface were characterized by harmonic frequency calculations. Energetic results are shown in Table I and salient geometrical features are summarized in Figures 1 and 2.

A wide variety of homodienyl hydrogen shifts have been studied experimentally.[5,8,9] The homodienyl 1,5-hydrogen shift of the parent, **1**, has an activation energy of 31 kcal/mol, and only the cis product, **2**, is formed.[48b-d,10] The calculated activation energy at the RHF level with the 3-21G basis set is 18 kcal/mol higher than the experimental value. This apparently alarming difference is actually quite normal for RHF calculations on such reactions, since correlation energy corrections are greater for transition states than for reactants. For the parent ene reaction of propene and ethylene[3] and the 1,5-sigmatropic hydrogen shifts of 1,3-pentadiene.[11] the RHF activation energies are 21 and 17 kcal/mol too high. MP2 correlation energy calculations correct these values to give activation energies close to experimental values.[3,11] The inclusion of MP2 correlation energy corrections with the 6-31G* basis set should give an activation energy for the homodienyl hydrogen shift that is much closer to the experimental value with little geometrical change of the transition structure. However, due to the large size of this MP2 calculation, these calculations were not performed for the reaction of **1**. Although our calculated activation energy is too high, the activation energy difference of 17 kcal/mol between the endo and exo transition structures should be relatively reliable, as has been found for substituent effects on related pericyclic reactions.[2] This difference agrees with Berson's experimental estimate of ≥12 kcal/mol. The major point of interest in this paper is the origin of this 17 kcal/mol endo preference, which appears even at the RHF level.

The geometrical features of the transition structure for the parent ene reaction of propene with ethylene, **5**, the ground-state conformation of **1**, the endo transition structure, TS-endo, and exo transition structure, TS-exo, of the homodienyl hydrogen shift are shown in Figure 1.

The lowest energy conformation of **1** has the vinyl group exo to the cyclopropane ring (*exo*-**1** in Figure 2). The $C_5C_6C_1C_2$ dihedral angle is -141° and the HC_6C_1H dihedral angle is -175°. A rigid rotation of the vinyl group was performed at 30° intervals on **1** to ensure that the global minimum was found. The 12 single-point calculations indicate that there are two energy maxima about 2.8 and 20.5 kcal/mol above *exo*-**1**, at $C_5C_6C_1C_2$ dihedral angles of 150° and 0°, respectively. Full-geometry optimizations were then performed on the two minima giving the *exo*-**1** conformer and an endo conformation (*endo*-**1**), which is disfavored by 0.6 kcal/mol. The *endo*-**1** conformation has $C_5C_6C_1C_2$ and HC_6C_1H dihedral angles of 98° and 60°, respectively.

There have been many theoretical[12] and experimental[13] investigations of vinylcyclopropane (**6**). Previously it was found that ab initio calculations using the STO-3G basis set show a twofold rotational barrier[12b,d] for **6**. However, by using 3-21G or a larger basis set, the rotational barrier becomes threefold.[12a-c] The most recent theoretical study[12a] of vinylcyclopropane (**6**) using a medium-sized basis set predicts a threefold rotational barrier. The global minimum occurs at the s-trans conformation (HC_1C_4H, = 180°) while two equivalent gauche conformations (HC_1C_4H, 62°) are 1.2 kcal/mol higher in energy. The s-trans and gauche conformers are separated by a barrier of 3.1 kcal/mol. Experimentally, the difference in energy between the s-trans and gauche conformers is 1.1 kcal/mol by electron diffraction[13d] and Raman spectroscopy.[13b] Another vapor-phase study by Raman spectroscopy[13a] shows a $\Delta H = 1.43 \pm 0.14$ kcal/mol with a rotational barrier of 3.92 kcal/mol between the s-trans and gauche conformers.

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(5) Glass, D. S.; Boikess, R. S.; Winstein, S. *Tetrahedron Lett.* **1966**, 999–1008.

(6) Binkley, J. S.; Whiteside, R. A.; Raghavachari, K.; Seeger, R.; Defrees, D. J.; Schlegel, H. B.; Frisch, M. J.; Pople, J. A.; Kahn, L. R. GAUSSIAN 82; Carnegie-Mellon University, Pittsburgh, **1982**.

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(9) For references to related 1,5-homodienyl shifts, see: (a) Glass, D. S.; Zirner, J.; Winstein, S. *Proc. Chem. Soc., London* **1963**, 276. (b) Roth, W. R. *Justus Liebigs Ann. Chem.* **1964**, *671*, 10. (c) Grimme, W. *Chem. Ber.* **1965**, *98*, 756. (d) Crandall, J. K.; Watkins, R. J.; *Tetrahedron Lett.* **1967**, 1717. (e) Roberts, R. M.; Landolt, R. G.; Greene, R. N.; Heyer, E. W. *J. Am. Chem. Soc.* **1967**, *89*, 1404. (f) Ohloff, G. *Tetrahedron Lett.* **1965**, 3795.

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(11) Jensen, F.; Houk, K. N. *J. Am. Chem. Soc.* **1987**, *109*, 3139.

(12) (a) Klahn, B.; Dyczmons, V. *Theochem* **1985**, *122*, 75 and references therein. (b) De Maré, G. R.; Peterson, M. R. *Theochem.* **1982**, *89*, 213. (c) Skancke, A.; Boggs, J. E. *J. Mol. Struct.* **1979**, *51*, 267. (d) Hehre, W. J. *J. Am. Chem. Soc.* **1972**, *94*, 6592.

(13) (a) Carreira, L. A.; Towns, T. G.; Malloy, T. B., Jr. *J. Am .Chem. Soc.* **1978**, *100*, 385. (b) Salares, V. R.; Murphy, W. F.; Bernstein; H. J. *J. Raman Spectrosc.* **1978**, *7*, 147. (c) Codding, E. G.; Schwendeman, R. H. *J. Mol. Spectrosc.* **1974**, *49*, 226. (d) De Meijere, A.; Lüttke, W. *Tetrahedron* **1969**, *25*, 2047. (e) Lüttke, W.; de Meijere, A. *Angew. Chem., Int. Ed. Engl.* **1966**, *5*, 512. (f) Günther, H.; Klose, H.; Wendisch, D. *Tetrahedron* **1969**, *25*, 1531. (g) Günther, H.; Klose, H.; Cremer, D. *Chem. Ber.* **1971**, *104*, 3884. (h) De Maré, G. R.; Martin, J. S. *J. Am. Chem. Soc.* **1966**, *88*, 5033.

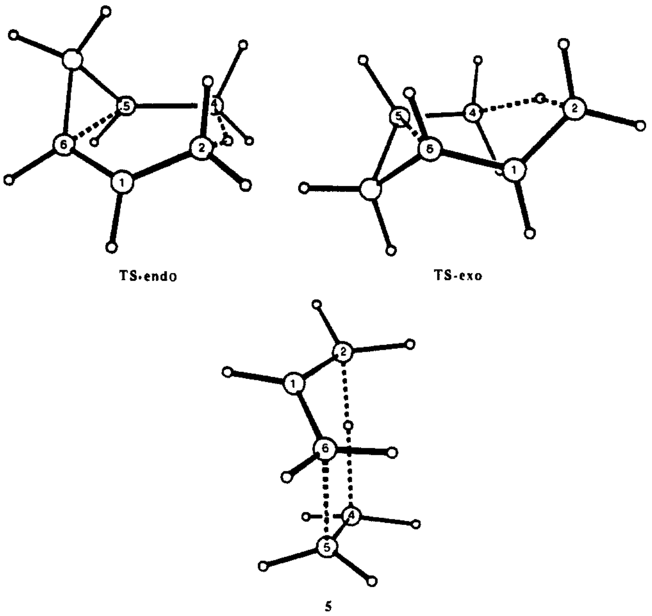

Figure 3. Views of the 3-21G transition structures of propene with ethylene, TS-endo, and TS-exo.

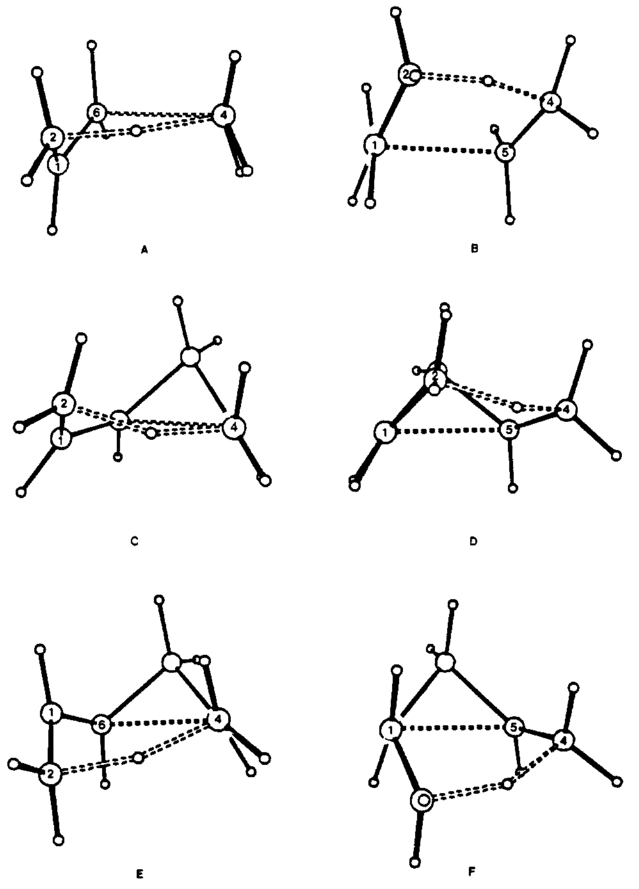

Figure 4. 3-21G transition structures of reactions of propene with ethylene, TS-endo, and TS-exo. Shown are Newman projections along the C_4C_5 and C_1C_6 bonds of all the transition structures. Numbering scheme is the same as in Figure 1.

The endo transition structure, TS-endo in Figure 3, can be viewed as a seven-membered ring with chairlike geometry. The atoms involved in bond reorganization resemble a six-membered ring of half-chair geometry. The exo transition structure, TS-exo, can also be viewed as a seven-membered ring with chairlike geometry, but differs from TS-endo in that the atoms of the six-membered ring are in a boatlike conformation. The origins of these geometrical tendencies are discussed below.

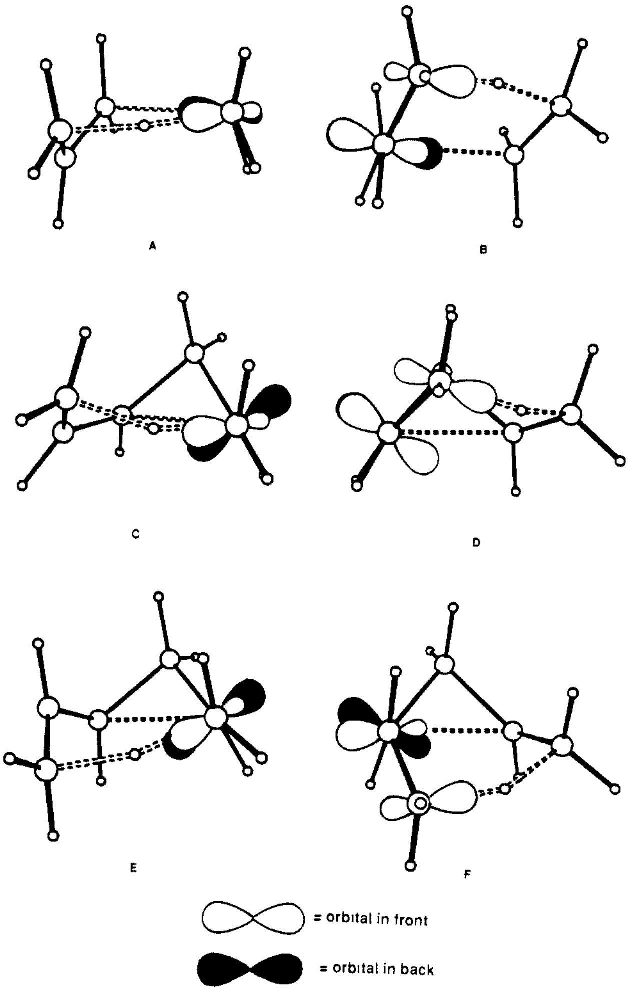

Figure 5. Orbital overlap between breaking cyclopropane σ-bond orbital and p orbitals on adjacent carbons.

The transition structure for the reaction of propene with ethylene resembles the envelope conformation of cyclopentane (**5** in Figure 3). The structure looks like an allyl radical attached to an ethylene moiety by two long CC bonds, and a hydrogen atom floating near the center of one of the bonds. As seen in Figure 4A, the breaking C_4H bond and forming C_5C_6 bond are nearly parallel, so that the hybrid orbital at C_4 overlaps with that on C_5. Thus, the ethylene π overlap is well-maintained in the transition structure. As shown in an alternate view of this structure (Figure 4B), the central atom of the propene moiety distorts slightly from planarity in order to maximize overlap of the p orbital with the slightly hybridized orbitals of the adjacent atoms. This maximizes π-overlap of the developing double bond while maintaining π-overlap of the breaking double bond. The allyl fragment resembles that deduced for the S_N2' transition state[14] and that present in some metal η^3 complexes.[15]

As shown in Figures 1 and 4, the major difference in the endo and exo transition structures occur in the dihedral angles about the C_1C_2, C_4C_5, and C_5C_6 bonds. The orbitals on C_5 and C_6 of the breaking CC bond appear to be Walsh orbitals.[16] In the highest occupied molecular orbital (HOMO) of both TS-endo and TS-exo the orbitals on C_5 and C_6 are directed toward each other and resemble the 1e′ symmetric orbital of vinylcyclopropane.

The differences between the endo and exo transition structure geometries occur in order to maximize overlap of the breaking

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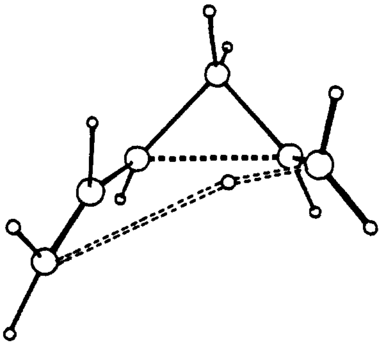
[14] Houk, K. N.; Paddon-Row, M. N.; Rondan, N. G. *Theochem* **1983**, *103*, 197.

[15] Boche, G.; Etxrodt, H.; Marsch, M.; Massa, W.; Baum, G.; Dietrich, H.; Mahdi, W. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 104 and references therein.

[16] Walsh, A. D. *Trans. Faraday Soc.* **1949**, *45*, 179.

CH bond with the breaking CC bond of the cyclopropane ring, as shown in Figures 4C,D and 5C,D. Small movement of the transferring hydrogen occurs in TS-endo. The CH breaking bond length is 1.351 Å in the endo transition structure. Here, little distortion from reactant is required in order to orient the molecule so that the hybridized orbital of C_4 aligns with the hybridized orbital on C_5 (see Figure 5C). Figure 4D shows a Newman projection along the C_1C_6 bond of TS-endo. As sketched in the corresponding orbital representation in Figure 5D, the π-orbital of C_1 is oriented as to maximize overlap with the orbital of C_6 of the developing double bond, while still maintaining π bonding with the hybrid orbital on C_2.

If we imagine a 180° rotation about the C_1C_6 bond, to produce the exo transition structure from TS-endo, structure **7** is obtained. This clearly has C_2 very far from the H, so that significant bonding between C_1 and the transferring H is not possible without significant distortion of the allyl moiety.



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In the resulting exo transition structure, the overlap of the hybrid orbitals on C_4 and C_5 is diminished somewhat (Figure 5E). In order to have overlap of the hydrogen 1s orbital with a p orbital at C_2, which now points away from the cyclopropane ring in this transition structure (Figure 4E), and still have overlap of the hybrid orbitals on C_4 and C_5, the CH breaking is much more advanced (1.446 Å). The nature of this distortion, which is brought about by the need to complete the hydrogen transfer, is easily seen by the staggered position of the methyl group and is reflected by the similar-forming CH bond lengths of 1.480 and 1.453 Å for TS-endo and TS-exo, respectively. As seen in Figure 4F and 5F, the π-orbital of C_1 is again oriented to maximize overlap of the developing double bond while maintaining overlap of the hybrid orbital of the former double bond.

The orbital overlap argument used to explain the origin of the endo preference of reaction can also be rephrased to focus on the conformational preference of a double bond in a seven-membered ring. The endo transition structure with the developing C_1C_6 double bond is analogous to a seven-membered ring containing a cis double bond, while the exo transition structure is analogous to a seven-membered ring with a trans double bond. In both transition structures, the C_1C_6 bond is about 65% double bond in character in comparison to the geometries of reactant **1** and products. In this respect the endo preference is easily understood as equivalent to the preference of a cis double bond, rather than a trans double bond in a seven-membered ring. The 17 kcal/mol difference results from the strain in forming the seven-membered ring in the exo transition state.

An interesting feature of TS-endo is that the Mulliken charge on the transferring hydrogen is 0.27 electron. This value is intermediate between the charge found on hydrogen in concerted 1,5-sigmatropic hydrogen shifts of 1,3-pentadiene (0.22) and 1,3-cyclopentadiene (0.31).[17] The Mulliken charge on the transferring hydrogen of TS-exo is much less at a value of 0.22. This implies a "tighter" transition state for the endo transformation,[17] which proceeds at a faster rate as compared to TS-exo.

Acknowledgment. We are grateful to the National Science Foundation and to the Harris Corporation for financial support of this research. We also thank Dr. Julius Rebek, Jr. and Weston T. Borden for discussions and their inexpensive intuitions ("it is a trans double bond in a seven-membered ring").

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Electronic Spectra and Chemical Reactivity

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Contribution from the Chemistry Department, University of California, Santa Barbara, California 93106. *Received August 17, 1987*

Abstract: Perturbation theory suggests a close relationship between the electronic spectra of molecules and energy barriers to possible unimolecular and bimolecular reactions. Considering only ν_{max}, the vertical frequency of the lowest excited state (of the same multiplicity), a number of interesting correlations can be made. It is necessary (a) to compare only groups of related molecules and (b) to use elementary spectroscopic theory to identify the nature of the lowest excited state. The relationship between vis-UV spectra and the stability of isomers is discussed.

For some chemists the presence of color in a molecule is an indication of reactivity, e.g. free radicals, but there are enough stable colored species to make the generalization of dubious value. Nevertheless, the vis-UV spectrum of a substance should contain much useful information about its chemical behavior. Certainly a detailed analysis of the spectrum in terms of the usual MO theory would yield information on valence shell MO's. Since chemical reactivity can also be discussed in terms of MO theory, a close connection must exist.

When detailed analysis is not available, what information can be gained from the gross features of the spectrum? The most obvious feature is the first absorption band, defining the lowest energy excited state. The purpose of this article is to show what information on chemical reactivity is contained in this band and to point out the pitfalls in the interpretation.

Table I contains the experimental data for a number of common, polyatomic molecules. The sources are the admirable reviews by Herzberg[1] and by Robin.[2] The convention is adopted of

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(1) Herzberg, G. *Electronic Spectra of Polyatomic Molecules*; Van Nostrand: Princeton, NJ, 1967.

(2) Robin, M. B. *Higher Excited States of Polyatomic Molecules*; Academic: New York, Vol. I, 1974; Vol. II, 1975; Vol. III, 1985.

(3) Note that Herzberg gives estimated term values for the equilibrium geometry of the excited state. These can differ substantially from ν_{max}. An extreme example is CO_2, where $\nu_{max} = 68\,000$ cm^{-1}, but the term value for the bent configuration in excited CO_2 is only $46\,000$ cm^{-1}.