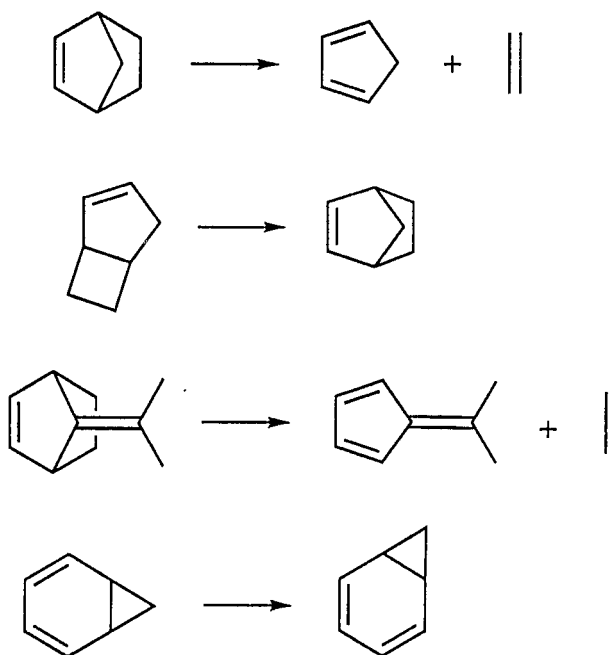


Retro-cycloadditions and sigmatropic shifts: The C_7H_8 and C_7H_{10} potential energy surfaces

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Abstract: Retro-cycloadditions and thermal rearrangements of hydrocarbons have been investigated with density functional theory (B3LYP) and complete active space multiconfiguration self consistent field theory (CASSCF and CASPT2). We review recent results from our laboratories. Subjects are the laser-induced retro-Diels-Alder reactions of norbornene, thermal retro-Diels-Alder reactions of norbornenes and isopropylidenenorbornene, 1,3-sigmatropic shifts of vinylcyclopropane and bicyclo[3.2.0]heptenes, and the 1,5-sigmatropic shifts of norcaradienes. The competition between concerted and stepwise processes and the nature of diradicals formed in these processes are described.



Thermal rearrangements of hydrocarbons have occupied the attention of many prominent physical organic chemists - Doering, Roth, Berson, Klärner, Grimme, Gajewski, Baldwin, to name a few - and, more recently, theoretical organic chemists and their physical chemistry and physical organic colleagues - Borden, Schaefer, Morokuma, Davidson, Doubleday, and Carpenter. At this IUPAC gathering of physical organic chemists in Florianópolis, I have the pleasure of describing our latest studies of these reactions. We have explored the four reactions shown below using modern theoretical methods - hybrid density functional theory and complete active space multiconfigurational self-consistent field theory.

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Our results give a consistent picture of concerted and stepwise mechanisms and evidence for the origin of stereoselectivities occurring even in reactions involving diradical species. Our results are summarized here, and I refer you to full accounts of each of these subjects for more details.¹⁻⁵

Thermal Retro-Diels-Alder reaction

Klärner reported that the retro-Diels-Alder reaction of *cis*-dideuterated norbornene occurs stereospecifically to give *cis*-dideuteroethylene. By contrast, the isopropylidene derivative reacts non-stereospecifically, and the loss of *cis* stereochemical integrity drops as the temperature is raised. These results are summarized in Table 1.⁶

Table 1. Stereoselectivities of Retro-Diels-Alder Reaction.

<u>cis-dideutero</u>	<u>T(K)</u>	<u>%<i>cis</i></u>
Norbornene	593	>97
7-Isopropylidenenorbornene	483	94
	663	87

Our B3LYP and CASSCF calculations on the synchronous concerted and stepwise retro-Diels-Alder processes of norbornene are summarized in Figure 1. The concerted process is favored by 7-12 kcal/mol and occurs through a synchronous concerted transition state structure.

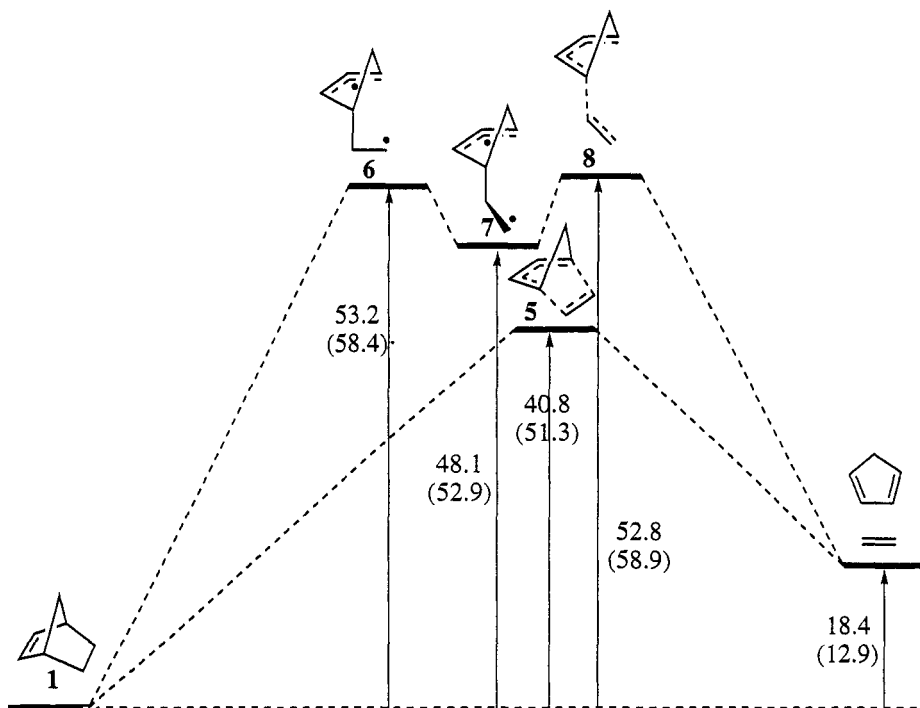


Figure 1. B3LYP (CASSCF)/6-31G* Energies of Stationary Points.

Intermediates are formed only when rotation about the C₄-C₅ bond occurs; this motion moves the radical centers away from each other. Merely stretching the C₁-C₆ bond gives a vibrationally excited concerted transition state, but no energy minimum. The very large preference for the concerted mechanism is consistent with the complete stereospecificity of this reaction observed by Klärner.⁶

Addition of the isopropylidene group alters the surface by lowering the concerted transition state by a small extent and the stepwise transition states and diradical by a larger amount. Consequently, the energy of concert drops for this case, and a non-stereospecific stepwise reaction compete can with the stereospecific concerted pathway. Our calculations of the degree of stereospecificity agree very well with observed values.³

The retro-Diels-Alder reaction of norbornene clearly goes through a concerted pathway, while the diradical mechanism may become competitive when the diradical is adequately stabilized.

Zewail and coworkers studied the decomposition of norbornene induced by femtosecond laser pulses.⁷ The experiments involve two-photon femtosecond pulse excitation to a state 184 kcal/mol above the ground state of norbornene. Two transients are observed, one with mass 94 (the same as norbornene) and a half-life of 165 fs, and a second, with the mass of cyclopentadiene, and a lifetime of 220 fs.⁷ With CASSCF calculations, we find that cleavage of either allylic bond (C1-C6 or C1-C7) occurs readily from the $\pi\pi^*$ state. Conical intersections - regions in space where excited and ground state surfaces cross and become degenerate - exist on the energy surfaces. The structure of the conical intersection formed by cleavage of the C1-C6 bond is shown in Figure 2.

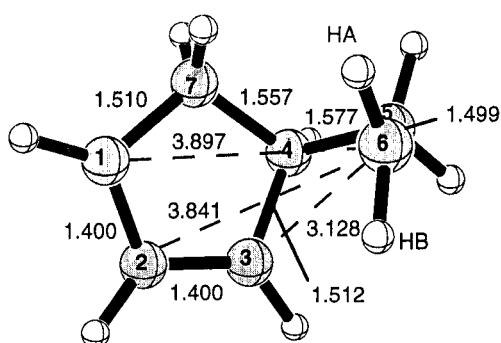


Figure 2. A Conical Intersection on the Norbornene Potential Energy Surface.

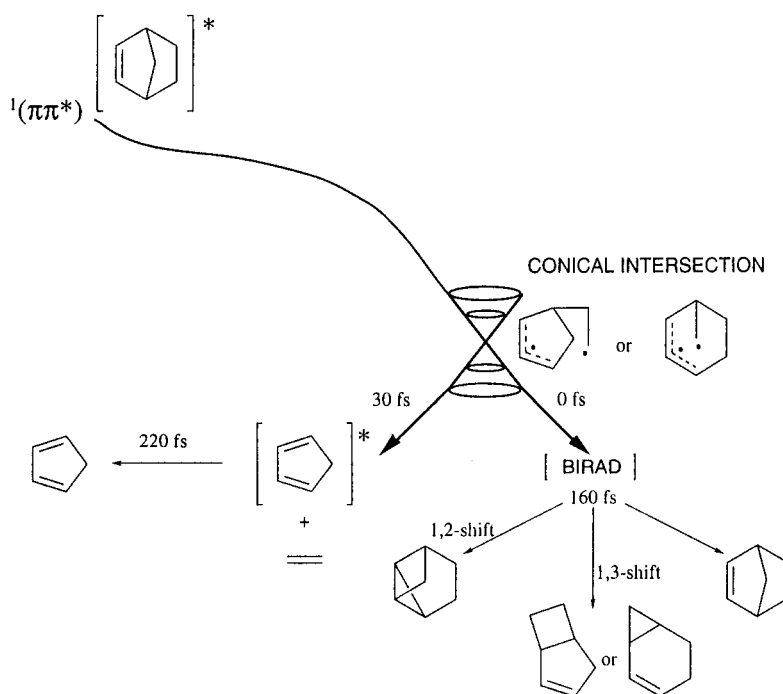


Figure 3. Schematic of Fate of $\pi\pi^*$ Excited State of Norbornene in Zewail Experiments.^{2,7}

From the conical intersections, many processes can occur on the ground state. Figure 3 shows species which likely to be formed from the conical intersection, of course as vibrationally excited species in the Zewail gas-phase experiments. The collapse of the diradical to norbornene or cleavage to vibrationally excited cyclopentadiene can occur rapidly, while species leading to 1,3- or 1,2-shift products may have lifetimes around 165 fs.

We conclude that the excited state reaction of norbornene occurs by one-bond cleavage in the excited state, and subsequent rapid cleavage of the second bond, or slower biradical processes. The femtosecond-pulse excitation leads to species different from those explored in the thermal reaction, where biradical species are not formed.

1,3-shifts

One very interesting region of the norbornene potential surface involves the 1,3-sigmatropic shift process which interconnects norbornene and bicyclo[3.2.0]hept-2-ene. Berson, Klärner, and Baldwin have reported the results shown in Figure 4.

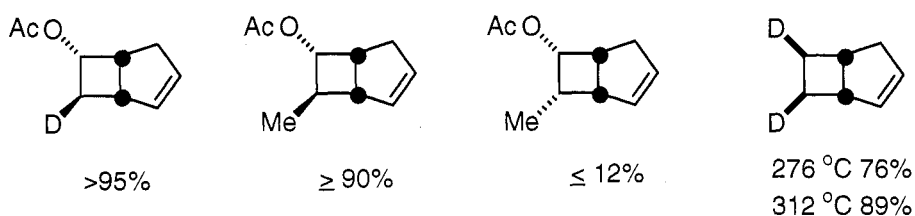


Figure 4. Stereoselectivities (% of 1i,3s) of Thermal 1,3 Shifts.

The results of our computations by UB3LYP¹ or CASSCF² methods are summarized in Figure 5. The surface is characterized by two transition states and a broad flat biradical region.

Starting from bicyclo[3.2.0]heptene, the transition state at 50.5 kcal/mol has the methylene partially rotated in the 1i sense. Continuation along the broad, flat plateau and then collapse to norbornene occurs with inversion. The broad plateau is definitely diradical in character, but the preferred stereochemistry follows Woodward and Hoffmann prediction. A second transition state at 49.2 kcal/mol, about 1 kcal/mol higher than the flat plateau, leads to retention of configuration.

This is reminiscent of our findings,⁴ and those of Davidson and Gajewski,⁸ on the vinylcyclopropane to cyclopentene rearrangement. In all of these cases, a single transition state for bond cleavage is found, and passage from the transition state to 1,3-shift product occurs along a flat surface which leads to product with inversion of configuration. The geometry agrees with the Woodward-Hoffmann prediction, but the mechanism involves diradical species. A second transition state involving rotation of the CH₂ group leads to the 1r,3s product, or those involving 3a processes, which lead to the minor products.

These results indicate that there are no energy minima in the region of the diradicals. While dynamics are important on such a flat surface, the deep minimum for diradicals found on the AM1 and PM3 surfaces are not found. The Carpenter dynamics⁹ treatment is not required to explain the quantitative stereochemical results, although quantitative understanding will require consideration of dynamics.

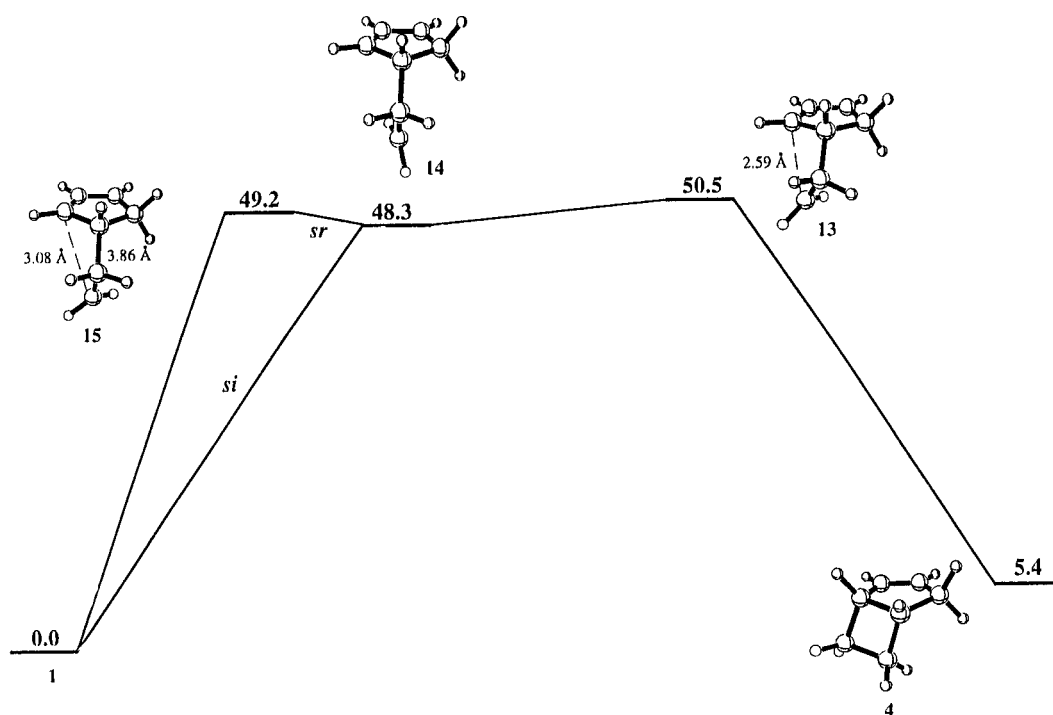


Figure 5. The B3LYP/6-31G* Stationary Points for the 1,3-Shift of Bicyclo[3.2.0]heptene to Norbornene.

1,5-shift of norcaradiene

Finally, we turn to the remarkable 1,5 rearrangement studied by Klärner.¹⁰ The [1,5]-sigmatropic carbon shift is a classic example of a Woodward-Hoffmann pericyclic process, potentially involving a six-electron aromatic transition state. The concerted reaction is predicted to occur with retention of configuration at the migrating carbon atom. Klärner reported a series of elegant studies that established that this reaction occurs mostly with inversion of configuration at the migrating carbon.¹⁰ Compounds bearing substituents on the cyclopropane ring (C-7) of the norcaradiene exhibit inversion with stereoselectivities of 92 to $\geq 99\%$. Other reaction channels, which could explain the experimental results, such as an epimerization at C-7 or two subsequent [1,3]-sigmatropic carbon shifts, have been excluded by labeling experiments.¹⁰

Norcaradiene rearranges via one of two possible transition structures shown in Figure 6. Both transition structures for the [1r,5s] and [1i,5s] processes have pentadienyl radical substructures which are essentially identical to the cyclohexadienyl radical in both geometry and natural bond orders.

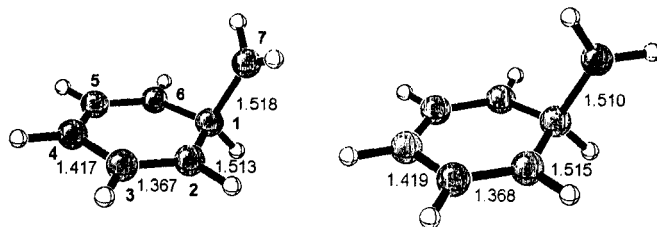


Figure 6. The 1r,5s and 1i,5s Transition States for Norcaradiene Rearrangements.

The distances from the radical center, C7, to the pentadienyl radical termini, C2 and C6, are 2.450 Å and 2.478 Å in these transition states. In neither case is there any significant bonding between C7 and either C2 or C6. These distances are similar to those in the transition structure for the analogous 1,3-shift rearrangement of vinylcyclopropane, which has breaking and forming CC bond lengths of 2.443 Å and 2.482 Å, respectively.⁴ The forbidden [1i,5s] transition structure is computed to be 0.9 kcal/mol more stable by CASSCF (6,6) calculations, and less stable by 0.2 kcal/mol by CASPT2N. Thus, there is essentially no difference in energy between the two reaction pathways. By contrast, disubstituted cases give high 1i,5s stereoselectivity, most likely a steric effect.⁵ The results can be reproduced by B3LYP and CASSCF calculations.

Conclusion

This survey of hydrocarbon rearrangements and retrocycloadditions provides new insights into the nature of diradical species involved in such processes, especially the absence of significant minima on the potential energy surface. Computations provide new details of the potential surfaces first explored by experimentalists.

Acknowledgment

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