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The Iconoclastic Dynamics of the 1,2,6-Heptatriene Rearrangement

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This communication reports trajectory calculations on the nominal [3,3] sigmatropic rearrangement of 1,2,6-heptatriene, **1**. The reaction has been studied experimentally by Roth et al.,[1] who reported trapping biradical intermediate **2** with O_2. This result was consistent with earlier studies on a dimethyl derivative[2] of **1** and on a bicyclic analogue,[3] both of which had provided stereochemical evidence for at least some component of a biradical pathway. However, by extrapolation of product ratios to infinite O_2 pressure, Roth et al. deduced that roughly half of the rearrangement of **1** to **3** occurred concertedly, without formation of an interceptible intermediate.[1]

If the mechanism of Roth et al. were correct, three transition structures ought to exist on the PES between **1** and **3**: $\mathrm{TS}_{1\rightarrow2}$, $\mathrm{TS}_{2\rightarrow3}$, and the concerted $\mathrm{TS}_{1\rightarrow3}$. However, two of us (D.A.H. and W.T.B.) have reported that $\mathrm{TS}_{1\rightarrow3}$ cannot be found at either the CASSCF-(8,8) or (U)B3LYP level of theory.[4,5] To rationalize the theoretical and experimental results, a reaction-path bifurcation, following the rate-determining $\mathrm{TS}_{1\rightarrow2}$, was proposed.[4] The present trajectory calculations were designed to test whether this hypothesis would produce reaction dynamics that were consistent with Roth's experimental results.

A direct-dynamics CASSCF(8,8) trajectory[6] was launched from $\mathrm{TS}_{1\rightarrow2}$ with just 0.1 kcal/mol kinetic energy in the **1** → **2** reaction coordinate. Not unexpectedly, it led to biradical **2**. However, two things were interesting about this trajectory. First, it revealed the existence of a secondary minimum, **2a**, for the biradical. At the CASPT2(8,8)//CASSCF(8,8) level[7,8] **2a** was found to be 0.14 kcal/mol higher in enthalpy than conformation **2b**, previously located.[4] Second, the formation of **2a** was followed by an oscillation of the C4−C5 bond that increased in amplitude and then decreased again over ~200 fs.

No other bond in **2** exhibited this behavior. A second trajectory, identical in all respects to the first, except with deuterium in place of H10, failed to show a C4−C5 oscillation of similar character (Figure 2). Apparently the out-of-plane bend of the C3−H10 bond is nearly in resonance with the C4−C5 stretch, and this resonance is detuned by the H/D substitution. In fact, **2a** has two normal modes of CASSCF(8,8) harmonic frequency[8] 741 and 805 cm^{-1}, which are combinations of C3−H10 out-of-plane bend and C4−C5 stretch.

The C3−H10 bend becomes highly activated on formation of **2a** from $\mathrm{TS}_{1\rightarrow2}$ because, as previously noted,[4] allylic stabilization of the biradical is not possible in $\mathrm{TS}_{1\rightarrow2}$, but can be achieved in **2** by bringing H10 into the C1−C2−C3 plane. The drop in potential energy accompanying the development of allylic resonance must be matched by an increase in kinetic energy, which appears initially in a C3−H10 local bending mode. The conversion of this local mode into the 741 and 805 cm^{-1} normal modes of **2a** involves exchange of the kinetic energy between the C3−H10 out-of-plane bend and the C4−C5 stretch. We believe that this is responsible for the oscillation seen in Figure 2.

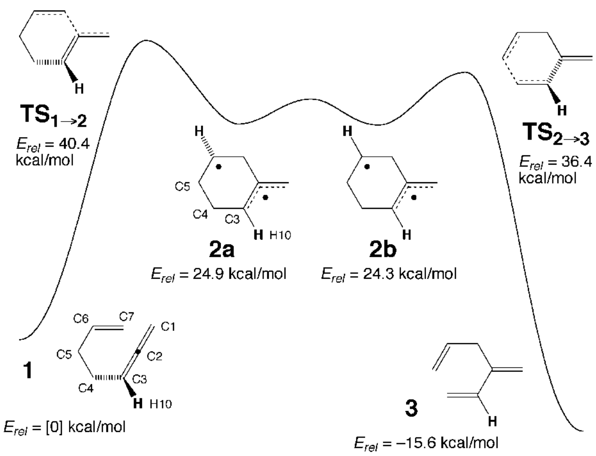

Figure 1. CASSCF(8,8)/6-31G* relative potential energies of the key stationary points for the title reaction.

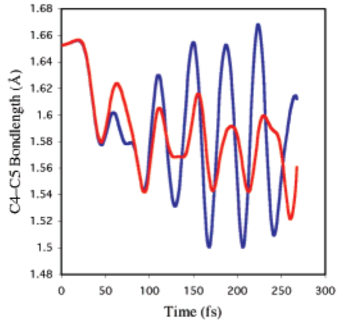

Figure 2. Oscillation of the C4−C5 bond of biradical **2** following its formation from $\mathrm{TS}_{1\rightarrow2}$. Blue line: unlabeled compound. Red line: D in place of H10.

The semiempirical simulation described below suggests that there are chemical consequences of this dynamic behavior. They arise from the fact that conversion of **2** to **3** requires *both* the C3−H10 bond to be bent back out of the plane and the C4−C5 bond to be broken.[4] Neither geometry change alone can convert **2** into **3**, via $\mathrm{TS}_{2\rightarrow3}$.

Since a trajectory from $\mathrm{TS}_{1\rightarrow2}$ solely along the reaction coordinate leads to **2a**, we hypothesized that any direct path from $\mathrm{TS}_{1\rightarrow2}$ to **3** via $\mathrm{TS}_{2\rightarrow3}$ must require some combination of real-frequency vibrational modes, as well as motion along the reaction coordinate. To assess what combination of modes might be effective, we

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calculated a linear-synchronous-transit (LST) path from TS$_{1\rightarrow2}$ to TS$_{2\rightarrow3}$ in mass-weighted Cartesian coordinates. The normalized vector was then expressed as a linear combination of the normal modes.[9] The signs of the linear-combination (LC) coefficients were taken to be the relative phases of the normal-mode motions that should be combined to effect the desired transformation. Indeed, a trajectory, started from TS$_{1\rightarrow2}$ with zero-point-energy (ZPE) in each of the normal modes and 1.04 kcal/mol (*RT* at 250 °C) in the reaction coordinate avoided the biradical **2** and gave the product **3**. We then repeated the procedure with a LST vector calculated from TS$_{1\rightarrow2}$ to **2a**. A trajectory that was isoenergetic with the previous one, but with phases of the ZPE motions dictated by the signs of the new LC coefficients, went to the biradical **2**.

Two questions were raised by these results. The first was whether a few key normal modes controlling the trajectory bifurcation could be identified. The second was whether the existence of the bifurcation was sufficient to explain the experimental results of Roth et al.[1] We addressed the first question by examining the normal modes whose coefficients had the largest absolute values in each of the LST decompositions. For the LST leading to TS$_{2\rightarrow3}$ the reaction coordinate had a weight (square of its coefficient) of 70%. The next most important modes (ν_{10} and ν_{11}) had weights of 5% and 11% respectively. Modes ν_{10} and ν_{11} are combinations of the C4−C5 stretch and C3−H10 bend. For the LST leading to **2a**, the largest contributor, with a weight of 69%, was ν_2, a torsion about the C1−C2 bond that is necessary to establish allylic resonance. The reaction coordinate and ν_3, another skeletal torsion that helps establish allylic resonance, contributed 9% and 6%, respectively.[10]

Determining whether the bifurcation can provide an explanation of the results of Roth et al. requires a full-scale molecular dynamics simulation. Unfortunately, such a study is currently not computationally feasible using the ab initio trajectories described above. Consequently we adopted Truhlar's approach[11] of reparametrizing a semiempirical MO model (AM1-SRP) to fit the results of ab initio calculations on the key stationary points of the PES. Although the fit of the AM1-SRP geometries and relative energies to the CASPT2//CASSCF results was quite good (see Supporting Information for details), the LST decompositions gave rather different results from those for the CASSCF suface. Specifically, the AM1-SRP mode ν_2 (similar to the CASSCF ν_2) was the largest contributor to both LSTs, with weights of 47% for the LST to TS$_{2\rightarrow3}$ and 59% for the one to **2a**.

Nevertheless, using quasiclassical normal-mode sampling of the initial states from a canonical ensemble at 438 K, we found that 17% of 400 AM1-SRP trajectories run from the vicinity of TS$_{1\rightarrow2}$ by-passed the biradical **2** and gave **3**. Of the trajectories entering the PES local minimum around **2**, 8% exited to **3** in $<$500 fs. These would not have been interceptible under Roth's experimental conditions,[1] and so should be counted in with the "concerted" component of the reaction. We ascribe this nonstatistical behavior, at least in part, to the C3−H10/C4−C5 resonance described above.[12]

In summary, our calculations suggest that the mechanism described above can explain the results of Roth et al at least qualititatively.[1] In addition, there follow two general and apparently iconoclastic conclusions. First, the dynamics of biradical **2** suggests that even intermediates in relatively deep PE minima can exhibit nonstatistical behavior. Second, the bifurcation occurring at TS$_{1\rightarrow2}$ shows that mechanisms in which more than one product arises from the same TS are not necessarily prohibited.[13,14] While it is true that the steepest-descent path from a TS can lead only to one product,[13] additional products may sometimes be formed by dynamically favored non-steepest-descent paths.[15]

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Supporting Information Available: AM1-SRP parameters and fits to the ab initio results (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(12) If this hypothesis is correct, deuterium substitution at the H10 site should reduce the nonstatistical behavior of biradical **2**. AM1-SRP calculations to test the hypothesis are in progress.
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(15) It is well-known that several products can arise from a common "plateau" region on a PES, but the present PES does not have such a feature, and so the dynamic bifurcation at the first TS is all the more striking.

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