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“H/Vinyl” and “Alkyl/Vinyl” Conical Intersections Leading to Carbene Formation from the Excited States of Cyclohexene and Norbornene

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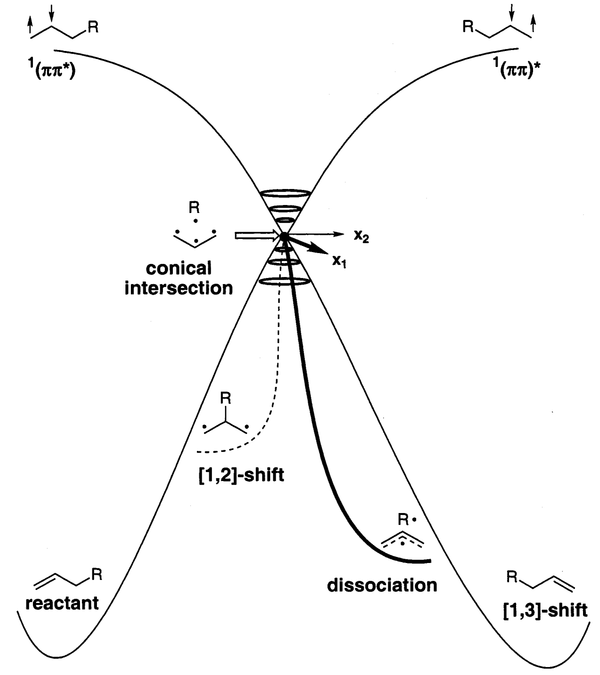
Received November 19, 2001. Revised Manuscript Received June 5, 2002

Abstract: The photochemical [1,2]-shifts leading to carbene intermediates from cyclohexene and norbornene have been studied using CASSCF calculations and a 6-31G* basis set. In each case, a S_1/S_0 conical intersection hyperline was identified that extends from the region of the reactant excited state to the carbene product. It is traditionally thought that the Rydberg R(π,3s) state is responsible for carbene formation on photolysis of cyclic alkenes, but these new results indicate an efficient mechanism for carbene formation following excitation to the $^1(\pi\pi^*)$ state. This pathway is essentially barrierless and involves internal conversion to the ground-state surface via conical intersections between the excited zwitterionic valence state and the ground-state surface, similar to those responsible for cis−trans isomerization in ethene and other acyclic alkenes. These results are in excellent agreement with recent experimental data obtained using femtosecond spectroscopy.

Introduction

Conical intersections control the products of many photochemical reactions. We recently characterized “alkyl/allyl” and “H/allyl” conical intersections that are involved in the photochemical [1,2]- and [1,3]-sigmatropic shifts of cyclic alkenes and dienes.[1] These structures occur at the intersection of the $^1(\pi\pi^*)$ state and the ground state and involve partial β-cleavage of a C−C or C−H bond (Scheme 1). Decay to the ground-state surface at these points can lead back to reactants, to fragmentation products (retro-Diels−Alder or hydrogen atom loss), or to [1,2]- and [1,3]-sigmatropic shift products. However, the photochemistry of alkenes is even more complicated than indicated in Scheme 1.[2] Cleavage of vinylic, as well as allylic, bonds can occur; the [1,2]-shifts of vinylic σ-bonds can produce carbenes and a number of derived products. Although these processes are often proposed to arise from Rydberg states,[2,3] we have located three types of conical intersection involving the lowest valence states of cyclohexene and norbornene leading to carbene ground states. In addition, we find that the surface topology of these systems along these [1,2]-shift coordinates is remarkably similar to the hydrogen migration coordinate in ethene itself.

Scheme 1



Experimental Background

The photochemistry of alkenes is exceedingly complex due to the presence of several low-lying Rydberg and valence excited states that are close in energy.[4] It is generally believed that irradiation of simple alkenes populates the valence $^1(\pi\pi^*)$ and Rydberg R(π,3s) states.[2] The Rydberg state normally lies below

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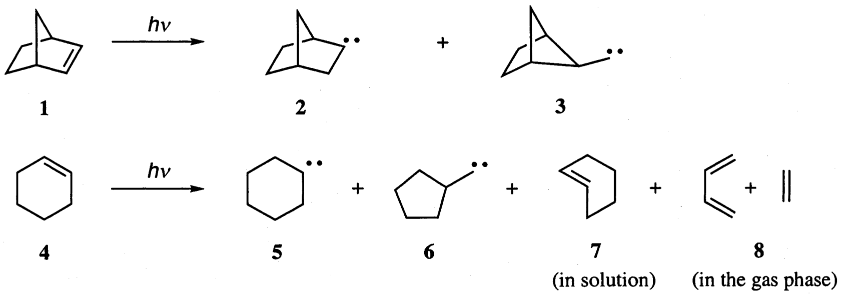
Scheme 2



the valence state at planar geometries, while the valence state is stabilized by rotation around the central C−C bond and falls below the Rydberg state at twisted geometries. $E-Z$ isomerization is believed to occur from the $^1(\pi\pi^*)$ state, while carbene formation is presumed to occur from the Rydberg state. In constrained alkenes $E-Z$ isomerization is inhibited, and carbene formation predominates.

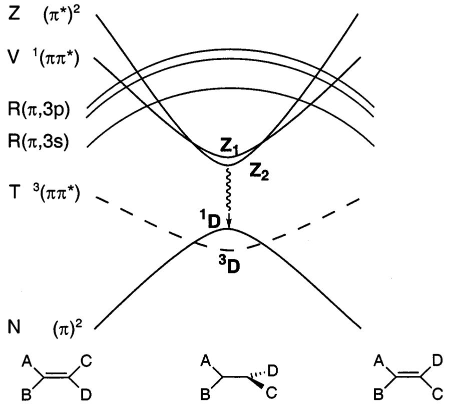
Solution-phase photolysis of norbornene **1** leads to the carbene intermediates **2** and **3**, formed via hydrogen and carbon shifts, respectively (Scheme 2).[5] Similarly, the solution-phase photolysis of cyclohexene **4** results in the formation of carbenes **5** and **6** and a small amount of the $E-Z$ isomerization product, *trans*-cyclohexene **7**.[5,6] The photolysis of cyclohexene in the gas phase leads to **5** and **6**, along with the retro-Diels−Alder products, butadiene and ethene (**8**).[6]

The suggestion of involvement of Rydberg states in these processes was originally based on the fact that carbene formation is totally suppressed on irradiation of 2-trifluoromethylnorbornene[7] and 2-cyanonorbornene,[8] where the Rydberg states are destabilized. However, more recent femtosecond experiments carried out by Fuss and co-workers have led to the suggestion that carbene formation in both norbornene and cyclohexene can arise directly from the $\pi\pi^*$ state.[9] It was proposed that the interconversion of Rydberg and $\pi\pi^*$ states is ultrafast, as they are so close in energy, and that the departure of the excited molecules from the Franck Condon region of both states takes place within about 20−30 fs. The molecules then evolve on the $\pi\pi^*$ state for 50−60 fs, before decaying to the ground-state surface via a dark zwitterionic state. While the study of the Rydberg states is beyond the scope of this work, we will show that a direct pathway leading from the $^1(\pi\pi^*)$ state to the carbene products via a zwitterionic state exists in both systems and that this pathway is essentially barrierless.

Theoretical Background

The classic paradigm for $E-Z$ isomerization in alkenes is shown in Scheme 3. Excitation from the ground-state surface to the valence $^1(\pi\pi^*)$ state (N and V, respectively, in Mulliken notation) at a D_{2h} geometry is followed by rotation and decay through an avoided crossing in the region of the perpendicular minimum onto the ground-state D_{2d} diradical, ^{1}D. This diradical is the transition state for rotation on the ground-state surface.[3] There is some difference of opinion in the literature as to the precise nature and energies of these states at the 90° geometry.[10−13] The most recent results of Ben-Nun and Martínez[12] suggest that the doubly excited zwitterionic state (Z) lies below the V state at the D_{2d} geometry as previously predicted by Brooks and Schaefer[11] and that decay to the ground-state surface occurs from this zwitterionic state in the region of Z_2 (Scheme 3). However, the Z/N energy gaps computed at the D_{2d} geometries were found to be too large to account for the short excited-state lifetimes of many alkenes.[15] In fact, the D_{2d} geometry of the Z state is not a minimum as the molecule is unstable with respect to pyramidalization of one of the methylene groups. The most recent theoretical methods estimate that the Z/N energy gap in ethene at the excited-state minimum is 0.4 eV (9 kcal/mol).[16] Crossing of the two surfaces is further facilitated by a partial hydrogen migration leading to ultrafast internal conversion in ethene. The excited-state lifetime of ethene has been quoted as being of the order of 10 fs,[17] although Martínez and co-workers suggested that it is most probably

Scheme 3



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closer to 180 fs, based on the results of their dynamics simulations.[12b]

The involvement of a partial hydrogen migration in the photochemical *E*−*Z* isomerization of ethene was first suggested by Ohmine[10] and has been corroborated more recently by the groups of Klessinger[14] and Martínez.[12] Ohmine identified a S_1/S_0 (Z/N) conical intersection for ethene along a hydrogen migration coordinate at a C_s-symmetry-constrained geometry.[10] Relaxation to the ground-state surface was predicted to lead directly to ground-state ethene or to the highly unstable ethylidene, which can then undergo a second, nearly barrierless, hydrogen migration to reform ethene. Freund and Klessinger[14] and Ben-Nun and Martínez[12] have since reported more extensive mappings of the excited states of ethene. They showed that decay to the ground-state surface requires both twisting and pyramidalization and leads to cis and trans isomers of ethene. It was found that the C_s-symmetry-constrained structure located by Ohmine is not the lowest energy conical intersection in this region.[12,14] Ben-Nun and Martínez proposed that the symmetry-constrained structure could be a “transition state” on a conical intersection seam between two lower energy structures.[12c] Our calculations on ethene have since confirmed this.[18]

We have explored the analogous S_1/S_0 (Z/N) conical intersections in norbornene and cyclohexene. We find that these conical intersections can be accessed directly from the $^1(\pi\pi^*)$ state with no barrier, in agreement with the results of Fuss and co-workers.[9] The results provide a much-expanded view of the mechanism of alkene photochemistry.

Computational Details

The excited-state and ground-state potential energy surfaces of cyclohexene and norbornene were investigated using the complete active space (CAS) SCF method in Gaussian94,[19] and compared with the results obtained for ethene at the same level of theory.[18] The conical intersections following α-cleavage of both C−C or C−H bonds in norbornene and cyclohexene were optimized using (6,6) active spaces and a 6-31G* basis set. The six active orbitals included the π-, π^*-, σ-, and σ^*-orbitals in the C═C bond and the σ- and σ^*-orbitals in the C−H or C−C bond that is cleaved. The reactant regions in cyclohexene and norbornene were studied with an active space of eight electrons in eight orbitals. The π-, π^*-, σ-, and σ^*-orbitals in the double bond were included, along with the σ- and σ^*-orbitals of the two adjacent C−C or C−H σ bonds.

Although the CASSCF calculations lack dynamic correlation energy, which will almost certainly affect the relative energies of the structures to an extent, previous results by the Martínez group have shown that the qualitative features of the potential energy surfaces are unchanged when this is taken into consideration.[12a] We are primarily interested in the existence of the crossing points and the mechanisms involved in reaching them, and therefore, we believe that the inclusion of dynamic correlation will not greatly affect our overall conclusions.

The conical intersections were optimized using the algorithm in Gaussian94 that finds the lowest energy point on an (n−2)-dimensional crossing seam, where n is the number of degrees of freedom in the molecule.[20] The remaining two dimensions are parallel to the gradient difference and derivative coupling vectors that describe the only two directions that break the two-state degeneracy. These two vectors are produced as part of the optimization procedure and indicate the immediate reaction paths that are available on the ground-state surface after instantaneous decay through the conical intersection. State-averaged orbitals were used at all conical intersection structures. State-averaging involves optimizing the average energy of two or more states simultaneously and has been shown to give a good approximation to the energies of excited states in cases of near-degeneracy.[21]

Results

(i) Conical Intersection Hyperlines in Cyclohexene and Norbornene. Previous results showed that, for ethene, two S_1/S_0 (Z/N) conical intersection structures exist, one in the region of the excited-state reactant following a partial hydrogen migration, and the second in the region of the carbene product.[12c] We refer to these conical intersections as type I and type II structures, respectively. These types of conical intersection structure also exist for cyclohexene and norbornene, following both C−H and C−C α-cleavage. In addition to these structures, a third type of conical intersection has also been identified at intermediate geometries between the type I and type II structures. We will refer to these conical intersections as type III, and they most probably arise because of steric constraints in the molecules. The existence of these three conical intersection minima is indicative of a hyperline of crossing points that extends from the region of the reactants to the carbene products. In principle, decay can occur anywhere along this hyperline. The most probable point of decay depends on factors such as the region in which the molecules first approach the degeneracy, the shape of the excited-state surface, and the shape of the conical intersections themselves.

The S_1/S_0 (Z/N) conical intersections corresponding to C−H and C−C α-cleavage in cyclohexene and norbornene were located at the CAS(6,6)/6-31G* level and the optimized geometries are shown in Figures 1−4. The energies are summarized in Table 1 and compared with the energies of the corresponding structures for hydrogen migration in ethene computed at the same level of theory. The geometries of the structures optimized for ethene can be obtained as Supporting Information.

The hydrogen migration conical intersection structures for cyclohexene are shown in Figure 1. Type I (1a), type III (1b), and type II (1c) structures were all located. The hydrogen atom migrates from left to right, and the degree of migration is best indicated by the $H_5C_3C_2$ angle, which varies from 46° in the type I structure to 116° in the type II structure. These angles are similar to those found in the type I and type II structures for ethene, which are 47° and 113°, respectively. The bond lengths of the breaking C−H bond in the type I conical intersections are also similar—1.23 and 1.22 Å in the ethene and cyclohexene structures, respectively. The gradient difference and derivative coupling vectors also resemble those found at the ethene conical intersections.[12c,14] In all three cases, one of

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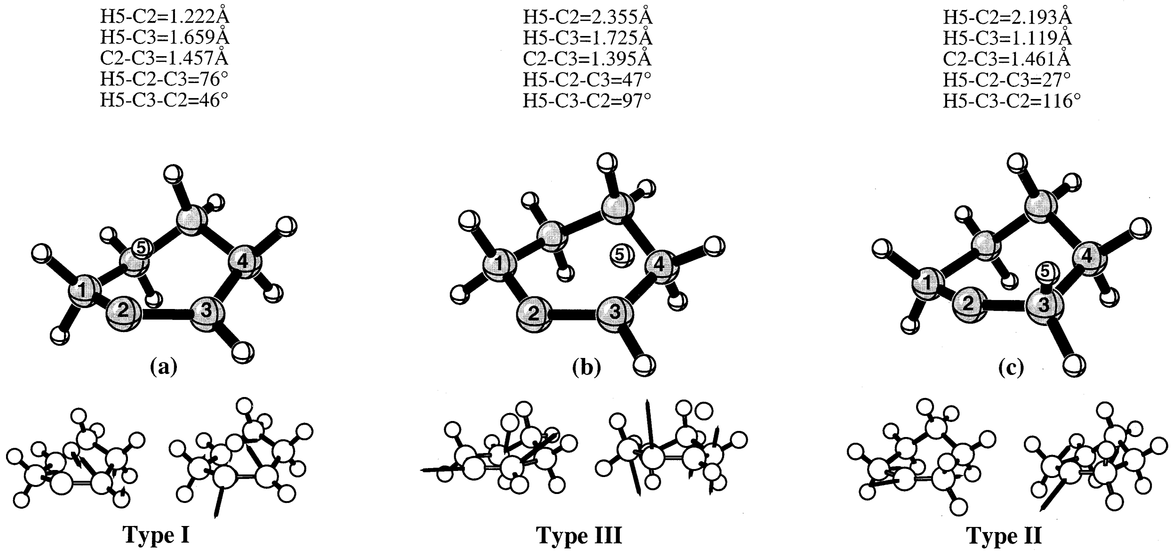

Figure 1. CASSCF(6,6)/6-31G* optimized structures for the [1,2]-hydrogen shift in cyclohexene. Gradient difference and derivative coupling vectors are shown below each structure. (a) Type I conical intersection, (b) type III conical intersection, and (c) type II conical intersection.

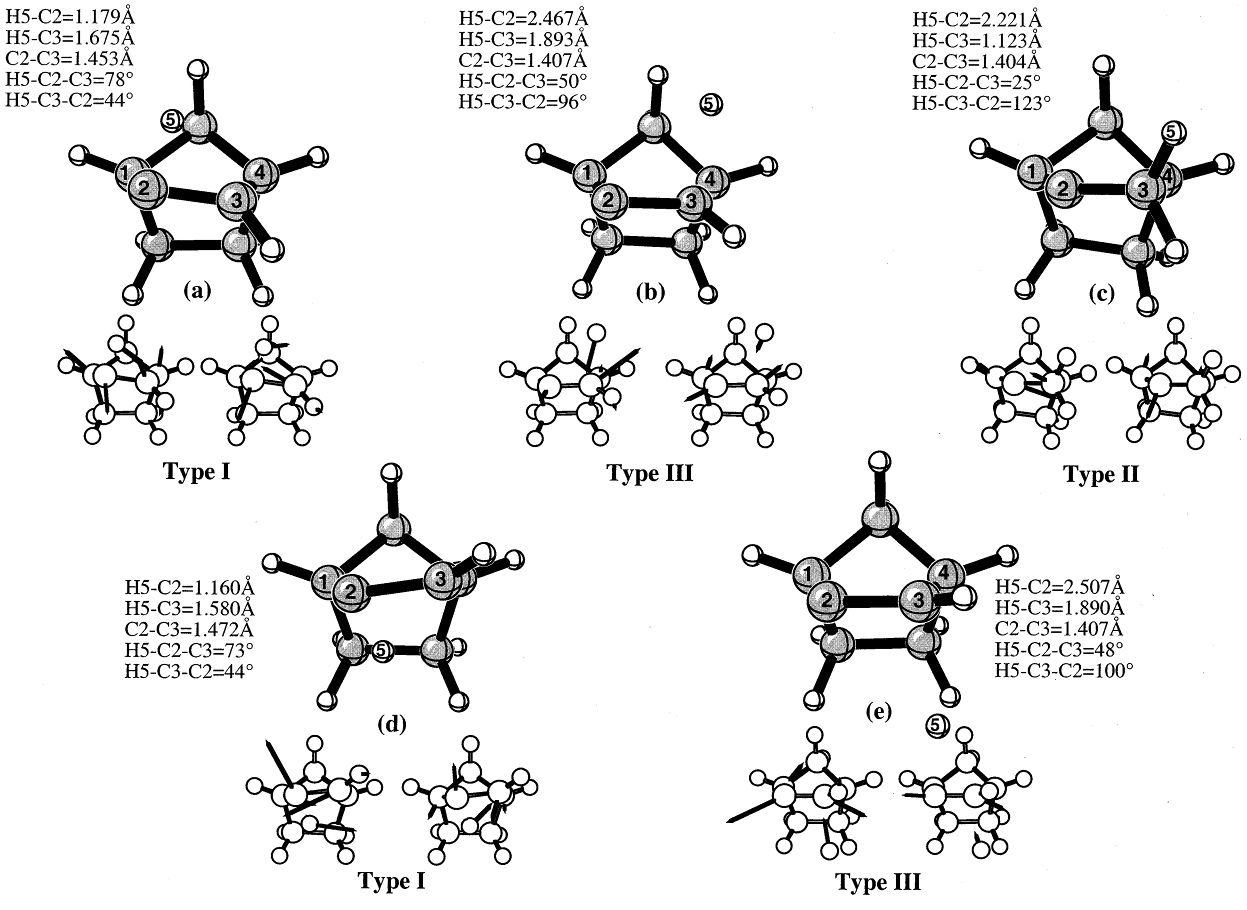

Figure 2. CASSCF(6,6)/6-31G* optimized structures for the [1,2]-hydrogen shift in norbornene. Gradient difference and derivative coupling vectors are shown below each structure. (a) Type I conical intersection for exo migration, (b) type III conical intersection for exo migration, (c) type II conical intersection, (d) type I conical intersection for endo migration, and (e) type III conical intersection for endo migration.

the vectors corresponds to motion of the hydrogen or the vinylic carbons either in the plane of migration or perpendicular to it. Relaxation on the ground-state surface is expected to lead to a mixture of *cis*-cyclohexene or to carbene **5**, as *E*−*Z* isomerization cannot occur via these constrained structures.

Analogous hydrogen migration conical intersection structures were located for norbornene (Figure 2). Both exo and endo migration can occur leading to type I (Figure 2a and d) and type III (Figure 2b and e) structures in each case. Only one type II structure (Figure 2c) is obtained as the hydrogen is fully migrated at this point. The degree of migration is best indicated by the $H_5C_3C_2$ angle, which resembles that in both the ethene and cyclohexene conical intersections (44° in the type I structures, 96° and 100° in the type III structures, and 123° in

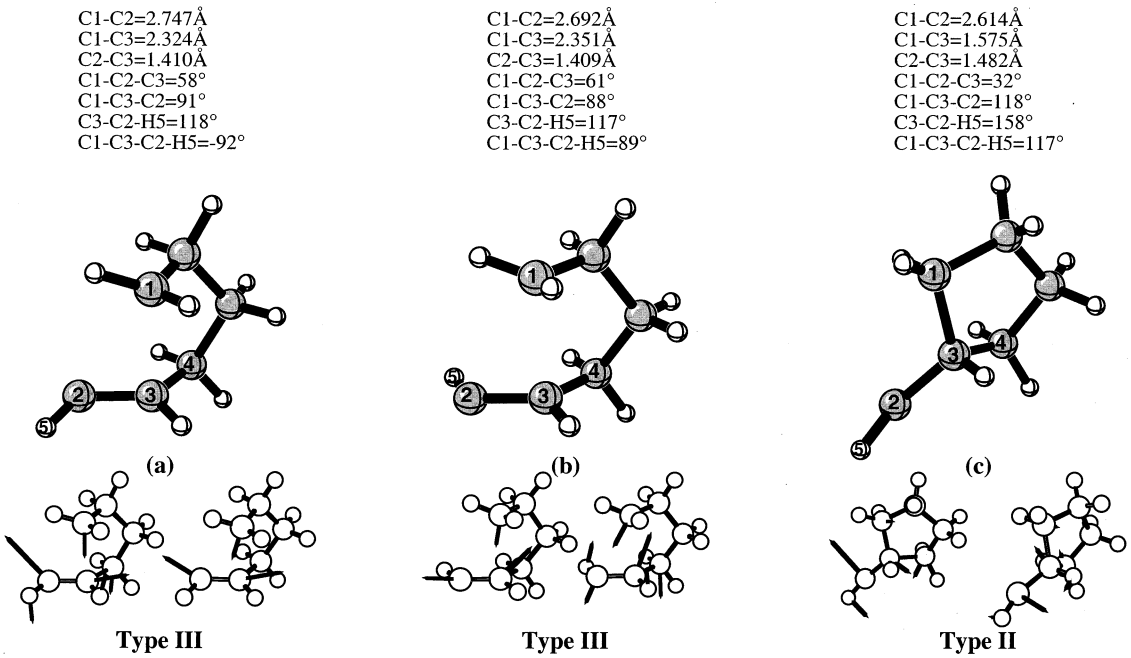

Figure 3. CASSCF(6,6)/6-31G* optimized structures for the [1,2]-carbon shift in cyclohexene. Gradient difference and derivative coupling vectors are shown below each structure. (a) Type III conical intersection with vinylic hydrogen atoms cis to each other, (b) type III conical intersection with vinylic hydrogen atoms trans to each other, and (c) type II conical intersection.

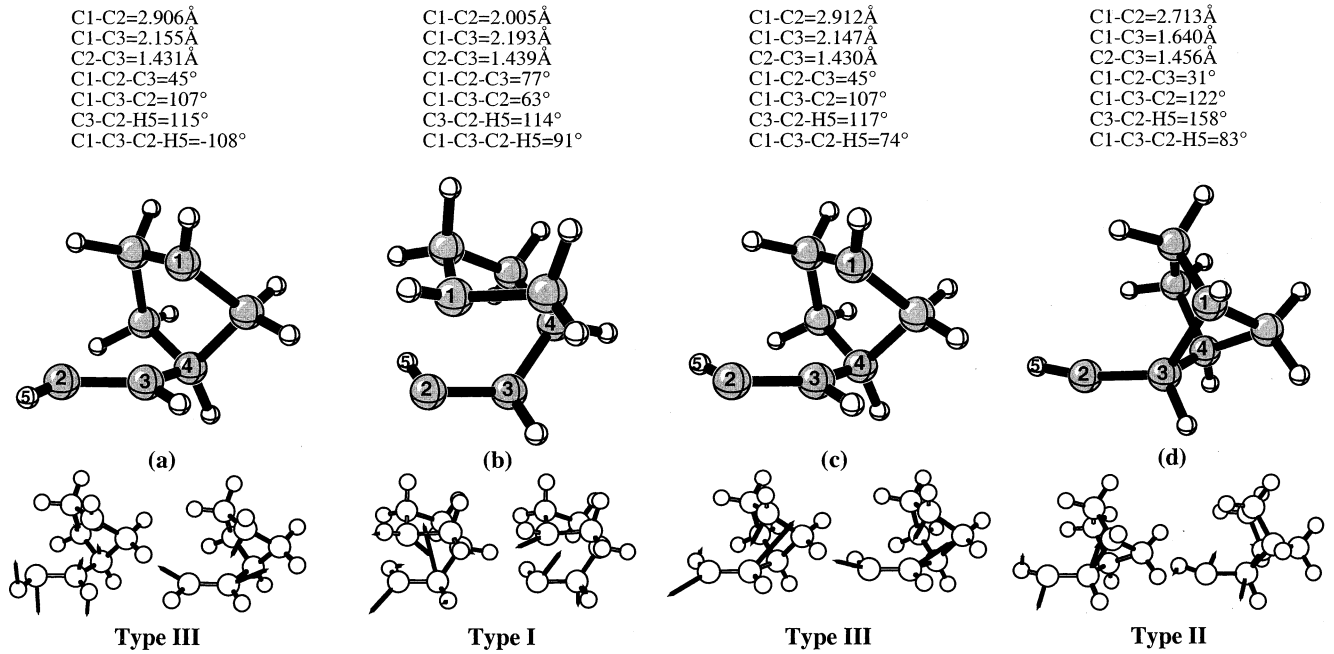

Figure 4. CASSCF(6,6)/6-31G* optimized structures for the [1,2]-carbon shift in norbornene. Gradient difference and derivative coupling vectors are shown below each structure. (a) Type III conical intersection with vinylic hydrogen atoms cis to each other, (b) type I conical intersection with vinylic hydrogen atoms trans to each other, (c) type III conical intersection with vinylic hydrogen atoms trans to each other, and (d) type II conical intersection.

the type II structure). However, the type I conical intersections occur somewhat earlier along the hydrogen migration coordinate with breaking C−H bond lengths of 1.18 (Figure 2a) and 1.16 Å (Figure 2d). *E*−*Z* isomerization is prohibited due to ring constraints, such that relaxation on the ground-state surface will only give rise to norbornene or to carbene **2**.

The conical intersection structures involving carbon migration in cyclohexene and norbornene are shown in Figures 3 and 4, respectively. The degree of migration in these structures is best indicated by the $C_1C_3C_2$ angle. For carbon migration in cyclohexene, the first structures that could be optimized along the migration coordinate are shown in Figure 3a and b. These are both type III structures with the hydrogen atoms on the C_2−C_3 bond cis and trans to each other, respectively. As we will show in the next section, both of these structures can be achieved following relaxation from the Franck Condon region, and the formation of *trans*-cyclohexene is most likely to occur via the structure shown in Figure 3b. Type I structures could not be optimized even though degenerate structures exist in these regions; i.e., although the hyperline is still present in this region, there are no conical intersection minima early along the migration coordinate.

Table 1. CAS(6,6)/6-31G* Computed Relative Energies (in kcal/mol) of the Structures Optimized along the [1,2]-Shift Pathways for Ethene, Cyclohexene, and Norbornene

	state	ethene H shift	cyclohexene H shift	norbornene H shift	cyclohexene C shift	norbornene C shift
reactant	S_0	0.0	0.0	0.0	0.0	0.0
trans reactant	S_0				61.9	
type I CI	S_1	127.5[a]	130.7[a](**1a**)	140.7[a] (**2a**)		136.5[a] (**4b**)
	S_0	127.2[a]	130.7[a]	140.6[a]		136.5[a]
	S_1			154.6[a] (**2d**)		
	S_0			154.5[a]		
type III CI	S_1		135.1[a] (**1b**)	133.2[a] (**2b**)	127.0[a] (**3a**)	126.0[a] (**4a**)
	S_0		135.0[a]	133.1[a]	126.9[a]	126.0[a]
	S_1			136.6[a] (**2e**)	127.3[a] (**3b**)	127.5[a] (**4c**)
	S_0			136.6[a]	127.2[a]	127.5[a]
type II CI	S_1	146.7[a]	134.5[a] (**1c**)	151.5[a] (**2c**)	128.3[a] (**3c**)	136.8[a] (**4d**)
	S_0	146.7[a]	134.5[a]	151.5[a]	128.3[a]	136.4[a]
carbene product	S_0	80.6	78.0	65.3	88.2 (cis) 89.0 (trans)	100.6 (cis) 101.6 (trans)

[a] Energies calculated using state-averaged orbitals, with states weighted 0.5:0.5.

For norbornene, type I, II, and III structures were all located. The type I structure (Figure 4b) could only be located at a geometry where the vinylic hydrogens are trans to each other. The corresponding cis structure could not be optimized as a conical intersection minimum even though the degeneracy persists in this region. Type III structures (Figure 4a and c) were located for both cis and trans conformers. However, unlike cyclohexene, a "stable" trans conformer does not exist for norbornene, so relaxation from both conformers is likely to lead back to norbornene or to carbene **3**.

In all cases, it is found that the gradient difference and derivative coupling vectors (shown below each optimized structure) resemble those in ethene, although $E-Z$ isomerization is often impossible in the more constrained systems. In general, internal conversion at the type I structures can give a mixture of reactant (with $E-Z$ isomerization where possible) and carbene product. In the intermediate (type III) structures, where the C_1-C_2 or H_5-C_2 distances are significantly longer, decay to the ground-state surface will lead predominantly to C_1-C_3 or H_5-C_3 bond formation and hence to carbene product, with movement of C_2 either in or out of the plane of the migrating atom. Likewise, decay through the type II structures will lead predominantly to carbene products with $C_3-C_2-H_5$ bending (for carbon migration) or $C_3-C_2-C_1$ bending (for hydrogen migration) either in or out of the plane of the migrating atom.

(ii) $^1(\pi\pi^*)$ Reactant Regions. It was previously believed that carbene formation occurs from the Rydberg states of norbornene and cyclohexene. However, our results indicate the existence of an efficient pathway on the $^1(\pi\pi^*)$ surface that channels the reaction toward these S_1/S_0 (Z/N) conical intersections. Similar results are known for ethene, and the reactant region of ethene has been well-documented.[10−14] For all the species studied here, and presumably alkenes in general, relaxation on the $^1(\pi\pi^*)$ surface involves C═C stretching and torsion around the central bond. For ethene, when the molecule is constrained to be planar, a relaxed D_{2h} minimum can be located on S_1 (Figure 5a). This D_{2h} structure is a second-order saddle point where the two negative directions of curvature correspond to moving all four hydrogen atoms out of the plane together (pyramidalization of the methylene groups) or to torsion around the central C−C bond. The molecule undergoes both pyramidalization and twisting around the central C−C bond, and as it relaxes, the $^1(\pi\pi^*)$ (or V) state couples strongly with the Z state, and the molecule acquires zwitterionic character. A higher energy Z/V conical intersection (Figure 5d) was located by Ben-Nun and Martínez, but this structure was thought to be irrelevant to chemistry as the type I conical intersection can be accessed directly from the $^1(\pi\pi^*)$ state by following the adiabatic surface.[12c]

The surface topology in norbornene and cyclohexene is remarkably similar to that in ethene, and carbene formation from the $^1(\pi\pi^*)$ state is essentially a barrierless process. In both cases, we find a second-order saddle point at a geometry where the vinylic group is nearly planar and the C═C bond is elongated, analogous to the D_{2h} structure in ethene (Figure 5). The second-order saddle points were optimized using two different active spaces—one containing the C−C σ-bond orbitals and one containing the C−H σ-bond orbitals. The energies of both are given in Table 2. The two negative directions of curvature in these cases correspond to out-of-plane distortions of the vinylic hydrogen atoms, either in-phase or out-of-phase with each other. In our previous work on norbornene, we suggested that relaxation on the $^1(\pi\pi^*)$ surface leads to this type of second-order saddle point (Figure 5c).[22]

Intrinsic reaction coordinate (IRC) calculations from these second-order saddle points were carried out using both active spaces and following both negative directions of curvature. State averaging was required to achieve convergence. For cyclohexene, all of the IRC calculations led to α-cleavage and migration of a C−C or C−H bond (depending on the active space used) and to a conical intersection region close to a type I structure. The IRCs indicated that H_5, H_6, C_1, and C_4 can all migrate and that $E-Z$ isomerization occurs directly from the second-order saddle points before reaching the conical intersection region.

The IRC calculations for norbornene were more difficult to converge but showed that both exo and endo migrations of the hydrogen atoms were possible, and both cis and trans conformers of the carbon migration conical intersection structures were accessible.

We have also located Z/V conical intersections in both cyclohexene (Figure 5e) and norbornene (Figure 5f) with active spaces containing the C−C σ-bond orbitals. At these geometries, the vinylic hydrogens are out of plane in an out-of-phase fashion and the H−C−C−H torsional angles are 111° and 156°, respectively. These structures are analogous to the 90° twisted

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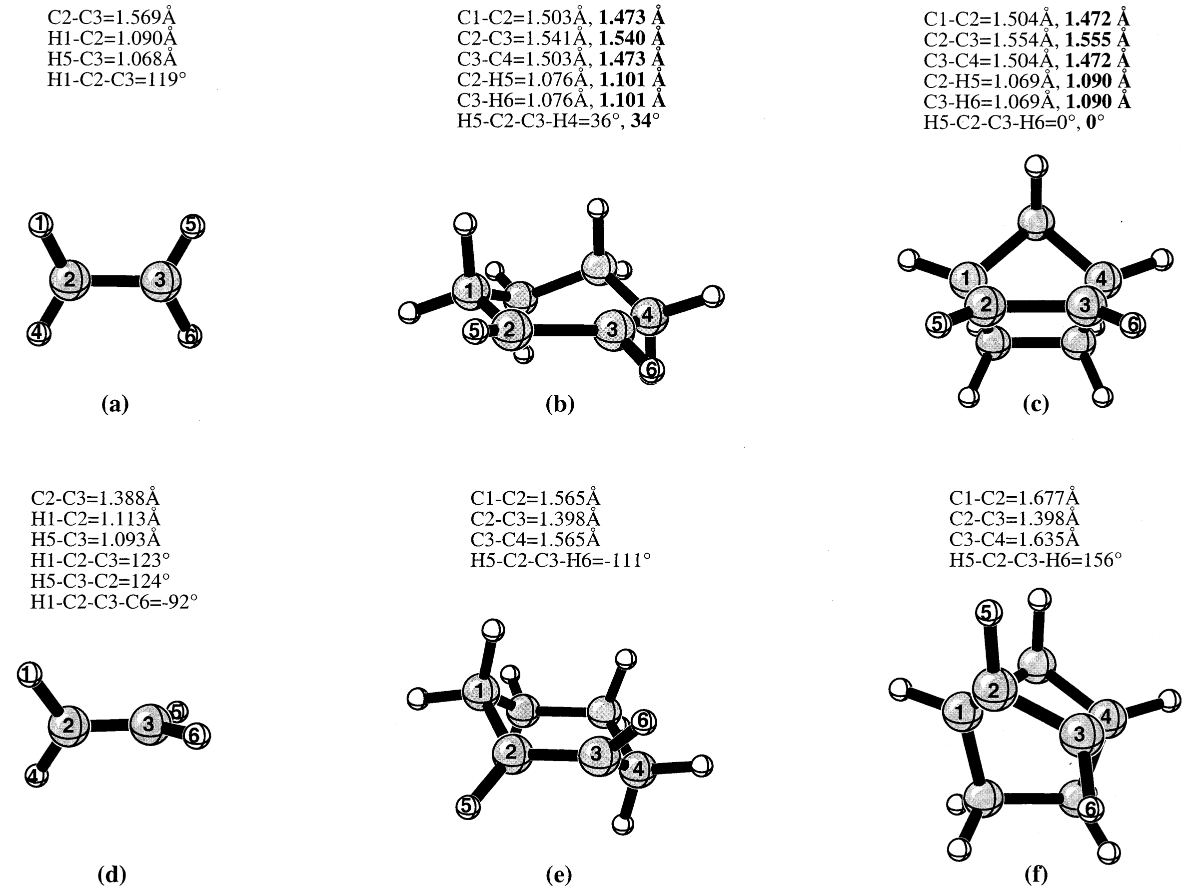


Figure 5. CASSCF/6-31G* optimized structures of the second-order saddle points and Z/V conical intersections in ethene, cyclohexene, and norbornene. (For cyclohexene and norbornene geometries, the parameters optimized with the active space containing the C−C σ-orbitals are given in regular type and those optimized with the active space containing the C−H σ-orbitals are in boldface type.): (a) CAS(6,6)/6-31G* optimized second-order saddle point in ethene, (b) CAS(8,8)/6-31G* optimized second-order saddle point in cyclohexene, (c) CAS(8,8)/6-31G* optimized second-order saddle point in norbornene, (d) CAS(6,6)/6-31G* Z/V conical intersection in ethene, (e) CAS(8,8)/6-31G* optimized Z/V conical intersection in cyclohexene, and (f) CAS(8,8)/6-31G* optimized Z/V conical intersection in norbornene.

Table 2. CASSCF/6-31G* Computed Relative Energies (in kcal/mol) of the S_1 Second-Order Saddle Points and Z/V Conical Intersection Structures

	state	ethene[a]	cyclohexene[b]	norbornene[b]
reactant	S_0	0.0	0.0 *0.0*	0.0 *0.0*
second-order saddle point	S_1	207.5 (**5a**)	198.1 *196.6* (**5b**)	190.6 *189.3* (**5c**)
Z/V conical intersection	S_2	163.0[c] (**5d**)	161.5[c] (**5e**)	176.5[c] (**5f**)
	S_1	162.8[c]	161.4[c]	176.0[c]

[a] Geometries optimized with active space containing six electrons in six orbitals. [b] Geometries optimized with active space containing eight electrons in eight orbitals. Values in regular type correspond to geometries optimized with an active space containing the σ- and σ*-orbitals of the adjacent C−C bonds. Values in italic type correspond to geometries optimized with an active space containing the σ- and σ*-orbitals of the adjacent C−H bonds. [c] Energies calculated using state-averaged orbitals, with states weighted 0.5: 0.5.

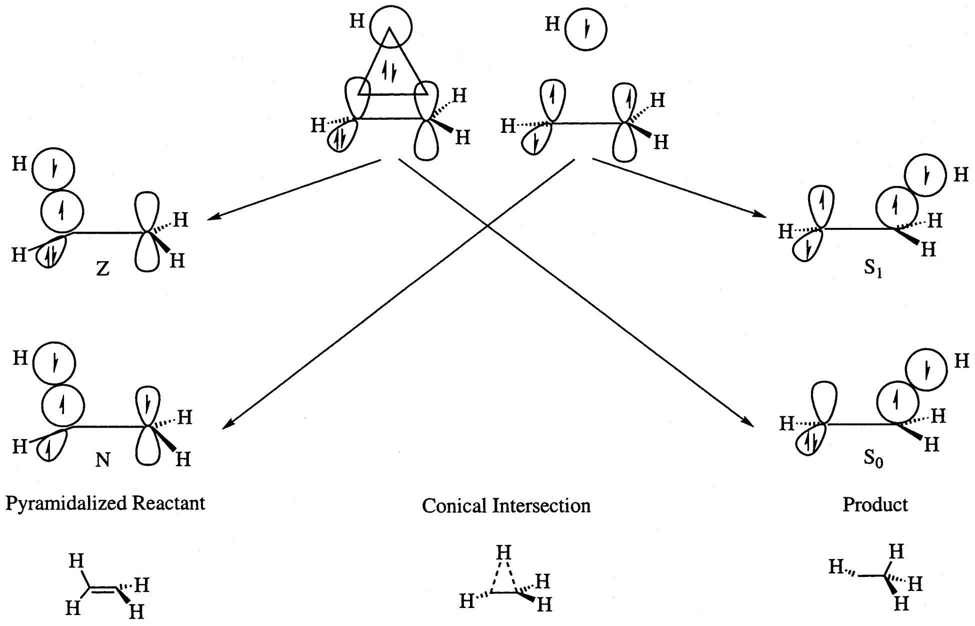
Z/V conical intersection located previously for ethene. However, as found in ethene, these structures do not appear to be relevant to the excited-state chemistry of these molecules, since the molecules evolve smoothly into the zwitterionic states as they relax on the S_1 adiabatic surface from the second-order saddle point.

Discussion

These studies show that the $^1(\pi\pi^*)$ excited states of cyclohexene and norbornene can readily achieve S_1/S_0 (Z/N) conical intersections with migration of vinylic C−H or C−C bonds. These results are in agreement with the recent experimental results of Fuss and co-workers.[9] The efficiency of ground-state carbene formation in these systems will depend on the topology of the S_1 surface, especially where the molecule first encounters the S_1/S_0 degeneracy. Freund and Klessinger[14] predicted that, in ethene, about 1 in 10 excited molecules would lead to ethylidene through the type I conical intersection structure. Similarly, the AIMS calculations of Martínez showed that decay to the ground-state surface at the type I structure can lead to the formation of ethylidene, but they did not observe any decay in the region of the type II structure.[12] These results suggest that, in ethene, quenching will occur predominantly via the type I structure.

For norbornene and cyclohexene, type I, type II, and type III conical intersections exist in most cases. However, the IRC calculations suggest that the conical intersection hyperlines are initially accessed in the region of the type I structures following passage over the second-order saddle points shown in Figure 5b and c. Decay is likely to occur early along the conical intersection hyperline. However, the efficiency of carbene formation should be much higher in cases where the type III conical intersection can be achieved, since this structure has essentially complete migration of the C−C or C−H bond.

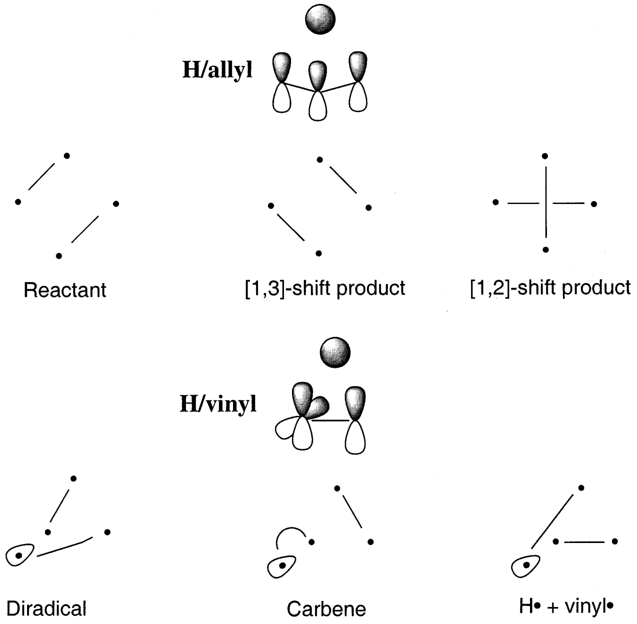
Scheme 4



The structures of the conical intersections located here are very different from the "H/allyl" and "alkyl/allyl" structures located previously.[1] We describe these vinylic hydrogen and carbon migration structures as "H/vinyl" and "alkyl/vinyl" conical intersections, respectively. These conical intersection structures consist of four electrons distributed over a triangular arrangement of atoms in two degenerate configurations, representing the ground- and excited-state configurations. For the type I−type II hyperline of a "H/vinyl" conical intersection, in one configuration, there are two electrons in the plane of the migrating hydrogen atom and two electrons in the perpendicular n-orbital, essentially the picture one would draw for the transition state for hydrogen migration in a singlet carbene. In the other configuration, there are three electrons in the plane of the migrating hydrogen atom and one electron in the perpendicular n-orbital. This could be considered a transition state for hydrogen migration in the excited state of the carbene. A simple schematic representation of the electronic states of the distorted alkene reactants, conical intersection, and carbene products is shown in Scheme 4. It should also be noted that the picture in Scheme 4 only describes the hydrogen migration coordinate. At the conical intersection, there are two motions that break the degeneracy. In this case, there is an orthogonal coordinate corresponding to torsion around the C−C bond leading to cis or trans isomers of ethene.

These results are compared with those reported earlier for "H/allyl" and "alkyl/allyl" conical intersections using Scheme 5.[1,21] In both cases, four electrons are distributed in four orbitals that can couple in three different ways. In the "H/allyl" and "alkyl/allyl" conical intersections, the four orbitals are on different centers and recoupling the electrons leads to reactant, [1,3]-shift product, and [1,2]-shift product. In the "H/vinyl" and "alkyl/vinyl" conical intersections, two of the orbitals are on the same center. At the conical intersection, the original alkene molecule is twisted and one of the methylene groups is pyramidalized, so instead of leading directly to the alkene reactant, recouplingthe electrons leads initially to the ground-state diradical ^{1}D, or to H and vinyl radicals, which in turn can relax, forming the alkene or its isomer. Alternatively, the electrons on the same center can couple, leading to the carbene product.

Scheme 5



The energies of the "H/vinyl" and "alkyl/vinyl" conical intersections are higher than those of the "H/allyl" and "alkyl/allyl" conical intersections.[1,22] The energies of the "alkyl/allyl" conical intersections are 118 kcal/mol for cyclohexene and 105 and 113 kcal/mol for norbornene depending on whether initial cleavage occurs at the ethano or methylene bridges, some 10−20 kcal/mol lower than the conical intersection structures we have optimized here. However, in our study of the potential energy surfaces of norbornene, we found barriers of 3−5 kcal/mol separating the second-order saddle point from the "alkyl/allyl" conical intersections. More importantly, the motion required to break these bonds is orthogonal to the negative directions of curvature foundat the second-order saddle point. In contrast, we have shown here that relaxation along the negative directions of curvature leads directly to the “H/vinyl” and “alkyl/vinyl” conical intersections without a barrier. This is in good agreement with the experimental results, which indicate that in solution, where the excess energy is readily lost to the solvent, photolysis of alkenes leads to carbene products and to $E-Z$ isomerization.[5,6] However, in the gas phase, where the excess energy cannot be dissipated so easily, other products can be formed. In the case of cyclohexene, retro-Diels−Alder products have been observed that may be the result of decay through the “alkyl/allyl” conical intersection.[6] In the case of larger cycloalkenes, other products of allylic cleavage (vinylcycloalkanes and α,ω-dienes) have been detected, implying the involvement of “alkyl/allyl” conical intersection structures on the gas-phase photolysis of these molecules also.[6]

Finally, the support for the involvement of Rydberg states in these processes originally came from the results observed for the substituted norbornene systems, 2-trifluoromethylnorbornene[7] and 2-cyanonorbornene.[8] On photolysis of these molecules, only products corresponding to decay through the “allyl/alkyl” conical intersections are observed. This has been attributed to the destabilization of Rydberg states by electron-withdrawing substituents. Fuss and co-workers have suggested that the CF_3 and CN groups stabilize the zwitterionic states, leading to activation barriers for both carbon and hydrogen migration.[9] This will be the subject of a future investigation.

Conclusions

Alkenes possess conical intersection hyperlines, which invoke significant migration of vinylic hydrogen or carbon atoms toward carbene structures. For ethene, two types of conical intersection were located along the hydrogen migration coordinate; for cyclic alkenes, three types of conical intersection were found. The most probable point of decay along these hyperlines will depend predominantly on the surface topology of the S_1 surface and where the molecule first encounters the S_1/S_0 degeneracy. The type I conical intersection is highly nonplanar and can lead to both $E-Z$ isomerization, when this is geometrically feasible, and to carbene formation. The type II or III conical intersections have nearly complete carbon or hydrogen migration, and carbene formation will be the dominant process through such structures.

These calculations indicate that carbene formation can occur directly from the valence $^1(\pi\pi^*)$ state and that a barrierless process via second-order saddle points leads directly to the type I Z/N conical intersection structures. These results provide support for the assignment of the time constants in the experimental results of Fuss and co-workers.[9]

Acknowledgment. We are grateful to the National Science Foundation for financial support of this research and to the NCSA (Illinois), NPACI (San Diego), and the UCLA Office of Academic Computing for computational resources. S.W. would also like to thank the Violette and Samuel Glasstone Trust for financial support, the Royal Society for an equipment grant, and the UK Computational Chemistry Facility and the Oxford Supercomputing Centre for supercomputer time. We thank Professor Werner Fuss for helpful discussions.

Supporting Information Available: Cartesian coordinates and absolute energies of all optimized critical points. One figure showing the CAS(6,6)/6-31G* optimized conical intersection structures for ethene. This material is available free of charge via the Internet at http://pubs.acs.org.

JA012565G