J. Am. Chem. Soc. **1993,** *115,* 2073-2074 2073

A Concerted Nonadiabatic Reaction Path for the Singlet Di-π-methane Rearrangement

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Received September 17, 1992

The reaction path of the photochemical di-π-methane rearrangement of 1,4 dienes **1** to yield vinylcyclopropanes **4** is usually written[1-3] as shown in Scheme I. However, such a mechanism is only *formal*, and in any actual case some or all of the steps may merge into one step and the reaction may become concerted.[1-3] While 1,4-diradical intermediates have been characterized by theoretical work,[4,5] in one particular case there is experimental evidence[6,7] that appears to suggest that the 1,4-diradical is bypassed. However, a singlet photochemical reaction can only be concerted[8] if it starts on an excited-state potential surface and proceeds directly to a ground-state bonding structure via a Born–Oppenheimer violation region where the excited state and ground state cross (at a conical intersection[9-11]). In the di-π-methane rearrangement, this Born–Oppenheimer violation may or may not occur in the 1,4-diradicaloid region. In this communication we will demonstrate that the preferred relaxation pathway from S_1 to S_0, for the *model* singlet reaction of 1,4-pentadiene, occurs in the region of the 1,3-diradical (structure **3** in Scheme I), thus avoiding formation of the intermediate **2**. The diradical **3** is unstable and undergoes a ground-state barrierless ring-closure process leading to the final vinylcyclopropane product directly.

A conical intersection provides the *transition point* (where the decay from an excited state is fully efficient[11]) between the excited and ground states in a photochemical reaction. For a thermal reaction, at a transition state there is a single vector that corresponds to the reaction path through the saddle point. In a photochemical reaction, at a conical intersection there are *two* characteristic directions[10] (the gradient difference vector and the nonadiabatic coupling vector). If the energy is plotted in the plane defined by those two directions, the energy of the ground and excited states forms a double cone with the degeneracy occurring at the apex of the cone. When the system decays, at the minimum energy point of the conical intersection the initial ground-state reaction path lies in the plane formed by these directions (since the gradient of the energy of ground and excited states is 0 in all other directions).

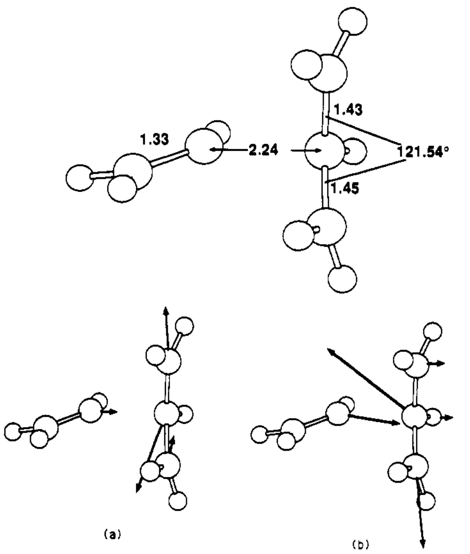


Figure 1. CASSCF/4-31G optimized geometry of the lowest energy point on the conical intersection between the lowest energy singlet states ($E_1 = E_2 = -193.5644$ E_h). (a) Nonadiabatic coupling vector, $\langle \Psi_1 | \partial \Psi_2 / \partial \mathbf{q} \rangle$ and (b) gradient difference vector, $\partial(E_2 - E_1)/\partial \mathbf{q}$.

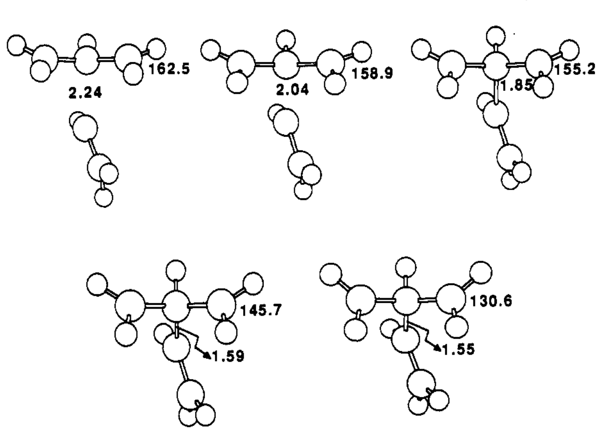
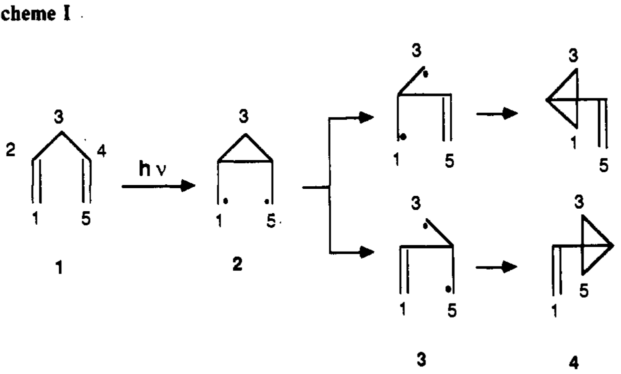


Figure 2. Geometries along the intrinsic reaction coordinate beginning from the conical intersection. The bond length indicated (Å) is that of the forming C–C bond. The angle (deg) is the dihedral angle H–C–C–C involving one of the terminal methylene H. (The energies of the structures from left to right are −193.5669, −193.5922, −193.6133, −193.6348, and −193.6407 E_h).

Scheme I



We now discuss the central features of a nonadiabatic reaction path for the *model* singlet di-π-methane rearrangement. Cal-

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culations were carried out using the CASSCF/4-31G method (with six-orbital active space comprising the four ethylenic p^π orbitals and the two C p^σ orbitals of C atoms 2 and 3) as implemented in a development version of Gaussian.[12] We have fully optimized, using the method described in ref 10, *three* conical intersection points: structure **a** similar to that of the reactant, where both π bonds are broken by rotation of the terminal methylenes, thus creating a tetraradicaloid; structure **b** that corresponds to a rhomboid arrangement of the two ethylenic π systems (i.e., with a partial *cross* σ-bond between atoms 1 and 4 in **1**); and structure **c** (shown in Figure 1), the lowest energy conical intersection that occurs in the region of **3**. Decay from **a** (23 kcal mol^{-1} higher than **c**) would lead only to cis-trans isomerization or back to starting material. Structure **b** (31 kcal mol^{-1} higher than **c**) has a geometry similar to the conical intersection[9h,i] for the ethylene + ethylene [2 + 2] cycloaddition. Decay from **b** could lead to [2 + 2] cycloaddition products or the 1,4-diradical **2** (which arises from an asynchronous [2 + 2] cycloaddition of the two π bonds). However, this intersection point will probably be unimportant (except in the case of structural constraint) because of its high energy and the fact that the reactant must assume an eclipsed conformation. Structure **c** would be reached via a formal 1,2-vinyl shift and can lead to **3** and **4**. The two directions that define the space of the double cone for structure **c** are plotted in Figure 1 and correspond to bond stretching in the allylic fragment and the motion of the ethene fragment to form the central bond of the 1,3-diradical. We attempted to follow reaction paths in the plane of these two directions using the IRC method. The only path that did not lead to disproportion is shown in Figure 2. It can be seen that the ground-state reaction path leads directly to the 1,3-diradical region of the potential energy surface.

We now briefly discuss the way in which the various experimental features are consistent with a concerted pathway which passes through a conical intersection point with the structure given in Figure 1. Firstly, the regiospecificity observed in 1,5-substituted reactants is readily rationalized via the different stability of the two different conical intersections leading to the 1,3-diradicaloids (**3** in Scheme 1). The most stable conical intersection will be the one with the most stable allyl radical moiety so that the vinyl radical that migrates will be the one without radical stabilizing substituents. Secondly, the integrity of the migrating vinyl radical double bond is found to be maintained. The optimized conical intersection structure and the structures optimized on the IRC show that this double bond does indeed retain its original geometry along the excited-ground-state relaxation pathway. A third "classical" stereochemical feature is the observed inversion of configuration of carbon 3 (where the migrating vinyl radical corresponds to carbon 1 and 2). This feature can be seen in the IRC (Figure 2) involving the evolution of the conical intersection structure toward the 1,3-diradicaloid structure. The final 1,3-diradicaloid structure on the IRC has the two terminal methylene radical centres oriented to form a new σ-bond (via a barrierless process). From Figure 2, it is obvious that this σ-bond will be formed on the *opposite side* of the -CH_2 fragment from the position where the migrating vinyl radical was initially attached.

We have assumed that the product of the reaction is determined by the point where the system returns to S_0 and the nature of the subsequent ground-state reaction path beginning at this point. Further, one assumes that the excess energy of the reaction is rapidly removed by equilibration in solution as the system moves on the potential energy surface. The reaction path on the excited surface immediately after vertical excitation will be determined by behavior of the vertical S_1 state (a $^1(\pi\pi^*)$ state best described as partly Rydberg ionic C^+–C^-). After adiabatic geometrical relaxation, the system enters a region where S_1 is a covalent excited state (essentially doubly excited with respect to S_0). The only features of the covalent region of S_1 that we have been able to locate are the three conical intersections just discussed (i.e., the *minima* on the covalent excited-state surface are conical intersections). Thus our theoretical characterization of the Born-Oppenheimer violation region in the region of **3** shows that there is a point where fully efficient decay from the excited-state surface is possible *avoiding* the 1,4-diradicaloid region **2** and that the subsequent ground-state reaction path leads directly to the 1,3-diradicaloid **3**. Thus a concerted path for the *model* singlet di-π-methane reaction exists. The higher energy conical intersection points can lead back to reactants, to [2 + 2] cycloaddition, or to **2**. The triplet reaction is well known in more rigid systems and probably proceeds by a different mechanism,[3] such as that studied in ref 4.

Acknowledgment. This research has been supported by the SERC (U.K.) under Grant Number GR/G 03335 and GR/G 11941 (CCP1). The authors are also grateful to IBM for support under a Joint Study Agreement. All computations were run on an IBM RS/6000.

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Resonance Raman Spectroelectrochemistry of the C_{60} Radical Anion

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Received October 19, 1992

We report the first resonance Raman spectrum of the C_{60} monoanion in solution. This spectrum resolves a significant issue regarding the extent of electron transfer during fullerene doping with alkali metals. When C_{60} films are doped with alkali metals, they show conducting and superconducting[1] behavior. These electronic effects are associated with the partial filling of the degenerate LUMO orbitals by electrons transferred from the alkali metal ions. The resulting decrease in average bond order can be monitored via vibrational spectroscopy. In particular, the totally symmetric "pentagonal pinch" mode of C_{60}, which appears as a strong band in the Raman spectrum,[1,2] shifts to lower frequencies when C_{60} is doped. The band has been found by Haddon and co-workers[1,8] to be at 1467 cm^{-1} in an undoped film, but at 1445

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