[5,5] Sigmatropic Rearrangement. DFT Prediction of a Diradical Mechanism for a Woodward−Hoffmann "Allowed" Thermal Pericyclic Reaction

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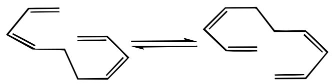
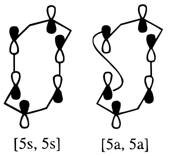
Abstract: The mechanisms of the degenerate [5,5] sigmatropic rearrangements of 5,5a,10,10a-tetrahydroheptalene and (*Z,Z*)-1,3,7,9-decatetraene were explored with restricted and unrestricted Becke3LYP/6-31G* hybrid HF-DFT calculations. The restricted DFT wavefunctions for the synchronous, concerted transition structures for these formally Woodward−Hoffmann allowed 10-electron rearrangements are unstable with respect to unrestricted wavefunctions. A stepwise diradical mechanism is predicted for both reactions. The 9 kcal/mol preference for the [5s,5s] mechanism over the [5a,5a] pathway in the rearrangement of decatetraene results primarily from the geometric distortions that the system must adopt in the [5a,5a] transition structure. The geometric and electronic characteristics of the [5,5] and [3,3] (Cope) rearrangements are compared.

Introduction

After decades of experimental and theoretical studies and some heated debates in the literature, concerted mechanisms have been established for the parent hydrocarbon Diels−Alder reaction of butadiene and ethylene, the [3,3] sigmatropic (Cope) rearrangement of 1,5-hexadiene, and other pericyclic reactions involving simple hydrocarbons.[1] Firmly established paradigms in physical organic chemistry including orbital symmetry conservation,[2] frontier molecular orbital theory,[3] and the idea of the "aromatic" transition state[4] predict concerted mechanisms for these reactions. Concerted pathways are generally assumed for the prototypical pericyclic reactions of simple hydrocarbons.

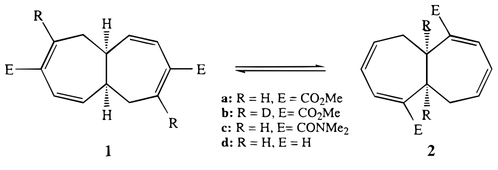
One pericyclic reaction for which a stepwise diradical mechanism may be favored over a concerted pathway in the absence of substituent electronic and steric effects is the [5,5] sigmatropic rearrangement. Chemical systems capable of this 10-electron process are large enough to allow both [5s,5s] and [5a,5a] sigmatropic shift stereochemistries.





The results of a prior experimental and computational study (AM1)[5] suggest that this reaction occurs via a stepwise diradical mechanism, although an "aromatic" orbital-symmetry-allowed concerted pathway[2] is not precluded by geometric or steric effects. The tendency of AM1 to predict stepwise mechanisms even when concerted mechanisms are favored[1] detracts from the definitiveness of this result.

The rearrangements of **1b**−**d** were reported by Hafner and co-workers in 1993.[5] The experimental $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for the rearrangement of **1c** to **2c** are 21 kcal/mol and −13 eu, respectively. For the reverse reaction, the values are 23 kcal/mol and −9 eu. The negative $\Delta S^{\ddagger}$ values for the forward and reverse rearrangements suggest a concerted mechanism. However, they are also consistent with a diradical mechanism in which the new C−C bond is formed to a large extent and the breaking C−C bond is only slightly elongated in the transition state. AM1/configuration interaction (CI) semiempirical calculations predict a stepwise mechanism involving a diradical intermediate for the reaction. However, semiempirical methods are known to favor open-shell stepwise over closed-shell concerted mechanisms in many cases.[6]



To elucidate the details of the mechanism for the [5,5] sigmatropic rearrangement and to increase our knowledge of the factors which bias pericyclic reactions toward concerted or stepwise mechanisms, we have explored the potential-energy surfaces for the [5,5] sigmatropic rearrangements of 5,5a,10,10a-tetrahydroheptalene (**1d**) and (*Z,Z*)-1,3,7,9-decatetraene (**3**) at the Becke3LYP/6-31G* level of theory (Figure 1). We have also studied the [3,3] (Cope)[7] rearrangement of 3,6-bismethyl-

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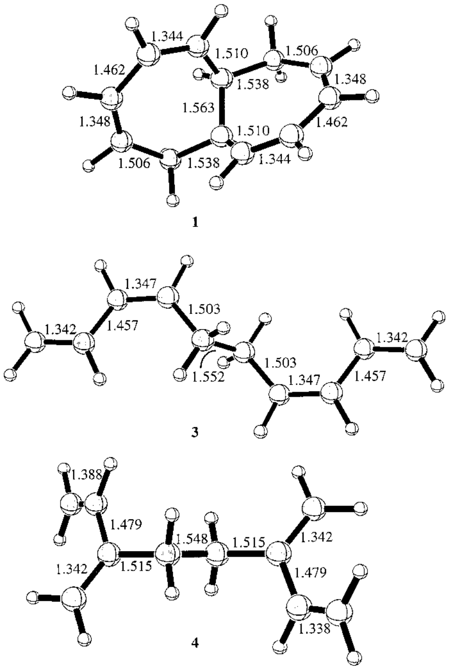


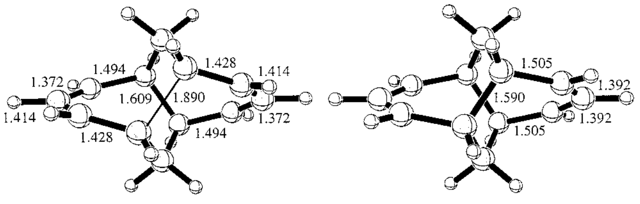
Figure 1. Becke3LYP/6-31G*-optimized structures of 5,5a,10,10a-tetrahydroheptalene (**1d**), (*Z*,*Z*)-1,3,7,9-decatetraene (**3**), and 3,6-bismethylene-1,7-octadiene (**4**). All bond lengths are in angstroms.

ene-1,7-octadiene (**4**) for comparison. The Becke3LYP hybrid HF-DFT method was used because it has been shown to provide a balanced treatment of both open- and closed-shell systems and has been used to predict activation barriers in excellent agreement with experimental results for many pericyclic reactions.[8]

This paper is organized as follows. First, the computational methods are outlined. Second, transition structures and intermediates in the [5,5] rearrangements of **1d** and **3** are then discussed. Third, the stationary points on the potential surface for the Cope rearrangement of **4** are presented. Finally, the mechanisms of the [3,3] and [5,5] sigmatropic rearrangements are compared.

Computational Methodology

Calculations were performed with the *Gaussian94* suite of programs.[9] All stationary points were fully optimized at the Becke3LYP/6-31G* level[10] and identified as either transition structures or minima with vibrational frequency calculations. Restricted (RBecke3LYP) and unrestricted (UBecke3LYP) wavefunctions were used for closed- and open-shell species, respectively. Stability calculations were performed on all closed-shell transition structures. All relative energies include zero-point energy corrections.



5 $<S^2> = 0.26$ **6** $<S^2> = 0.96$

Figure 2. UBecke3LYP/6-31G* diradical transition structure, **5**, and intermediate, **6**, for the [5a,5a] sigmatropic rearrangement of **1d**. All bond lengths are in angstroms.

Table 1. Energetics of the [5,5] Sigmatropic Rearrangements of **1a** and **3** and the [3,3] Sigmatropic Rearrangement of **4**[a]

		$\Delta E^{\ddagger}$	$\Delta E_{rxn}{}^{b}$
1a	[5a,5a]	29.1	23.9
3	[5s,5s]	34.3	28.3
3	[5a,5a]	43.3	34.4
4	[3,3]	21.9	10.8

[a] All energies are in kcal/mol and are corrected for zero-point energy. [b] Energy of reaction for formation of diradical intermediate.

Results and Discussion

[5a,5a] Sigmatropic Rearrangement of 5,5a,10,10a-Tetrahydroheptalene (1d). During this degenerate rearrangement, one C−C bond in **1d** is broken and another is formed. A D_2 synchronous, concerted transition structure for this process was located at the RBecke3LYP/6-31G* level. In this transition structure, the breaking and forming bonds are of equal lengths. However, a stability calculation predicted a lower energy unrestricted wavefunction for the structure. Subsequently, unrestricted DFT (UBecke3LYP/6-31G*) was utilized in order to locate the diradical transition structure **5** (Figure 2), which is 1.0 kcal/mol more stable than the structure obtained with the restricted wavefunction.

Transition structure **5** leads to diradical intermediate **6** with a predicted $\Delta E^{\ddagger}$ of 29.1 kcal/mol and a ΔE_{rxn} of 23.9 kcal/mol (Table 1). In **5**, the length of the forming C−C bond is 1.890 Å, only 0.3 Å longer than that in diradical intermediate **6**, and the C−C bond which is broken during the reaction is still completely formed. In intermediate **6**, the new C−C bond is fully formed, and the second has not yet begun to break.

[5,5] Sigmatropic Rearrangement of (*Z*,*Z*)-1,3,7,9-Decatetraene (3). Because of its conformational flexibility, orbital-symmetry-allowed [5s,5s] and [5a,5a] concerted mechanisms are possible for **3**. However, as with **1d**, attempts to locate synchronous, concerted transition structures for both of these reaction pathways with restricted DFT wavefunctions resulted in stationary points which have instabilities with respect to unrestricted wavefunctions. Diradical transition structures (**7** and **9**, Figure 3) and intermediates (**8** and **10**) were located at the UBecke3LYP/6-31G* level.

In diradical transition structures **7** and **9**, the forming C−C bonds are 1.932 and 1.923 Å in length, respectively, while the lengths of the C−C bonds which are broken during the reaction are 1.619 and 1.583 Å. Bond formation has progressed to a large extent in these transition structures, while the second C−C bond is stretched by less than 0.1 Å in each structure.

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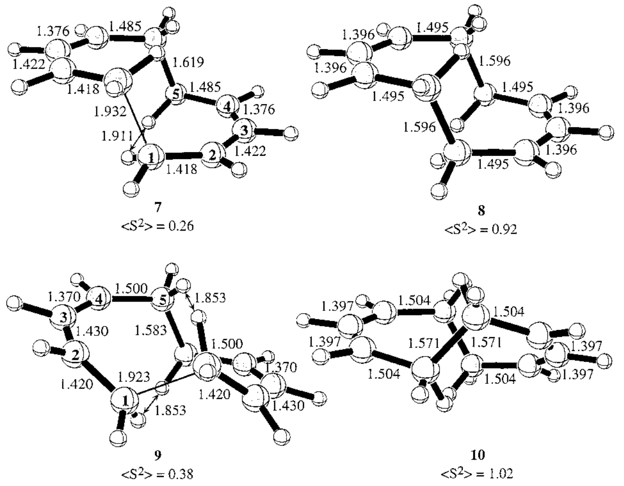
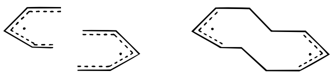


Figure 3. UBecke3LYP/6-31G* diradical transition structures, **7** and **9**, and intermediates, **8** and **10**, for the [5s,5s] and [5a,5a] sigmatropic rearrangements of **3**. All bond lengths are in angstroms.

The [5s,5s] transition structure **7** leads to the diradical intermediate **8** with a $\Delta E^{\ddagger}$ of 34.3 kcal/mol. The ΔE_{rxn} for formation of **8** is 28.3 kcal/mol. The $\Delta E^{\ddagger}$ for the [5a,5a] pathway is 9.0 kcal/mol higher than that for the [5s,5s] route, and this large preference for the [5s,5s] mechanism is reflected in the relative energies of the diradical intermediates as well. The [5a,5a] diradical **10** is 6.1 kcal/mol less stable than the [5s,5s] diradical **8**.

Transition structures **7** and **9** can be considered resonance hybrids of the two species shown below. At one extreme, each transition structure may be represented as two weakly interacting pentadienyl radicals. Alternatively, the transition structures may be better represented as a bis-allyl diradical species. The UBecke3LYP/6-31G*-optimized transition structures **7** and **9** are consistent with the latter alternative.



The greater stabilities of [5s,5s] transition structure **7** and intermediate **8** relative to [5a,5a] transition structure **9** and intermediate **10** are attributed primarily to the geometric distortions required for the [5a,5a] process. In [5s,5s] structures **7** and **8**, the pentadienyl moieties are planar or nearly so, with C1−C2−C4−C5 torsional angles of 1.9 and 0.0°, respectively, whereas in **9** and **10**, the pentadienyl fragments are distorted from planarity with C1−C2−C4−C5 torsional angles of 32.0 and 6.9°, respectively.

Based on UBecke3LYP/6-31G* single-point energies of the pentadienyl fragments in **7** and **9**, geometric distortions destabilize the [5a,5a] transition structure **9** by 9.0 kcal/mol relative to the [5s,5s] transition structure **7**. This energy difference is exactly the same as the difference between the $\Delta E^{\ddagger}$ values predicted for the two pathways.

The $\Delta E^{\ddagger}$ for the [5a,5a] shift of **1d** is 14.2 kcal/mol below the barrier for the [5a,5a] rearrangement of **3**. This large difference in activation barriers is the result of an unfavorable steric interaction present in the [5a,5a] transition state for **3** but absent in the [5a,5a] transition structure for **1d**. In transition structure **9**, two methylene hydrogens are within 1.85 Å (Figure 3) of each other. In **5**, the [5a,5a] transition structure for **1d**, the two hydrogens have been replaced by a methylene unit, and the repulsive H−H interaction is eliminated.

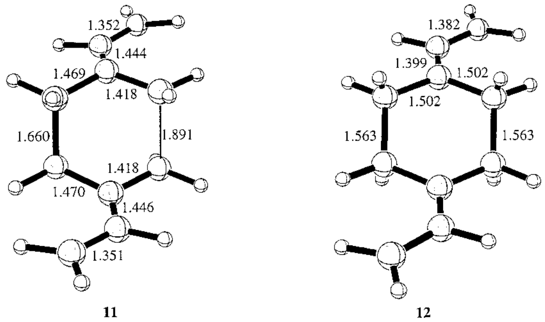


Figure 4. UBecke3LYP/6-31G* diradical transition structure, **11**, and intermediate, **12**, for the [3,3] sigmatropic (Cope) rearrangement of **4**. All bond lengths are in angstroms.

[3,3] Sigmatropic (Cope) Rearrangement of 3,6-Bismethylene-1,7-octadiene (4). The [5,5] sigmatropic shift, in contrast to the [3,3] sigmatropic shift, favors a diyl intermediate.[7b−g] There is evidence that the 2,5-diphenyl substitution of 1,5-hexadiene causes the substituted case to react through a stepwise mechanism. To compare isoelectronic Cope and [5,5] systems, we explored the mechanism of the 2,5-divinyl Cope rearrangement. As with the systems discussed above, the closed-shell DFT wavefunction for the synchronous, concerted Cope rearrangement of **4** is unstable with respect to the unrestricted wavefunction. Attempts to locate a transition structure at the UBecke3LYP/6-31G* level resulted in **11** (Figure 4).[11] This is a true transition structure in which the lengths of the forming and breaking C−C bonds are similar to those found for the diradical pathways of the [5,5] sigmatropic rearrangements. However, the $\langle S^2 \rangle$ for this transition structure is 0.0. The lack of spin contamination suggests that the species is a closed-shell singlet. A true diradical intermediate, **12**, for this reaction was located. This species has an $\langle S^2 \rangle$ of 1.01 which is consistent with its diradical nature. The $\Delta E^{\ddagger}$ and ΔE_{rxn} for formation of intermediate **11** are 21.9 and 10.8 kcal/mol, respectively. The predicted ΔE_{rxn} is in good agreement with the 12.7 kcal/mol ΔH_{rxn} computed from Benson's group increments.[12]

In transition structure **11**, the forming C−C bond is 1.891 Å in length. Bond formation has progressed to a large extent, but the C−C bond which is broken during the reaction is only 0.11 Å longer than that of reactant **4**.

The $\Delta E^{\ddagger}$ predicted for this reaction, 21.9 kcal/mol, is in good agreement with the experimental $\Delta H^{\ddagger}$ of 21.3 ± 0.2 kcal/mol for the Cope rearrangement of 2,5-diphenyl-1,5-hexadiene.[13] On the basis of experimental and theoretical studies, a diradical mechanism has been predicted for the Cope rearrangement of this 1,5-diene,[13,14] in accord with our DFT prediction of a diradical mechanism for the rearrangement of **4**.

The $\Delta E^{\ddagger}$ for the [3,3] rearrangement of **4** is much lower than that for any of the [5,5] rearrangements examined. This

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(11) RHF/6-31G* calculations predict synchronous, concerted transition structures for the [5,5] sigmatropic shifts of **1d** and **3** and the Cope rearrangement of **4**. The forming and breaking bond lengths in the [5,5] transition structures are very short, with lengths which range from 1.690 to 1.744 Å. These transition structures have large amounts of diradical character. Both the forming and breaking C−C bonds in the RHF/6-31G* transition structure for the Cope rearrangement of **4** are 1.865 Å. The RHF/6-31G* activation barriers for the [5s,5s], [5a,5a], and [3,3] rearrangements follow the same relative ordering as the DFT results.

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difference is also reflected in the relative energies of the diradical intermediates and is due to both steric effects and the greater stability of the 1,1-dialkylallyl radical moieties present in [3,3] intermediate **12** relative to the 1,3-dialkylallyl radical moieties present in the [5,5] intermediates.

At the UBecke3LYP/6-31G* level, the 1,1-dimethylallyl radical is predicted to be 3.7 kcal/mol more stable than the 1,3-dimethylallyl radical. Thus, the [3,3] intermediate **12** is expected to be at least 7.4 kcal/mol lower in energy than the [5,5] intermediates. As the formation of the diradical intermediates is endothermic, much of this energy difference should be reflected in the transition structures as well. In addition, the [3,3] transition structure and intermediate lack the destabilizing transannular H−H steric interactions found in the [5,5] transition structures and intermediates.

Conclusions

DFT calculations predict that the [5,5] sigmatropic rearrangements of 5,5a,10,10a-tetrahydroheptalene and (*Z*,*Z*)-1,3,7,9-decatetraene occur via stepwise diradical mechanisms with activation barriers of 29.1 and 34.3 kcal/mol, respectively. For the rearrangement of (*Z*,*Z*)-1,3,7,9-decatetraene, both [5s,5s] and [5a,5a] reaction pathways are possible, and the [5s,5s] route is favored by 9.0 kcal/mol as a result of the greater planarity of the delocalized radical moieties in the [5s,5s] transition state. The [3,3] (Cope) rearrangement of 3,6-bismethylene-1,7-octadiene is also predicted to occur by a stepwise diradical mechanism. The barrier for this reaction, 21.9 kcal/mol, is much less than those for the [5,5] rearrangements due to greater stability of its constituent radical moieties and the lack of unfavorable steric interactions in the transition state.

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