

Can a Photochemical Reaction Be Concerted? A Theoretical Study of the Photochemical Sigmatropic Rearrangement of But-1-ene

Fernando Bernardi,^{*†} Massimo Olivucci,[‡] Michael A. Robb,^{*,‡} and Glauco Tonachini[§]

Contribution from the Dipartimento di Chimica "G. Ciamician" dell'Università di Bologna, Via Selmi 2, 40126 Bologna, Italy, Department of Chemistry, King's College, London, Strand, London WC2R 2LS, U.K., and Istituto di Chimica Organica, Torino, Italy.

Received August 13, 1991

Abstract: MC-SCF computations at the 4-31G level using a complete active space (CAS) of four orbitals demonstrate the existence of a concerted photochemical pathway for [1,2] and [1,3] alkyl sigmatropic shifts. The central feature of this concerted path is a conical intersection (e.g., a genuine crossing) between ground and excited state from which a fully efficient return to the ground state is possible. Thus the excited-state surface has no minimum with zero gradient (i.e., a critical point) but only a singularity which corresponds to the lowest energy point of a conical intersection between ground and excited states. Thus there is no bottleneck corresponding to a short-lived intermediate that would correspond to the minimum on the excited-state surface at an avoided crossing. Intrinsic reaction coordinate computations have been performed on the excited-state surface that demonstrate the existence of two "channels" on the excited-state surface that simply continue on the ground-state surface. One of these channels leads to a [1,2] sigmatropic shift, the other to a [1,3] sigmatropic shift. The proposed mechanism is consistent with experimental observations where both [1,2]- and [1,3]-shift products are observed, and where the migrating group moves according to a supra process with retention of configuration of the migrating group.

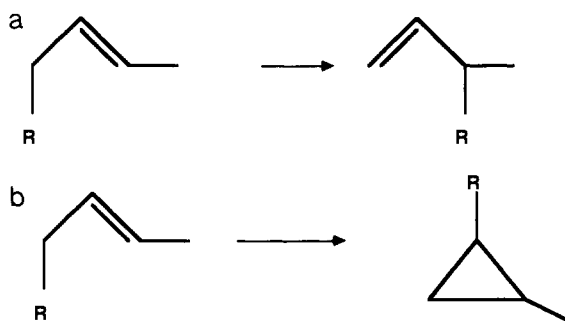
Introduction

In ground state reactivity problems the retention of rigid stereochemistry is usually assumed to imply a one-step concerted reaction mechanism. In contrast, one of the key features of the mechanism of a photochemical reaction is usually assumed to involve the existence of an excited-state minimum near an avoided crossing from which radiationless decay to the ground state occurs. However, this minimum must play the same role as an intermediate in a ground-state reaction, and unless the decay to the ground state is very rapid, the stereochemical integrity can be lost. Thus a minimum on the excited state corresponding to an avoided crossing not only forms a "bottleneck" for the reaction (since the decay probability will be less than 1) but also can lead to loss of stereospecificity.

Photochemical sigmatropic shift reactions are a class of reactions which have shown rigid stereochemistry and thus appear to be concerted.^{1a} For example, the stereochemistry of the photochemical sigmatropic shift on an allyl radical is rigid. The migrating group moves according to a supra process, and its configuration is retained.^{1b-f} However, there is some considerable variability in the distribution of products that one can observe even within the same group of reactions, i.e., mixtures of [1,2]- and [1,3]-shift products are obtained by irradiating the same reactant.^{1g,h} The purpose of this paper is to document a concerted photochemical mechanism that is consistent with the observed stereochemistry and the possibility of competing [1,2] and [1,3] shifts in a prototypical system: the sigmatropic shift of methyl on an allyl fragment in but-1-ene. The mechanism is shown to involve a conical intersection (i.e., a genuine crossing) between ground and excited states from which an efficient return from the excited state is possible. Thus there is no bottleneck in the decay process that can lead to loss of stereospecificity.

In a discussion of the mechanism of the photochemical sigmatropic shift of a group R on an allyl fragment (Scheme I), there are two issues: the distribution of products and the stereochemistry. The experimental information can be summarized as follows. The distribution of products resulting from a photochemical sigmatropic shift on a formal allyl radical fragment is affected by the nature of the system under investigation. For example, direct photolysis of cycloalkenes in the gas phase, where the

Scheme I



migrating group R is an alkyl radical, yields vinylcycloalkanes as a result of [1,3] sigmatropic shifts (path a of Scheme I) while no [1,2] sigmatropic shift (path b of Scheme I) products are observed.¹ⁱ The same behavior is observed when irradiating (dicyanomethylene)cyclohexanes where the migrating group is a formal benzyl or allyl radical. Direct irradiation of 1,5-hexadienes,^{1h} where the migrating group is an allyl radical, or of 7-phenylhepta-1,4-dienes,^{1g} where the migrating group is a benzyl radical, yields a mixture of [1,3]-shift products and cyclopropanes as a result of competing [1,3] and [1,2] sigmatropic shifts. Despite the variability in the distribution of products that one can observe even within the same group of reactants,^{1h} the stereochemistry of the photochemical sigmatropic shift on an allyl radical fragment

(1) (a) Turro, N. J. *Modern Molecular Photochemistry*; Benjamin Publishing: Reading, MA, 1978. Gilbert, A.; Baggott, J. *Essentials of Molecular Photochemistry*; Blackwell Scientific Publications: Oxford, 1991. Coxson, J. M.; Halton, B. *Organic Photochemistry*; Cambridge University Press: London, 1974; pp 47-57. (b) Cookson, R. C.; Gogte, J.; Hudec, J.; Mirza, N. A. *Tetrahedron Lett.* **1965**, 3955. (c) Brown, R. F. C.; Cookson, R. C.; Hudec, J. *Tetrahedron* **1968**, *24*, 3955. (d) Cookson, R. C.; Hudec, J.; Sharma, M. *Chem. Commun.* **1971**, 107-108. (e) Cookson, R. C.; Hudec, J.; Sharma, M. *Chem. Commun.* **1971**, 108. (f) Sharma, M. *J. Am. Chem. Soc.* **1975**, *97*, 1153-1160. (g) Sanford, E. C.; Hammond, G. S. *J. Am. Chem. Soc.* **1970**, *92*, 3497. (h) Manning, T. D. R.; Kropp, P. J. *J. Am. Chem. Soc.* **1981**, *103*, 889-897. (i) Inoue, Y.; Takamuku, S.; Sakurai, H. *J. Chem. Soc., Perkin Trans. 2* **1977**, 1635-1642. The direct irradiation of alkenes in the gas phase yields mainly fragmentation products through the production of carbenes. This behavior is related to the 189-201 nm region absorption maxima is isolated alkenes. However, in particularly strained bicycloalkenes the absorption maximum shifts to a region above 230 nm, and thus sigmatropic shifts become the main reactions (see, for example: Andrews, G. D.; Baldwin, J. E. *J. Am. Chem. Soc.* **1977**, *99*, 4851-4853).

^{*} Dipartimento di Chimica "G. Ciamician" dell'Università di Bologna.

[‡] Chemistry Department, King's College, London.

[§] Istituto di Chimica Organica, Torino.

does not appear to change. The migrating group moves according to a supra process, and there is no evidence for an antara path in the photochemical reaction. Furthermore, experimental studies on [1,3] allyl shifts of benzyl and allyl groups show a complete retention of configuration of the migrating centers.^{1b-f} This behavior is predicted by the Woodward-Hoffmann selection rules^{1a,2} for [1,3] concerted sigmatropic shifts. However, as pointed out by other workers,¹⁸ the same rules make no prediction that [1,3] and [1,2] shifts should be competitive in the same system with the same stereochemistry.

In this paper we shall be concerned with a theoretical and computational study of the thermal and photochemical sigmatropic shift on the model system but-1-ene. In agreement with experimental evidence we will assume that triplet excited states are not involved in the process since triplet sensitization normally diverts the reaction toward cis-trans isomerizations and, where possible, cycloadditions rather than sigmatropic shifts. Thus we will concentrate on the relationship between ground state and covalent singlet excited state.

Now let us elaborate briefly on the difference between a photochemical mechanism that involves a conical intersection and a mechanism via an avoided crossing. The existence of a *concerted* reaction pathway for a photochemical reaction must involve initial downhill motion on a valley on the excited-state potential energy surface which "continues" on the ground-state potential energy surface at a *point of intersection*. (Two states *even with the same symmetry* will intersect in an $(n-2)$ -dimensional hyperline as the energy is plotted against n nuclear coordinates.^{3a-d} In the simplest case of three nuclear coordinates this will yield a point.) The dynamics of the decay through conical intersections has been rigorously investigated elsewhere.^{3m-o} Results for realistic model systems show that the decay occurs rapidly within less than 1 vibrational period from the excited to the ground adiabatic state.^{3o} Here we will give only a qualitative pictorial view of this process, which we have illustrated schematically in Figure 1b.

The picture of motion through a conical intersection differs in a fundamental way from the classical picture of the decay at the "funnel" corresponding to an avoided crossing (Figure 1a). In the case of an avoided crossing, the system, after excitation, undergoes decay to the lowest energy singlet excited state and stabilizes on the minimum on the excited state corresponding to an avoiding crossing. It then undergoes a process of radiationless decay to the ground state. (For a good discussion of these points the reader is referred to textbooks.^{3j,4a}) The decay probability P from excited state to ground state can be approximated by the Landau Zener formula (see the discussion of Salem^{4a} or Tully and Preston^{4b}):

$$P = \exp(-\pi^2 g^2 / h\nu\delta s)$$

where ν is the nuclear velocity along the reaction coordinate, g is the energy gap at the avoided crossing, and δs is the difference in slopes between the intersecting "diabatic" states. Clearly the

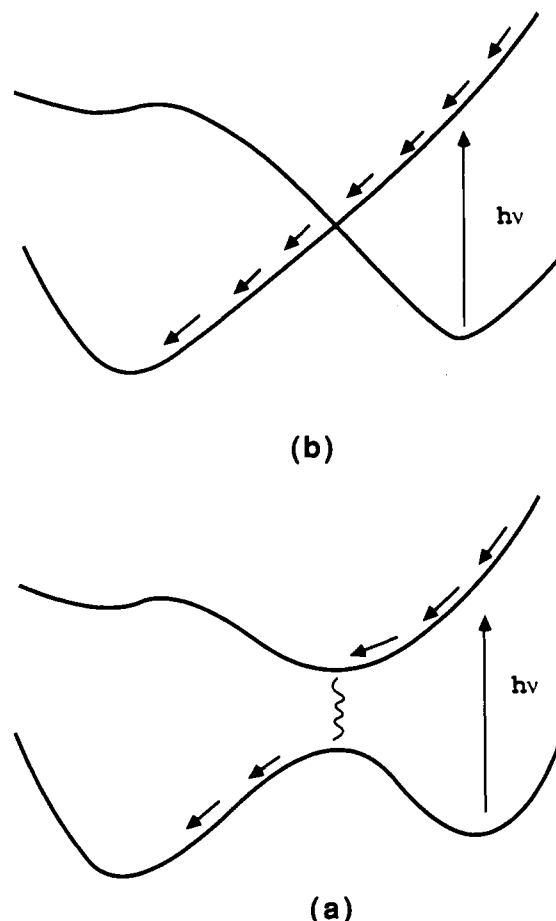


Figure 1. Schematic representations of the radiationless decay between states of the same spin multiplicity. (a) Decay through an avoided crossing. (b) Passage through a conical intersection.

larger the value of g , the smaller is P . At a conical intersection, on the other hand, $g = 0$ and $P = 1$, so the decay occurs within a single vibrational period and thus follows a *concerted* route from the excited state to the ground state.

We have recently documented⁵ the existence of a conical intersection between the singlet excited state and ground-state potential energy surfaces for the $2s + 2s$ photochemical cycloaddition of two alkenes. As we will now show, the stereochemistry and possible product distribution observed for the photochemical sigmatropic shift are also consequences of the existence of a conical intersection. We now give some insight into the way in which such conical intersections can arise using a simple valence bond (VB) model.

VB Model of a Conical Intersection in But-1-ene

A detailed mathematical discussion of conical intersections can be found in refs 3e-h. A discussion from a more chemical point of view can be found in the book of Michl^{3j} and in refs 3k,l. In two previous papers^{5a,b} we have discussed the VB treatment of a system with four active orbitals (i.e., those involved in bond breaking/making) and four electrons in some detail. In other work, we have demonstrated explicitly how an MC-SCF wavefunction can be transformed to this VB basis showing that the energies are unchanged from the MC-SCF results.^{5c,6} Here we shall limit our discussion to a demonstration of the way in which a conical intersection can occur on the potential energy surface for the sigmatropic shift of methyl in but-1-ene.

(2) Woodward, R. B.; Hoffmann, R. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 781.

(3) (a) Von Neumann, J.; Wigner, E. *Physik. Z.* **1929**, *30*, 467. (b) Teller, E. *J. Phys. Chem.* **1937**, *41*, 109. (c) Herzberg, G.; Longuet-Higgins, H. C. *Trans. Faraday Soc.* **1963**, *59*, 77. (d) Herzberg, G. *The Electronic Spectra of Polyatomic Molecules*; Van Nostrand: Princeton, 1966; pp 442. (e) Mead, C. A.; Truhlar, D. G. *J. Chem. Phys.* **1979**, *70*, 2284. (f) Mead, C. A. *Chem. Phys.* **1980**, *49*, 23. (g) Keating, S. P.; Mead, C. A. *J. Chem. Phys.* **1985**, *82*, 5102. (h) Keating, S. P.; Mead, C. A. *J. Chem. Phys.* **1987**, *86*, 2152. (i) Gerhartz, W.; Poshusta, R. D.; Michl, J. *J. Am. Chem. Soc.* **1977**, *99*, 4263. (j) Michl, J.; Bonacic-Koutecky, V. *Electronic Aspects of Organic Photochemistry*; Wiley: New York, 1990. (k) Bonacic-Koutecky, V.; Koutecky, J.; Michl, J. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 170-189. (l) Davidson, R. E.; Borden, W. T.; Smith, J. *J. Am. Chem. Soc.* **1978**, *100*, 3299-3302. (m) Mead, C. A. *The Born-Oppenheimer approximation in molecular quantum mechanics. In Mathematical frontiers in computational chemical physics*; Truhlar, D. G., Ed.; Springer: New York, 1987; Chapter 1, pp 1-17. (n) Blais, N. C.; Truhlar, D. G.; Mead, C. A. *J. Chem. Phys.* **1988**, *89*, 6204-6208. (o) Manthe, U.; Koppel, H. *J. Chem. Phys.* **1990**, *93*, 1658-1669.

(4) (a) Salem, L. *Electrons in Chemical Reactions: First Principles*; Wiley: New York, 1982. (b) Tully, J. C.; Preston, R. K. *J. Chem. Phys.* **1971**, *55*, 562.

(5) (a) Bernardi, F.; De, S.; Olivucci, M.; Robb, M. A. *J. Am. Chem. Soc.* **1990**, *112*, 1737-1744. (b) Bernardi, F.; Olivucci, M.; Robb, M. A. *Acc. Chem. Res.* **1990**, *23*, 405-412. (c) Bernardi, F.; Olivucci, M.; Robb, M. A. *J. Am. Chem. Soc.* **1992**, *114*, 1606.

(6) Bernardi, F.; Olivucci, M.; McDouall, J. J. W.; Robb, M. A. *J. Chem. Phys.* **1988**, *89*, 6365.

In the following discussion we shall not make use of any group-theoretical arguments. In the Appendix we give a formal discussion of the way in which some of these ideas can be viewed as having their origin in symmetry effects. The arguments presented in what follows will remain valid even when symmetry is not present (i.e., when substituents are present).

There are four active orbitals involved in the sigmatropic shift: the three singly occupied p orbitals belonging to the allyl π -system (p^π orbitals) and the singly occupied p orbital of the methyl radical as shown in Figure 2a. There are only two independent VB structures (spin couplings) which can be chosen in an arbitrary way (see Appendix and ref 5). The nature of these two possible spin couplings is irrelevant to the present discussion. The two possible energy levels can be written in terms of coulomb Q and exchange T energies as

$$E_{gs} = Q - T \quad (1a)$$

$$E_{ex} = Q + T \quad (1b)$$

The term Q is the "coulomb energy" and includes all the energy effects associated with the inactive orbitals (plus nuclear-nuclear repulsion) in addition to the nuclear-electron attractions and electron-electron repulsions of the active space electrons. The term T is the "total exchange energy", and its value is given in terms of exchange integrals K_{ij} involving pairs of active orbitals i and j by the London formula:⁷

$$T = (K_a^2 + K_b^2 + K_c^2 - K_a K_b - K_a K_c - K_b K_c)^{1/2} \quad (2)$$

where K_a , K_b , and K_c are defined⁵ in terms of the two-center exchange integrals as

$$K_a = K_{12} + K_{34} \quad (3a)$$

$$K_b = K_{14} + K_{23} \quad (3b)$$

$$K_c = K_{13} + K_{24} \quad (3c)$$

The two-center exchange integrals K_{ij} involving pairs of nonorthogonal active orbitals i and j that occur in the London formula (eq 2) have the same interpretation as those that occur in the Heitler-London treatment of H_2 and can be written as

$$K_{ij} = [ij|ij] + 2s_{ij}\langle ih|j \rangle \quad (4)$$

The $[ij|ij]$ is the usual two-electron-exchange repulsion integral, $\langle ih|j \rangle$ is the one-electron-exchange integral (kinetic plus nuclear electron attraction), and s_{ij} is the overlap integral between orbitals i and j . The three different sums of exchange integrals in eqs 3 are illustrated in Figure 2 for later reference.

The exchange integral K_{ij} plays a particularly important role in our discussion due to its simple and predictable behavior, which we will now briefly discuss. The exchange integral is dominated by the overlap (s_{ij}) factor in eq 4. In the present case the overlaps involve the three allyl p^π orbitals and the p orbital of the methyl. When an overlap (s_{ij}) drops to 0, the value of K_{ij} drops as well. This occurs when the distance between sites i and j gets large or when the dihedral angle between two p orbitals becomes 90° .

The existence of molecular structures corresponding to conical intersections between singlet excited state and ground-state potential energy surfaces can be predicted in a straightforward way on the basis of eqs 1a,b. At a conical intersection the "total exchange energy" T is 0 since the two states are, by definition, degenerate (i.e., $E_{gs} = E_{ex}$), and therefore, by virtue of eq 2, the following two independent relationships must hold:

$$K_a = K_b \quad (5a)$$

$$K_a = K_c \text{ (or } K_b = K_c) \quad (5b)$$

Expressions 5a and 5b, when combined with the schematic representation of eq 3 in Figure 2b-d, enables the a priori prediction of these molecular structures belonging to conical inter-

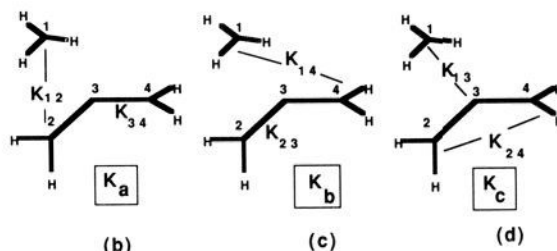
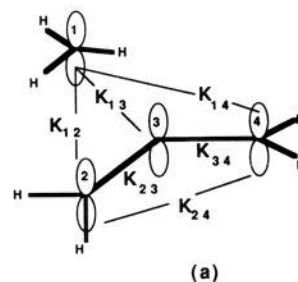


Figure 2. Exchange integrals in but-1-ene. (a) Exchange integrals between pairs of singly occupied atomic orbitals. The pairs of exchange integrals contributing to (b) K_a , (c) K_b , and (d) K_c (eqs 2, 3, and 5).

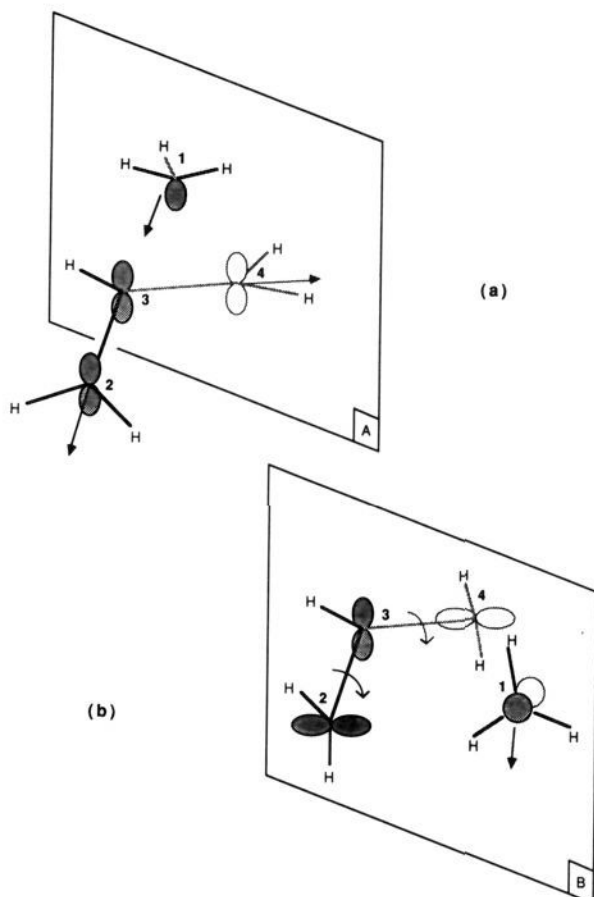


Figure 3. Two-dimensional cross sections (shaded areas on planes A and B) of the set of molecular structures associated with two conical intersections in but-1-ene. Region a corresponds to a supra-like conical intersection. Region b corresponds to an antara-like conical intersection.

sections. This is possible because the behavior of the exchange integrals K_{ij} (eqs 3a-c) is easily predicted as a function of the geometrical coordinates. Thus a structure corresponding to a conical intersection can be predicted by distorting the molecular structure of the system in such a way as to satisfy those two equations.

(7) Eyring, H.; Walter, J.; Kimball, G. *Quantum Chemistry*; Wiley: New York, 1944.

Using this approach one is led to predict two general regions (regions a and b in Figure 3) of geometrical structures where the ground- and excited-state surfaces must intersect. These are shown in Figure 3 as shaded areas on planes *A* (supra-like) and *B* (antara-like). Region a (Figure 3a) is characterized by a pyramidalized CH_3 radical fragment with its singly occupied orbital overlapping with the orbital on carbon 3. Region b (Figure 3b) is characterized by a planar CH_3 radical fragment with its singly occupied orbital overlapping with the orbitals on carbons 2 and 4. This region can be spanned by distorting the geometries of the system according to the arrows in Figure 3a,b. We now proceed to justify this prediction using qualitative considerations based upon the conditions of eq 5 and the schematic representation of the exchange integrals of Figure 2.

In region a (Figure 3a), eq 5a (compare parts b and c of Figure 2) is always satisfied if we maintain a symmetry constraint corresponding to plane *A*. Under that constraint, we find that $K_{12} = K_{14}$ and $K_{23} = K_{34}$. Condition 5b (compare parts b and d of Figure 2) can only be satisfied when the distance between carbon 1 and carbon 3 is such that $K_{13} + K_{24} (=K_c)$ matches $K_{12} + K_{34} (=K_a)$. It is then very easy to imagine how that situation could be reached in an infinite and continuous number of cases, i.e., for any value of the $\text{C}_2\text{-C}_3$ bond length (assumed equal to the $\text{C}_3\text{-C}_4$ bond length), we can always find a value of the bond length $\text{C}_1\text{-C}_3$ such that $K_a = K_c$.

In region b eq 5a is always satisfied if we maintain, by analogy with region a, a plane of symmetry *B*. Equation 5b (compare parts b and d of Figure 2) will be satisfied only if the distance between carbon 2 and carbon 4 is such that K_{24} is equal to K_a , since K_{13} is 0 by symmetry. Again a continuous region of geometries can be found by suitable rotation of the CH_2 group in the allyl radical fragment about the $\text{C}_2\text{-C}_3$ and $\text{C}_3\text{-C}_4$ bonds which changes K_{24} .

A more formal discussion which traces the conical intersection via descent in subgroups from a Jahn-Teller effect in T_d symmetry is given in the Appendix.

The preceding discussion illustrates that a conical intersection is not a single point on the potential energy surface but rather a smooth subset of points. Rigorously, a conical intersection is an $(n-2)$ -dimensional subset of the two n -dimensional potential energy surfaces (ground- and excited-state potential energy surfaces) where n is the number of independent geometrical coordinates of the system (i.e., number of degrees of freedom). Of course, we are interested in the lowest energy point on this $(n-2)$ -dimensional hyperline. From a practical point of view, we can simply minimize the energy on the excited-state surface. The lowest energy point on the excited-state surface corresponds to a minimum of the energy; however, it is a singularity where the gradient is not 0 (the left and right gradients are different) and two of the second derivatives are undefined. In spite of this, we can treat the molecular structure corresponding to the lowest energy point on the conical intersection in the same way as any other well-defined point (e.g., transition state) in a reaction mechanism.

Results and Discussion

(i) **Global Representation of the Reaction Surface.** In two previous papers^{5a,b} we have shown how MC-SCF results can be transformed to a valence bond representation and the coulomb and exchange integrals fitted to simple analytic functions as a function of the distance and orientation of the orbitals on the two centers. This procedure enables one to obtain a global representation of the potential surface whose accuracy is limited only by the accuracy of the fitting procedure used. Recently,^{5c} we have extended this method and combined it with molecular mechanics to produce a general modeling algorithm which we shall refer to as molecular mechanics-valence bond (MM-VB). This method yields a global representation of the potential surface that is accurate enough to reproduce the surface topology correctly. Thus in order to illustrate the global structure of the potential surface we shall present some preliminary results obtained with this technique first. The interesting features will then be documented with MC-SCF computations using a complete active space (CAS).

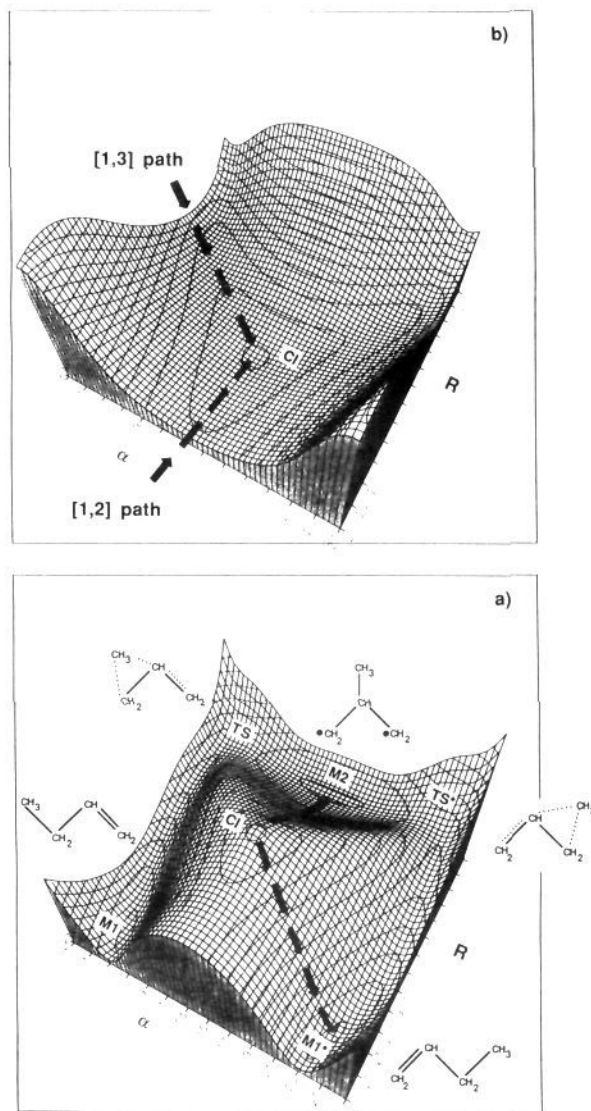


Figure 4. (a) Ground-state and (b) excited-state potential energy surfaces for [1,2] and [1,3] sigmatropic shifts in but-1-ene. The *R* and α axes are based upon linear interpolation (*R* axis) and parabolic interpolation (α axis) passing through six structures including the optimized minima. The *R* axis corresponds mainly to the distance *R* and the α axis to the angle α defined in Scheme II. M1, TS, M2, TS*, M1*, and CI indicate the location of the various critical points and the conical intersection on the surfaces. The "[1,3] path" and "[1,2] path" arrows show the possible "pathways" for the photochemical [1,3] and [1,2] shifts. (Because of the resolution of the grid and the smoothing of the contouring algorithm used in plotting, one sees the conical intersection as two opposed smooth surfaces rather than singularities.)

In Figure 4 we show the potential surface for the ground and excited states for the sigmatropic shift of a methyl fragment. The independent variables in these surfaces are dominated by *R* (bottom left to top right in Figure 4) and α (bottom right to top left) as shown in Scheme II. The values of the remaining variables are obtained using an interpolation of geometrical parameters from optimized structures.

The most important features of the thermal and photochemical reactions can now be discussed. We begin with a discussion of the ground-state surface (Figure 4a). There is a concerted pathway for the thermal [1,2] sigmatropic shift of CH_3 following one of the two valleys connecting one of the equivalent minima M1 (but-1-ene) to a transition state for a [1,2] sigmatropic shift TS and then to a diradical minimum M2. The other important feature of the surface is the very high energy region at the center of the surface which corresponds to the lower part of a conical intersection CI. The upper part of the *same* conical intersection

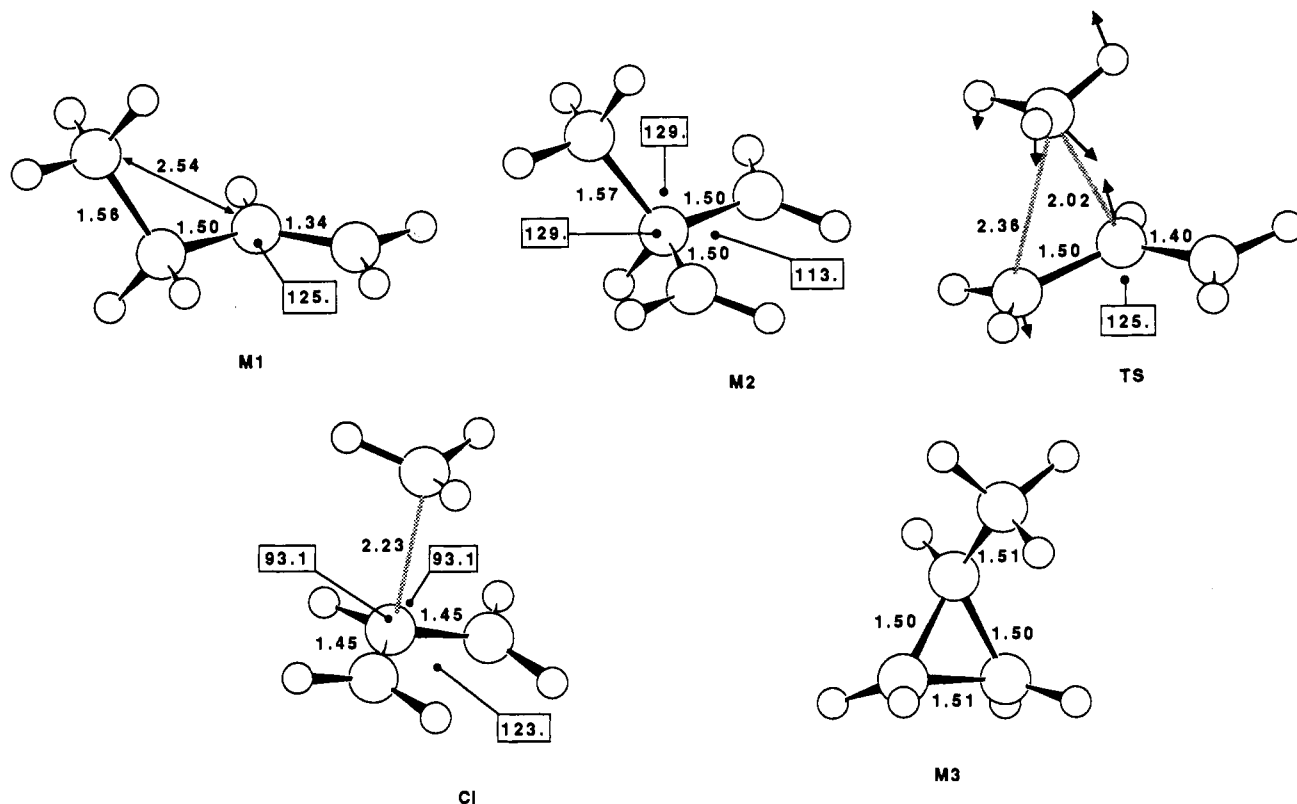
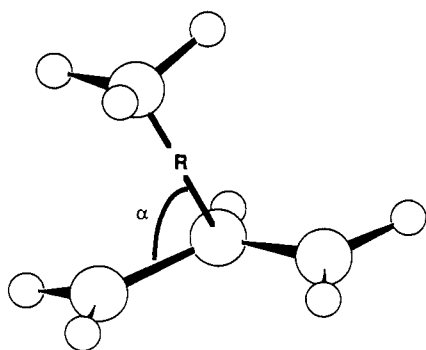


Figure 5. CAS-SCF/4-31G optimized molecular structures for the ground-state critical points M1, M2, M3, and TS and for the conical intersection CI. The arrows drawn on structure TS represent a displacement along the eigenvector corresponding to the imaginary frequency. The values of bond lengths are given in angstroms and the values of planar angles in degrees.

Scheme II



can be found on the excited-state potential energy surface as shown in Figure 4b. In fact, the bottom of the conical intersection at the center of the surface occurs at exactly the same energy of the high-energy region on the ground-state surface. Because of the resolution of the grid and the smoothing of the contouring algorithm used in plotting this figure, the singularities get smoothed somewhat and one sees the conical intersection as two opposed smooth surfaces.

The excited-state potential energy surface (Figure 4b) shows some additional features which are important from a mechanistic point of view. Notice that there are three different valleys starting at the edges of the surface leading to the conical intersection structure CI. There are two symmetric valleys indicated as "[1,3] path" and a valley marked "[1,2] path". We shall discuss the "[1,3] path" valleys first. The two "[1,3] path" valleys start (on the excited-state surface) at geometries similar to TS (i.e., the transition state for the [1,2] shift on the ground-state surface), and then they disappear at the conical intersection. If we now turn our attention to the ground-state potential energy surface (Figure 4a), we observe the path that has started out on the two "[1,3] path" valleys on the excited-state surface, "continues" on two ground-state valleys, and ends up at the two but-1-ene minima M1 and M1*. Thus a reaction path that starts on one of the "[1,3]

path" valleys on the excited state ends up on the ground-state potential energy surface after passing through the conical intersection CI. A mechanistic picture involving a concerted process for the photochemical [1,3] shift of M1 to M1* can now be easily formulated. The excited species, which arrives on the singlet excited-state surface after irradiation of M1, populates the "[1,3] path" valley before undergoing a fully efficient decay to M1*.

In an analogous way we can visualize a concerted photochemical reaction mechanism for the [1,2] shift of M1 to M2. In fact, the "[1,2] path" valley, which starts from a geometry in which the CH₃ radical attacks carbon 3 on the allyl radical, reaches the conical intersection and emerges on a ground-state-surface valley just near the diradical M2. Thus if the "[1,2] path" becomes populated, the diradical M2 is reached through a concerted pathway, and the system undergoes subsequent cyclization to the cyclopropane M3.

It now remains to verify these features from *ab initio* computations.

(ii) **Ab Initio Computations of Ground- and Excited-State Critical Points.** Our purpose in this section is to confirm the mechanism proposed in the previous subsection using *ab initio* MC-SCF gradient optimizations. However, we must first emphasize that we shall be concerned only with the photochemical process. The initial photophysical process must involve direct excitation to some highly excited state which decays rapidly via internal conversion to the lowest energy singlet excited state on which the photochemical reaction takes place. We have made no attempt to study this photophysical process, which probably involves Rydberg states and would require a very careful choice of basis sets.

The optimized geometries, IRC (intrinsic reaction coordinate) structures, and energies presented in this paper have been calculated via *ab initio* CAS-SCF/4-31G calculations. The only exception is structure M3 (methylcyclopropane), which has been optimized using SCF theory in the same basis set. The nature of the transition structure (TS) and radical intermediate (M2) has been confirmed by frequency calculation. The relevant geometrical parameters of the critical points for the ground-state

Table I. Energies of Minima, Transition States, and the Lowest Energy Point of the Conical Intersection for the Sigmatropic Rearrangement of But-1-ene

structure (Figure 5)	energy (E_h) CAS-SCF/4-31G
M1	-155.9284
M2	-155.8182
M3	-155.8643 ^a
TS	-155.7703
CI	-155.7512
reactants ($^{\cdot}\text{CH}_3$, $^{\cdot}\text{C}_3\text{H}_5$)	-155.8248

^aSCF/4-31G.

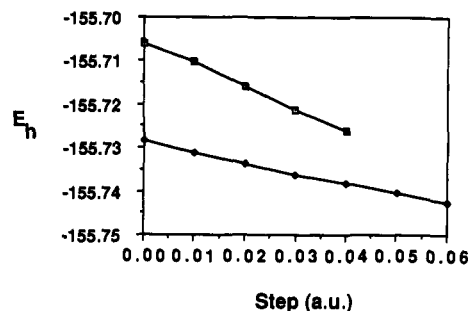
(thermal) sigmatropic shifts in 1-butene are shown in Figure 5. The normal mode corresponding to the imaginary frequency for TS is also indicated.

Some aspects of the technique used to optimize the structure of the conical intersection (CI), which corresponds to a singularity where the energy is minimized but the gradient is not 0, on the excited-state surface need a brief mention. Firstly, at a conical intersection point, the excited state and the ground state are degenerate and a standard CAS-SCF calculation on the excited state will not converge. Thus one must use "state-averaged" CAS-SCF in the final stages of the optimization. Secondly, a conical intersection is not really a critical point on the potential energy surface but rather a singularity. Thus the gradient at the conical intersection will never be 0. Consequently, we have minimized the energy of the excited state using a small maximum step size (~ 0.02 Å) and have terminated the optimization when no further improvement on the energy is observed. The optimized geometry of the lowest energy point on the conical intersection is shown in Figure 5.

The thermal [1,2] shift occurs via a concerted mechanism involving the transition structure TS. The proposed product for this process, the diradical intermediate, M2, is characterized by two very small vibrational frequencies ($103.52i$ and 137.60 cm^{-1}) corresponding respectively to the conrotatory and disrotatory (nearly-free) rotation of the two terminal methylenes. Since one of the two frequencies is imaginary, the structure clearly corresponds to a transition state between two different rotamers. The flatness of the diradical region was also confirmed by the failure of various attempts at finding a net transition structure for the ring closure of M2 to methylcyclopropane M3 which, therefore, seems to occur without a barrier.

In the case of the thermal [1,3] shift we attempted to locate two types of C_s symmetry transition structures, one consistent with retention of configuration at the migrating center, the other consistent with inversion. However, both optimizations led only to dissociation of the CH_3 radical. Thus the thermal [1,3] shift appears to occur through a nonconcerted process consistent with a dissociation-reassociation of the methyl radical fragment to the two terminal methylenes of the allyl fragment. Of course, one could expect to find two such critical points if the migrating center were permanently connected to the allyl radical fragment as is the case in cyclic compounds. Indeed CAS-SCF/3-21G calculations⁸ performed on bicyclo[2.1.0]pent-2-ene for a [1,3] shift have demonstrated the existence of these two C_s critical points (a transition state and a minimum).

The energies for the critical points discussed above are reported in Table I. The CAS-SCF energy difference between but-1-ene and allyl + methyl is about 34 kcal/mol lower than the barrier for the [1,2] shift (M1 \rightarrow TS), which suggests that the fragmentation-[1,3] shift process is strongly favored. While the stereochemistry associated with the thermal [1,2] shift pathway is clearly consistent with a retention of configuration at the migrating center, the stereochemistry of the nonconcerted (i.e., via fragmentation) [1,3] shift can, in principle, involve racemization. However, during our attempts at optimization of [1,3] shift transition states, which always ultimately converged to a CH_3 radical and an allyl radical, the pathway involving inversion was always lower in energy than the pathway involving retention. In

**Figure 6.** Excited-state CAS-SCF/4-31G intrinsic reaction coordinate energies (E_h) for [1,3] (\square) and [1,2] (\blacklozenge) pathways.

the calculation performed on bicyclo[2.1.0]pent-2-ene,⁸ the author finds one C_s transition structure consistent with inversion of configuration and a 7.7 kcal/mol higher minimum whose structure is consistent with a retention of configuration process.

Now we turn our attention to the excited state. There appears to be no minimum (in the usual meaning of the word) in the excited state. Rather all attempts at optimizing a minimum on the singlet excited state potential energy surface converges to a point in which the energies of the ground state and excited state are nearly degenerate. Under such conditions, a standard CAS-SCF procedure diverges, and the optimization is thus continued using the technique described in the previous section. The resulting optimized structure, which is shown in Figure 5 (CI), represents the lowest energy point on the conical intersection corresponding to region a (see Figure 3a). The CAS-SCF energy of structure CI lies, as shown in Table I, only 12 kcal/mol above the highest ground-state critical point, namely, the [1,2] shift transition state (TS). Thus the surface topology of the excited-state surface discussed in the previous section is confirmed. Thus the rigorous ab initio CAS-SCF location of a conical intersection structure which coincides with a minimum (probably the absolute minimum) on the excited-state surface strongly supports the existence of a concerted reaction pathway starting on the excited state and ending on the ground state. Furthermore, the structure CI is completely consistent with a pathway characterized by a supra process with retention of configuration at the migrating center.

The search for a conical intersection structure belonging to the region b (Figure 3), which would be consistent with an antarafacial process with inversion of configuration at the migrating center, has also been attempted. While we can find structures that lie on the conical intersection, attempts at optimization lead only to dissociation. Thus this photochemical pathway does not appear to exist, and this is consistent with experiment.

While the ab initio results discussed above provide information on the critical points of both the ground- and excited-state surfaces and provide support for the existence of a photochemical concerted pathway via a conical intersection, they do not provide information on the global structure of those potential energy surfaces. In particular, it is not possible to gain any insight into the nature of pathways (valleys) on the excited-state potential energy surface and therefore on what type of process (for example, [1,2] or [1,3] shift) may pass through the conical intersection CI. In order to substantiate our earlier conjecture on this problem, we now report the results of two different ab initio intrinsic reaction coordinate (IRC) calculations on the n -dimensional excited-state potential energy surface. As we shall see, the mechanistic scenario for the photochemical [1,3] and [1,2] sigmatropic shifts, which was proposed on the basis of a simulated two-dimensional cross section, is consistent with the result of accurate CAS-SCF calculation.

The energy along an IRC corresponding to the [1,3] and [1,2] shift pathways is shown in Figure 6. The calculation of the [1,3] shift IRC has been started from the geometry TS, as suggested by the simulated "[1,3] path" in Figure 4b. For the "[1,2] path" we have used a geometry describing the attack ($R = 2.45$ Å) of a CH_3 radical on the central carbon of allyl radical. Since such geometries do not correspond to critical points on the excited-state surface, we have started the IRC calculation by following the

(8) Jensen, F. *J. Am. Chem. Soc.* 1989, 111, 4643-4647.

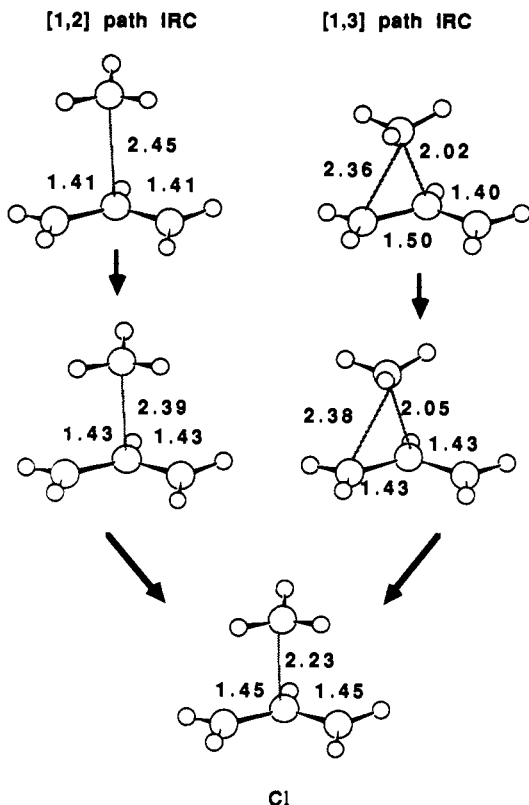


Figure 7. Excited-state CAS-SCF/4-31G intrinsic reaction coordinate optimized structures. The two structures corresponding to the starting point of the intrinsic reaction coordinate are shown at the top of the figure. The last structure obtained before the calculation failed to converge as shown in the middle of the figure with the conical intersection geometry shown at the bottom. The values of bond lengths are given in angstroms and the values of planar angles in degrees.

eigenvector of the Hessian which has the largest overlap with the gradient. The IRC calculation is stopped when a point on the conical intersection is reached (i.e., when the CAS-SCF energy fails to converge). As shown in Figure 6, the "[1,3] path" is higher in energy than the "[1,2] path" but, consistent with the results shown in Figure 4b, decreases more rapidly. The relevant geometrical parameters for the starting and final points of the two IRC are shown in Figure 7. One can see that both starting structures undergo a deformation toward the geometry of the conical intersection structure CI. The deformation along the "[1,3] path" is dominated by the asymmetric stretching of the allyl fragment which moves the system toward a structure with C_s symmetry. The starting point along the "[1,2] path" already has C_s symmetry, and thus the deformation toward CI is dominated by a symmetric stretching of the allyl fragment and by the distance R .

The geometry and orientation of the migrating CH_3 radical along the [1,2] and [1,3] pathways is consistent with a supra process and retention of configuration at the migrating carbon. Thus, not only the structure of the CI but also the whole pathway acts as a constraint to the stereochemistry of the two reactive processes. Although our results are in general consistent with the observed stereochemistry of sigmatropic shifts, they deal with the final part of the photochemical process which occurs when other events could have already taken place. For example, since the [1,2]-shift pathway starts on a very flat region of the potential energy surface, a certain amount of isomerization could also be expected.

Conclusions

MC-SCF computations at the 4-31G level using a CAS space of four orbitals and four electrons confirm the existence of a concerted photochemical pathway for [1,2] and [1,3] alkyl sigmatropic shifts. Following the initial photophysical process (direct excitation to some state which decays via internal conversion),

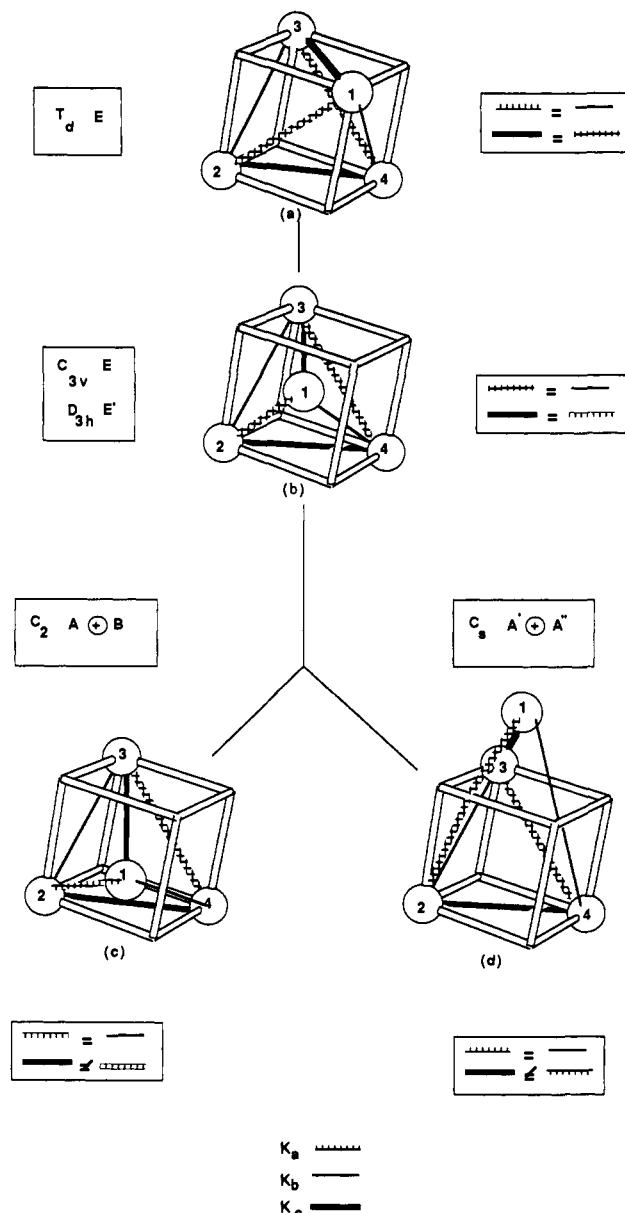


Figure 8. Symmetry analysis of the conical intersection region. The hashed, solid, and bold lines refer to the sums of exchange integrals K_a , K_b , and K_c . (a) T_d symmetry. (b) C_{3v} or D_{3h} symmetry. (c) C_2 symmetry. (d) C_s symmetry.

which has not been studied, the system arrives on the lowest energy excited-state surface. This surface does not appear to have a minimum in the normal sense (0 gradient) but rather a singularity which corresponds to the lowest energy point of a conical intersection (i.e., a genuine crossing) between ground and excited states. The occurrence of a conical intersection implies that the return to the ground state must be fully efficient. Thus there is no bottleneck corresponding to a short-lived intermediate that would correspond to the minimum on the excited-state surface at an avoided crossing. Consequently the stereochemistry is preserved, and the process is concerted. The IRC computations demonstrate the existence of two "channels" on the excited-state surface that simply "continue" on the ground-state surface. One of these channels leads to a [1,2] sigmatropic shift, the other to a [1,3] sigmatropic shift.

The proposed mechanism is consistent with experimental observations^{1b-h} where both [1,2]- and [1,3]-shift products are observed and where the migrating group moves according to a supra process with retention of configuration of the migrating group.

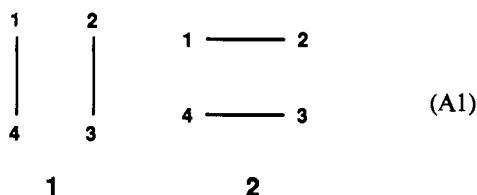
Acknowledgment. This work was supported by the SERC (U.K.) under Grants GR/F 48029, 46452, and GR/G 03335. All

ab initio computations were carried out using MC-SCF programs⁹ that are available in GAUSSIAN 90.¹⁰

Appendix. Symmetry Analysis of the Conical Intersection Region

We have demonstrated that the geometry of the conical intersection region can be predicted from simple geometrical considerations based on eqs 5a,b. While the geometry of the lowest energy point on the conical intersection has C_1 symmetry in this case, it is clear that the conditions can be satisfied when there is no symmetry present (e.g., when the methyl fragment is substituted). Nevertheless, it is of interest to analyze conditions 5a and 5b using symmetry arguments. There are two issues: (i) What are the symmetries of the ground and excited states? (ii) Is the condition $T = 0$ symmetry enforced or not? Two states even with the same symmetry will intersect in an $(n - 2)$ -dimensional hyperline as the energy is plotted against n nuclear coordinates.^{3a-d} Thus there are always two constraints on the system if it is at a conical intersection. Here we shall illustrate that one or both of these constraints can be supplied by symmetry.

The ground and excited states can be represented as two different spin couplings in a VB representation where the orbitals are chosen to be localized (see, for example, ref 5).



Thus we choose the two states, 1 and 2, in eq A1 as basis states for a diabatic representation. The adiabatic states are combinations of these two states and are necessarily symmetry adapted. The condition for a conical intersection (in a diabatic basis) is just

$$H_{11} = H_{22} \quad (\text{A2})$$

and

$$H_{12} = 0 \quad (\text{A3})$$

where H_{ij} in eqs A2 and A3 represents Hamiltonian matrix elements in the diabatic basis 1 and 2.

The two conditions 5a and 5b are completely equivalent to these two conditions but do not require the introduction of an arbitrary diabatic basis. If the two states 1 and 2 belong to different

irreducible representations of the point group, then condition A3 holds automatically for the subspace of all totally symmetric motions (i.e., those that do not break the symmetry); however, unless the two states belong to a degenerate irreducible representation, condition A2 is *not* automatically satisfied as well. Alternatively, either eq 5a or 5b (or both) may be satisfied automatically for the space of totally symmetric motions. While the two preceding statements are completely equivalent, using simple geometric considerations one can predict the conditions when eqs 5a,b can be satisfied when the symmetry is broken as well.

It is adequate (see refs 3i,j) to illustrate group-theoretical aspects of the problem with four localized s orbitals as illustrated in Figure 8. We can thus trace the origin of the conical intersection from the Jahn-Teller effect that occurs in T_d symmetry. Let us consider the symmetries of the states involved. In T_d , states 1 and 2 belong to the E representation and are necessarily degenerate. Thus both conditions A2 and A3 are satisfied. Now we turn to conditions 5a and 5b. In Figure 8 we have shown the K_{ij} 's that occur in K_a , K_b , and K_c of eq 5 as hashed lines, solid lines, and bold lines, respectively. It is easily seen that both conditions 5a and 5b are satisfied by symmetry. Now consider the distortion to D_{3h} or C_{3v} obtained by moving atom 1 down the C_3 axis of T_d . The E representation remains irreducible. Again, both conditions 5a and 5b remains satisfied. Thus $T = 0$ (eqs 5a,b) is enforced by symmetry as long as one retains the C_3 axis.

Now consider the distortion from D_{3h} to C_2 shown in Figure 8c. The E representation is reducible and splits into two different irreducible representations. The diabatic states 1 and 2 can be symmetry adapted to these one-dimensional irreducible representations, and thus condition A3 must hold. Equivalently, it is clear that only one condition from eq 5 is satisfied (i.e., $K_a = K_b$) and not the other. Thus in order to satisfy the second condition we must adjust the geometry so that $K_b = K_c$. A similar situation holds as we descend from C_{3v} to C_s .

Now when we lower the symmetry still further, both diabatic states have the same symmetry. Conditions 5a and 5b can still be satisfied by adjusting the geometry. Thus the conical intersection persists in general even when there is no symmetry (see the two examples in ref 5). Of course, we are interested in the lowest energy point on this conical intersection since this provides the obvious transition point for the radiationless decay from excited state to ground state. This may or may not occur at a geometry that has some symmetry properties.

The geometry of the lowest point on the conical intersection has C_s symmetry for this reaction. Thus as discussed in relation to Figure 3a, one of the conditions (i.e., $K_a = K_b$) is satisfied automatically. Alternatively, one can say that the two diabatic states can be chosen so that they belong to different irreducible representations (A' and A'') so that eq A3 is automatically satisfied. However, the second condition A2 or $K_a = K_c$ is not automatically satisfied.

Registry No. But-1-ene, 106-98-9.

(9) (a) Eade, R. H. A.; Robb, M. A. *Chem. Phys. Lett.* **1981**, *83*, 362. (b) Schlegel, H. B.; Robb, M. A. *Chem. Phys. Lett.* **1982**, *93*, 43.

(10) 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. A.; Melius, C. F.; Baker, J.; Martin, R. L.; Kahn, L. R.; Stewart, J. J. P.; Topiol, S.; Pople, J. A. *Gaussian 90*; Gaussian, Inc.: Pittsburgh, PA, 1990.