

Ab Initio and DFT Calculations on the Cope Rearrangement of 1,2,6-Heptatriene

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Abstract: (8/8)CASSCF, CASPT2, and B3LYP calculations have been performed on the potential surface for the Cope rearrangement of 1,2,6-heptatriene (**1**) to 3-methylene-1,5-hexadiene (**3**). Although an allylic diradical intermediate (**2**) has been located, the transition states connecting it to **1** and **3** show little allylic delocalization. The first of these transition states is higher in energy than the second; and, when the geometries of intermediate points are constrained so as to prevent allylic delocalization, a pathway from the former to the latter has been found along which the energy decreases monotonically. The existence of a second pathway from **1** to **3**, which bypasses **2**, is consistent with the experimental results of Roth and co-workers, who found that roughly half of this rearrangement proceeds without formation of a trappable intermediate. In the absence of appreciable allylic delocalization in the rate-determining transition state, the relative strengths of the π bonds broken and the σ bond formed in this transition state explain why ΔH^\ddagger for Cope rearrangement is lower for **1** than for 1,5-hexadiene and more highly unsaturated derivatives.

Calculations on the Cope rearrangement have proven to be unexpectedly challenging.¹ For example, although (6/6)CASSCF calculations with the 3-21G basis set gave fairly good results,² improvement of the basis set to 6-31G* gave an activation energy that was much too high and a potential surface with two reaction pathways for the chair Cope rearrangement.³ Subsequently, it was found that dynamic electron correlation must be included to obtain reasonable results.⁴

Ab initio calculations on the Cope rearrangement that included dynamic correlation,⁵ via either the CASPT2⁶ or CASMP2⁷ versions of multireference perturbation theory, gave computed activation parameters that were in excellent agreement with those measured.⁸ These calculations⁵ confirmed that the Cope rearrangement is a concerted reaction that proceeds via an aromatic transition state in which bond making and bond breaking occur synchronously.¹

Density functional theory (DFT) calculations, performed with the B3LYP functional,⁹ have also been shown to give excellent

results for the Cope rearrangements of 1,5-hexadiene¹⁰ and more highly unsaturated derivatives.¹¹ The magnetic properties, computed for the transition states of the Cope rearrangements of 1,5-hexadiene^{10b} and semibullvalene,¹² show that these transition states are, indeed, aromatic.

However, not all Cope rearrangements are concerted. A sufficient number of radical stabilizing groups¹³ or relief of strain^{12,14} can favor mechanisms in which bond breaking precedes bond making. Substituents can also favor mechanisms in which bond making precedes bond breaking, so that a derivative of cyclohexane-1,4-diyl is formed as an intermediate.¹⁵ In this paper, we report the results of CASPT2 and B3LYP calculations on an allenyl Cope rearrangement that involves such an intermediate.

In 1993, Roth and co-workers found that a diradical intermediate (**2**) could be trapped by oxygen and sulfur dioxide in the Cope rearrangement of 1,2,6-heptatriene (**1**) to 3-methylene-1,5-hexadiene (**3**).¹⁶ Extrapolation to infinite oxygen concentra-

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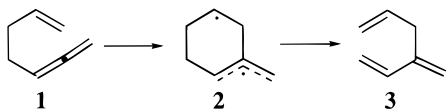
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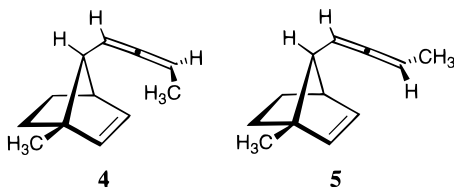
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tion of the ratio of trapping product to **3** indicated that roughly half of the rearrangement passes through diradical **2** and half of the rearrangement proceeds directly from **1** to **3**, without formation of a trappable intermediate.



Wessel and Berson adduced stereochemical evidence for the formation of a diradical intermediate in the Cope rearrangement of an optically active dimethyl derivative of **1**.¹⁷ They concluded that at least 16% of the reaction passes through the corresponding dimethyl derivative of **2**, but their experimental design precluded them from drawing any conclusion as to whether all of the reaction passes through this intermediate.

Prior to both of these studies, Duncan and co-workers had examined the stereochemistry of the allenyl Cope rearrangements of diastereomers **4** and **5**.¹⁸ Both were found to give



predominantly the products expected from concerted Cope rearrangements, but ca. 5% of the products formed from **4** consisted of the major products formed from **5** and vice versa. These findings were interpreted in terms of the existence of a minor reaction pathway, involving the formation of a diradical intermediate.

We undertook a study of the potential surface for the Cope rearrangement of **1** to address the question of why concerted and stepwise reaction pathways apparently compete in its Cope rearrangement to **3** and possibly in the Cope rearrangements of **4** and **5** as well. We were also interested in comparing some calculated energy differences involving **2** with those measured for this diradical. For example, from their experiments, Roth and co-workers obtained heights of ca. 11 and 8 kcal/mol for the enthalpic barriers separating **2** from respectively **1** and **3** and a singlet–triplet energy difference of 1.4 kcal/mol in **2**, with the triplet being the ground state.¹⁶ Finally, we wanted to assess to what extent allylic resonance in the transition state(s) is responsible for the lower enthalpy of activation for the Cope rearrangement of **1** ($\Delta H^\ddagger = 27.5$ kcal/mol¹⁹) relative to those for the Cope rearrangements of 1,5-hexadiene ($\Delta H^\ddagger = 33.5$ kcal/mol⁸) and of more highly unsaturated derivatives of this hydrocarbon ($\Delta H^\ddagger = 31$ – 34 kcal/mol¹¹).

As discussed above, both CASPT2 and B3LYP-DFT calculations give excellent results for Cope rearrangements that are concerted; but, because the reference wave functions for DFT calculations are single determinants of Kohn–Sham orbitals, DFT and its unrestricted variant (UDFT) each have some problems in dealing with diradicals.²⁰ Therefore, we were anxious to test the performance of B3LYP and UB3LYP

calculations against that of CASPT2 in the Cope rearrangement of **1**, to see whether the intermediacy of diradical **2** in this reaction would compromise the performance of these DFT methods. In this paper, we report the results of our CASPT2, B3LYP, and UB3LYP calculations.

Computational Methodology

CASSCF calculations were performed on **1**–**3** and the transition states connecting them, using an active space consisting of eight electrons in eight orbitals. The orbitals consisted of the four σ and π bonding orbitals involved in this reaction and an antibonding counterpart to each bonding orbital. (8/8)CASSCF vibrational analyses were used to characterize stationary points as energy minima or transition states and to obtain corrections for zero-point energy differences, which were not scaled. The CASSCF calculations were carried out with the Gaussian 94 suite of electronic structure programs.²¹

The effects of dynamic electron correlation⁵ were included by performing single-point CASPT2 calculations⁶ at all the stationary points. These calculations were carried out with MOLCAS 3.²² The 6-31G* basis set²³ was used for the CASSCF and CASPT2 calculations.

The same basis set was used to perform DFT calculations, using the hybrid, Becke, three-parameter, exchange functional^{19a} and incorporating the nonlocal correlation functional of Lee, Yang, and Parr.^{9b} Stationary points were located and vibrational analyses were performed at the (U)B3LYP/6-31G* level using Gaussian 94.

Results and Discussion

The CASSCF, CASPT2, and B3LYP energies of **1**–**3** and the two transition states (TS_{1–2} and TS_{2–3}) connecting them are given in Table 1. The relative enthalpies at 450 K are shown schematically in Figure 1, where they are compared with the experimental values.^{16,19} The C–C bond lengths in each of these species are given in Table 2. Complete descriptions of their geometries are available as Supporting Information.

Relative Energies of 1–3. At both 298 and 450 K, differences between the heat capacities (ΔC_p) of **1** and **3** are calculated to contribute less than 0.3 kcal/mol to the difference between the heats of formation of the two trienes. Combining the small $\Delta C_p \times 298$ K corrections with the differences in electronic and zero-point energies (ΔZPE) between **1** and **3** in Table 1 yields $\Delta\Delta H_f^\circ_{298} = -15.1$ kcal/mol at CASSCF, -13.8 kcal/mol at CASPT2, and -11.5 kcal/mol at B3LYP.

Group equivalents²⁴ give $\Delta\Delta H_f^\circ_{298} = -15.7$ kcal/mol, and Roth's experiments give $\Delta\Delta H_f^\circ_{298} = -14.5$ kcal/mol.¹⁶ The CASPT2 value of $\Delta\Delta H_f^\circ_{298} = -13.8$ kcal/mol is smaller than Roth's experimental value by only 0.7 kcal/mol. However, the B3LYP/6-31G* value of $\Delta\Delta H_f^\circ_{298} = 11.5$ kcal/mol is smaller than Roth's value by 3.0 kcal/mol.

B3LYP has previously been found to underestimate the energy of allene relative to propyne by 4.5 kcal/mol.²⁵ Therefore, it is not surprising that the enthalpy associated with the transformation of the allenic double bonds in **1** into the

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Table 1. Relative Energies, Differences in Zero Point Energy, and Heat Capacity Corrections for the Stationary Points on the Potential Surface for the Cope Rearrangement of 1,2,6-Heptatriene (**1**) to 3-Methylene-1,5-hexadiene (**3**), Computed with the 6-31G* Basis Set

structure	$\Delta E_{\text{CASSCF}}^a$	$\Delta E_{\text{CASPT2}}^a$	ΔZPE^b	$\Delta C_v^{450} \times 450^b$	$\Delta E_{\text{B3LYP}}^a$	ΔZPE^b	$\Delta C_v^{450} \times 450^b$
1	-270.9086	-271.7388	96.1	18.4	-272.6803 ^c	92.1	18.8
1 ²	24.3	13.4	1.4	-0.5	16.5 ^{d,e}	-0.4	-0.2
1 ³	25.2	14.9	1.3	-0.5	17.5 ^d	-0.5	-0.1
3	-15.6	-14.3	0.7	0.0 ^f	-11.9 ^c	0.5	0.0 ^g
TS _{1→2}	40.4	25.9	0.8	-0.8	31.9 ^d	-0.2	-0.5
TS _{2→3}	36.4	22.6	0.8	-0.9	30.6 ^d	-0.6	-0.5
midpoint ^h	33.9	22.5					

^a Absolute energies in hartrees. ^b Absolute energies in kcal/mol. ^c RB3LYP. ^d UB3LYP. ^e Energy for the UB3LYP "singlet" with $S^2 = 1$. As discussed in the text, the energy of the actual singlet ($S^2 = 0$) should be 1.0 kcal/mol lower. ^f $\Delta C_v^{298} \times 298 = -0.2$. ^g $\Delta C_v^{298} \times 298 = -0.1$. ^h See text for a description of this geometry and how it was obtained.

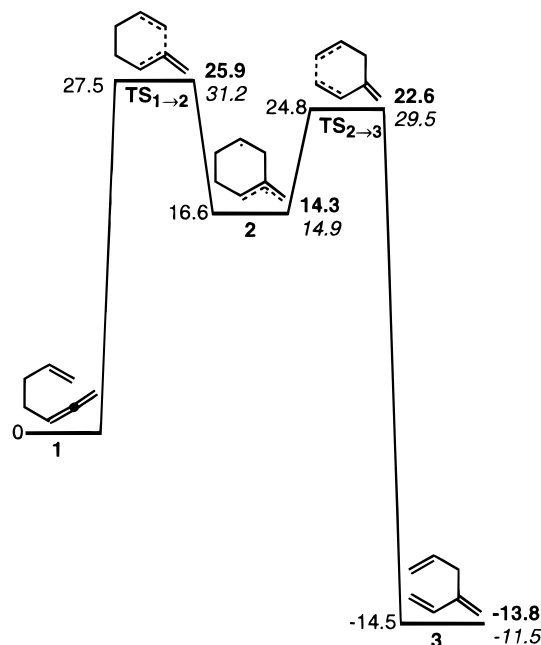


Figure 1. Experimental^{16,19} values for the differences between the enthalpies of **1**–**3** and the transition states connecting them. Enthalpy differences computed at the (8/8)CASPT2/6-31G*// (8/8)CASSCF/6-31G* level of theory are shown in boldface type, and (U)B3LYP/6-31G* ($S^2 = 0$) values are in italics.

conjugated diene moiety in **3** is also underestimated by a substantial amount.

Because **2** is a diradical, unrestricted (U)B3LYP calculations were performed²⁰ for this singlet intermediate in the transformation of **1** to **3**. As shown in Table 1, the UB3LYP energy of 16.5 kcal/mol for **1**² relative to **1** is 3.1 kcal/mol higher than that computed at the CASPT2 level of theory.

However, the UB3LYP "singlet" has $S^2 = 1.00$; so it is really a 1:1 mixture of singlet ($S^2 = 0$) and triplet ($S^2 = 2.00$) states. Since, as shown in Table 1, the UB3LYP energy of the triplet state (**1**³) is higher in energy than the "singlet" by 1.0 kcal/mol, a pure (i.e., $S^2 = 0$) singlet spin wave function for **1**² should have a UB3LYP energy that is 15.5 kcal/mol higher than the B3LYP energy of **1**.

It is of some interest that the CASSCF and (U)B3LYP ΔZPE corrections for **1** versus **2** have opposite signs. The 1.8 kcal/mol difference between these corrections results in the CASPT2 and (U)B3LYP enthalpies of respectively 14.3 and 14.9 kcal/mol for singlet **2** relative to **1**, being more nearly the same than the CASPT2 and (U)B3LYP ($S^2 = 0$) energies. As shown in Figure 1, the CASPT2 and (U)B3LYP values for ΔH_{450}^\ddagger of diradical **2** relative to the reactant (**1**) are respectively 2.3 and 1.7 kcal/mol lower than the value reported by Roth.¹⁶

The C₁–C₂ and C₂–C₃ bond lengths in **2** (cf. Table 2) show that this diradical is stabilized by allylic resonance. The allylic delocalization of the unpaired electron at C₃ of **2** decreases significantly the through-bond interaction²⁶ between it and the unpaired electron of opposite spin at C₆ compared to, for instance, the through-bond interaction between the analogous pair of electrons in the chair transition state for the Cope rearrangement of 1,5-hexadiene. Consequently, the CASSCF geometries of **1**² and **1**³ are nearly identical.

Roth and co-workers presented evidence, both from the temperature dependence of the EPR signal that they attributed to **1**³ and from oxygen trapping, that the triplet is the ground state of this diradical.¹⁶ Our CASSCF, CASPT2, and B3LYP calculations all predict a singlet–triplet energy difference of about the same size (1–2 kcal/mol) as that measured by Roth et al., but of the *opposite sign*. Even though both theory and experiment agree that the magnitude of ΔE_{ST} is small, the disagreement as to whether the singlet or the triplet is the ground state is disturbing; and the reason for this discrepancy is not currently known.²⁷

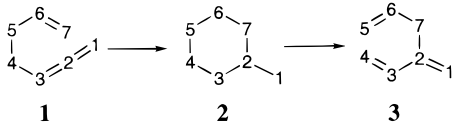
CASPT2 Energy and CASSCF Geometry of TS_{1→2}. Our CASSCF, CASPT2, and B3LYP calculations all find that the energy of TS_{1→2} is higher than that of TS_{2→3}. Therefore, passage over TS_{1→2} is the rate-determining step in the Cope rearrangement of **1**. Since the reactant is higher in energy than the product, it is not surprising that the transition state connecting diradical **2** to **1** is higher in energy than the transition state connecting **2** to **3**.

CASPT2 gives $\Delta H^\ddagger = 25.9$ kcal/mol for the Cope rearrangement of **1**, which is 1.6 kcal/mol lower than the experimental value of $\Delta H^\ddagger = 27.5$ kcal/mol.¹⁹ CASPT2 calculations with the 6-31G* basis set also underestimate the experimental value of $\Delta H^\ddagger = 33.5$ kcal/mol for the Cope rearrangement of 1,5-hexadiene,⁸ in that case by 2.7 kcal/mol.^{5a} Therefore, our CASPT2/6-31G* calculations find that ΔH^\ddagger for the Cope rearrangement is ca. 5 kcal/mol smaller for **1** than for 1,5-hexadiene, in good agreement with the experimental difference of $\Delta \Delta H^\ddagger = 6$ kcal/mol.

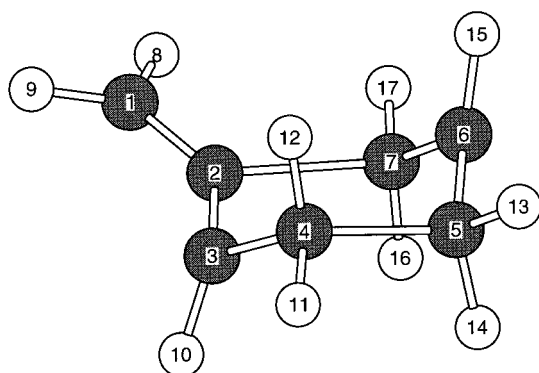
This good agreement between the CASPT2 calculations and the experiments^{8,19} indicates that the CASSCF optimized geometry for TS_{1→2} can, with some confidence, be used to provide information as to why ΔH^\ddagger for the Cope rearrangement

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Table 2. Carbon–Carbon Bond Lengths (Å) for the Stationary Points on the Potential Surface for the Cope Rearrangement of 1,2,6-Heptatriene (**1**) to 3-Methylene-1,5-hexadiene (**2**), Obtained with the 6-31G* Basis Set


structure	method	C ₁ –C ₂	C ₂ –C ₃	C ₃ –C ₄	C ₄ –C ₅	C ₅ –C ₆	C ₆ –C ₇	C ₂ –C ₇
1	CASSCF	1.316	1.317	1.509	1.565	1.505	1.339	
	RB3LYP	1.308	1.309	1.513	1.547	1.504	1.333	
2	CASSCF	1.398	1.389	1.504	1.562	1.499	1.498	1.552
	UB3LYP	1.391	1.390	1.500	1.545	1.492	1.492	1.527
3	CASSCF	1.399	1.389	1.504	1.560	1.499	1.502	1.554
	UB3LYP	1.392	1.391	1.501	1.543	1.493	1.497	1.529
TS₁₋₂	CASSCF	1.346	1.475	1.344		1.339	1.504	1.550
	RB3LYP	1.344	1.470	1.340		1.333	1.504	1.522
	CASSCF	1.336	1.404	1.477	1.652	1.472	1.413	1.919
	RB3LYP	1.333	1.394	1.441	1.755	1.432	1.412	1.841
	UB3LYP	1.333	1.394	1.441	1.753	1.432	1.412	1.838
TS₂₋₃	CASSCF	1.340	1.466	1.435	1.843	1.431	1.482	1.612
	UB3LYP	1.342	1.437	1.427	1.833	1.418	1.467	1.614
midpoint	CASSCF	1.341	1.471	1.489	1.620	1.484	1.490	1.589

**Figure 2.** (8/8)CASSCF/6-31G* optimized geometry of **TS₁₋₂** for the formation of 2-methylenecyclohexane-1,4-diyl (**2**) in the Cope rearrangement of 1,2,6-heptatriene (**1**) to 3-methylene-1,5-hexadiene (**3**).

of **1** is ca. 6 kcal/mol smaller than ΔH^\ddagger for the Cope rearrangement of 1,5-hexadiene. The CASSCF geometry for **TS₁₋₂** is shown in Figure 2, and the CASSCF and B3LYP C–C bond lengths in this transition state are given in Table 2.²⁸

The geometry for **TS₁₋₂** in Figure 2 confirms Roth's conclusion¹⁶ that allylic resonance in the transition state cannot be responsible for much of the 6 kcal/mol lower value of ΔH^\ddagger for the Cope rearrangement of **1** relative to ΔH^\ddagger for the Cope rearrangement of 1,5-hexadiene. In **TS₁₋₂**, the p- π AO at C₃ remains nearly orthogonal to the π bond between C₁ and C₂. The dihedral angle between the C₁–C₂ and C₃–H bonds is 79.6° in this transition state, compared to –0.9° in **1**² and –2.2° in **3**², both of which are allylically delocalized.

If allylic resonance stabilization were assumed to vary with the cosine of this dihedral angle, at most, ca. 2 kcal/mol of the allylic resonance energy²⁹ might be available to stabilize **TS₁₋₂**. However, the factor of 2.5 greater reduction in the value of ΔH^\ddagger

(28) (6/6)CASSCF/6-31G* calculations give transition state geometries for the Cope rearrangements of 1,5-hexadiene^{4,5} and of semibullvalene¹² that have too much diradical character, as shown by partial CASPT2 geometry reoptimizations. In contrast, B3LYP calculations are biased against giving transition state geometries with large amounts of diradical character.²⁰ This difference between CASSCF and B3LYP is seen in the lengths of the σ bonds being broken (C₄–C₅) and formed (C₂–C₇) in **TS₁₋₂**. These bond lengths, which are given in Table 2, are closer to being the same in the B3LYP than in the CASSCF transition state geometry. The CASPT2 energy is lower at the former than at the latter geometry for **TS₁₋₂**, but only by 0.5 kcal/mol.

that is computed for the Cope rearrangement of **1** compared to that of 1,5-hexadiene indicates that allylic resonance cannot be responsible for the majority of this reduction in the calculated enthalpy of activation.

Another indication of the relative unimportance of allylic resonance in stabilizing **TS₁₋₂** is the C₁–C₂ bond length. As shown in Table 2, this bond does lengthen by 0.02 Å at the CASSCF level on going from **1** to this transition state, but in diradical **2**, this bond has lengthened by an additional 0.06 Å. Moreover, in the product (**3**), this double bond is 0.03 Å longer than in the reactant (**1**), suggesting that some or all of the 0.02 Å lengthening of this bond in **TS₁₋₂** is due to partial rehybridization of C₂ from sp to sp².

In addition, the vibrational mode with the imaginary frequency (i.e., the transition vector) in **TS₁₋₂** consists almost entirely of motions of C₂ and C₇ that complete the formation of the C–C bond between them. There is little motion of C₄ and C₅ in the transition vector; and the C₄–C₅ bond, which is broken in the product (**3**), has lengthened by only 0.087 Å in **TS₁₋₂** (cf. Table 2).

Of particular significance is that the transition vector contains little or none of the rotation about the breaking C₂–C₃ π bond which is necessary to achieve the allylic delocalization that is present in diradical **2**. The absence of this rotation from the transition vector is additional evidence against allylic stabilization of **TS₁₋₂** providing much of the lowering of ΔH^\ddagger for the Cope rearrangement of **1** relative to that of 1,5-hexadiene.

We believe that most of the 5–6 kcal/mol lowering of the calculated and experimental values of ΔH^\ddagger between 1,5-hexadiene and **1** is due to the difference between the types of C–C σ bonds that are being formed in the transition states for these two Cope rearrangements. In the Cope rearrangement of **1** to **3**, an sp²–sp³ C–C σ bond is being formed in **TS₁₋₂**, whereas in the degenerate Cope rearrangement of 1,5-hexadiene, an sp³–sp³ C–C σ bond is being formed in the transition state.

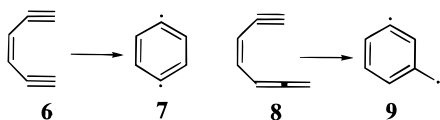
(29) Based on an allyl resonance energy of 13.5 kcal/mol. See: (a) Roth, W. R.; Bauer, F.; Beitz, A.; Ebbrecht, T.; Wüstefeld, M. *Chem. Ber.* **1991**, *124*, 1453. (b) Doering, W. v. E.; Roth, W. R.; Bauer, F.; Boenke, M.; Breuckmann, R.; Ruhkamp, J.; Wortmann, O. *Chem. Ber.* **1991**, *124*, 1461. (c) Berkowitz, J.; Ellison, G. B.; Gutman, D. *J. Phys. Chem.* **1994**, *98*, 2744. (d) Hrovat, D. A.; Borden, W. T. *J. Phys. Chem.* **1994**, *98*, 10460 and references therein.

Bonds to sp^2 carbons are stronger than bonds to sp^3 carbons. For example, the strength of the sp^2 C–H bond formed at the central carbon of allene in its hydrogenation to propene makes the heat of this reaction larger than the heat of hydrogenation of propene to propane.³⁰ In the latter reaction, an sp^3 C–H bond is formed at this carbon; and the difference of 10.7 kcal/mol between the two heats of hydrogenation³⁰ is about the same size as the difference between the C–H BDEs at an sp^2 carbon in ethylene and an sp^3 carbon in ethane.^{29c}

The experimental difference of $\Delta\Delta H_f^\circ_{298} = -14.5$ kcal/mol between **1** and **3**¹⁶ is comprised of the difference between the strengths of the sp^2 – sp^3 C–C bond in **3** and the sp^3 – sp^3 C–C bond in **1** plus the diene conjugation energy in **3**. The latter is known to be 4–5 kcal/mol,³¹ so that 9.5–10.5 kcal/mol also represents the difference between the strengths of the sp^2 – sp^3 C–C bond that is formed in the Cope rearrangement of **1** and the sp^3 – sp^3 C–C bond that is broken.

Only about half of the difference between the strengths of sp^2 – sp^3 and sp^3 – sp^3 C–C bonds is apparently available to stabilize TS_{1-2} relative to the transition state for the parent Cope rearrangement. In each of these reactions, the transition state geometry shows that the new C–C bond is only partially formed; so only a fraction of the difference between the strengths of these two types of C–C bonds is manifested in these two Cope transition states.

Replacement of a terminal acetylene by an allene also lowers the activation energy for the Myers–Saito cyclization of 1,2,4-heptatrien-6-yne (**8**) to β -dehydrotoluene (**9**), relative to that for the Bergman cyclization of 3-hexene-1,5-diyne (**6**) to 1,4-dehydrobenzene (**7**).³² Here too, ab initio calculations suggest that there is little benzylic stabilization of the transition state for cyclization of the hydrocarbon containing the allene moiety.^{33a,b} In addition, transannular bond formation in a cyclic derivative of **8** is also very fast, and the geometry of the resulting bicyclic diradical precludes its stabilization by benzylic resonance.³⁴



(30) Cox, J. P.; Pilcher, G. *Thermochemistry of Organic and Organometallic Compounds*; Academic Press: New York, 1970.

(31) (a) Kistiakowski, G. B.; Ruhoff, J. R.; Smith, H. A.; Vaughn, W. E. *J. Am. Chem. Soc.* **1936**, *58*, 146. (b) Fort, R. C.; Hrovat, D. A.; Borden, W. T. *J. Org. Chem.* **1993**, *58*, 211.

(32) (a) Myers, A. G.; Kuo, E. Y.; Finney, N. S. *J. Am. Chem. Soc.* **1989**, *111*, 8057. (b) Nagata, R.; Yamanaka, H.; Okazaki, E.; Saito, I. *Tetrahedron Lett.* **1989**, *30*, 4995. (c) Myers, A. G.; Dragovich, P. S.; Kuo, E. Y. *J. Am. Chem. Soc.* **1992**, *114*, 9369.

(33) (a) Koga, N.; Morokuma, K. *J. Am. Chem. Soc.* **1991**, *113*, 1907. (b) Engels, B.; Hanrath, M. *J. Am. Chem. Soc.* **1998**, *120*, 6356. (c) Koga and Morokuma suggested that the faster rate of **8** \rightarrow **9** compared to that of **6** \rightarrow **7** is due to the formation of a *transoid*-1,4-diradical in the former reaction and a *cisoid*-1,4-diradical in the latter. They obtained a value of 12 kcal/mol for this energy difference by computing the relative energies of anti and syn transition structures for formation of a σ bond between two acetylene molecules. However, their model does not contain the effects of some steric interactions that are present in the transition structure for the transformation of **8** to **9**. We find that an alternative model, consisting of the transition structures for formation of *cisoid*- and *transoid*-1,4-diradicals by attack of acetylene on the central carbon of allene, gives an (8/8)-CASSCF/6-31G* energy difference of only 3.8 kcal/mol. Nevertheless, our calculations leave little doubt that the effect postulated by Koga and Morokuma does contribute to the faster cyclization rate of **8** \rightarrow **9** compared to that of **6** \rightarrow **7**.

(34) (a) Meyers, A. G. *Tetrahedron Lett.* **1987**, *28*, 4493. (b) Meyers, A. G.; Proteau, P. J.; Handel, T. M. *J. Am. Chem. Soc.* **1988**, *110*, 7212. Meyers, A. G.; Proteau, P. J. *J. Am. Chem. Soc.* **1989**, *111*, 1146.

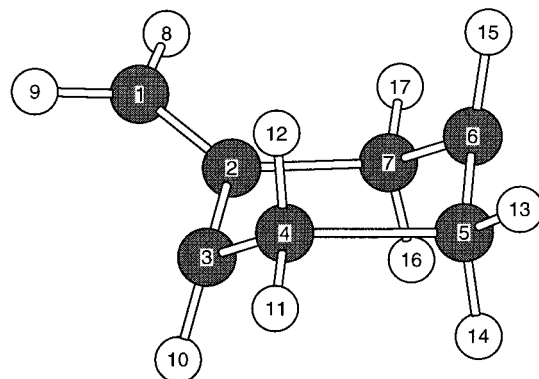


Figure 3. (8/8)CASSCF/6-31G* optimized geometry of TS_{2-3} , connecting 2-methylenecyclohexane-1,4-diyne (**2**) to 3-methylene-1,5-hexadiene (**3**), in the Cope rearrangement of 1,2,6-heptatriene (**1**).

In the cyclizations of both **6** and **8**, an sp^2 – sp^2 C–C bond is made, but one of the bonds that is broken in **8** is the π part of a double bond, whereas both π bonds broken in **6** are in triple bonds. Since an acetylenic π bond is 12 kcal/mol stronger than an ethylenic π bond,³⁵ the weaker π bond being broken in **8** contributes to its cyclizing faster than **6**.^{33c,36}

CASPT2 Energy and CASSCF Geometry of TS_{2-3} . Our CASPT2 calculations find that the transition state which connects diradical **2** to the product (**3**) lies 8.3 kcal/mol above **2**, which is in excellent agreement with Roth's experimental value of 8.2 kcal/mol.¹⁶ The CASPT2 difference of 3.3 kcal/mol between the energies of the two transition states is about the same size as Roth's estimated value.

As shown in Figure 3, the geometry of TS_{2-3} bears some superficial resemblance to that of TS_{1-2} . In TS_{2-3} , as in TS_{1-2} , the allylic conjugation, which stabilizes diradical intermediate **2**, is almost absent. In fact, the C_1 – C_2 – C_3 –H dihedral angle of 85.8° in TS_{2-3} indicates that there is even less allylic stabilization in this transition state than in TS_{1-2} . In TS_{2-3} , this dihedral angle is 6.2° farther from the values of $\sim 0^\circ$ that are found in the lowest singlet and triplet states of allylically stabilized diradical **2**.

In TS_{2-3} , the transition vector consists almost entirely of the motions of C_4 and C_5 that are necessary to break the bond between these two carbons. As in TS_{1-2} , in TS_{2-3} there is little, if any, of the motion that would promote the allylic conjugation that is present in **2** were TS_{2-3} to be traversed in the direction from the product (**3**) to this diradical intermediate.

Since, by definition, each transition state has only one vibrational mode with a negative force constant, the modes that would flatten the chair geometries of TS_{1-2} , and TS_{2-3} and thus develop the allylic conjugation that is present in **2** must have positive force constants. Therefore, it must only be at geometries that are intermediate between the two CASSCF transition states that molecular motions which lead to formation of **2** become energetically favorable.

Calculations at Geometries between TS_{1-2} and TS_{2-3} . To explore this region of the potential surface more thoroughly, we created a nine-point linear synchronous transit (LST)

(35) Nicolaidis, A.; Borden, W. T. *J. Am. Chem. Soc.* **1991**, *113*, 6750.

(36) The three Cope rearrangements, studied by Houk and co-workers,¹¹ which show "kinetic monotony" with the Cope rearrangement of 1,5-hexadiene, involve formation of a bond between one or two acetylenic carbons. In these three Cope rearrangements, the greater strength of the forming C–C bond at each carbon that becomes sp^2 hybridized in the product is almost exactly balanced by the greater strength of each acetylenic π bond in the reactant that is broken. It is for this reason that these reactions are nearly or exactly thermoneutral and that they also have nearly the same activation enthalpies as the Cope rearrangement of 1,5-hexadiene.

pathway^{37a} between **TS**_{1→2} and **TS**_{2→3}.^{37b} At each point, we then froze the lengths of the bond between C₂ and C₇, which is formed in **TS**_{1→2}, and the bond between C₄ and C₅, which is broken in **TS**_{2→3}, and fully optimized all of the remaining geometrical parameters at the CASSCF level. The CASSCF energy decreased smoothly and monotonically in going from **TS**_{1→2} to **TS**_{2→3} along this pathway; and no indication of allylic conjugation, involving C₁, C₂, and C₃, was found in any of the optimized geometries.

Since **TS**_{1→2} and **TS**_{2→3} must be connected by at least one intermediate and since neither of these transition states has appreciable allylic conjugation, it should be possible to find an intermediate between **TS**_{1→2} and **TS**_{2→3} that differs from **2** by being constrained to have no allylic conjugation. To confirm the existence of such a constrained intermediate, we froze the C₁–C₂–C₃–H dihedral angle at 81.1°, the value at the midpoint along the LST pathway between the two transition states; and, starting at the midpoint geometry, we performed a CASSCF geometry optimization.

The C–C bond lengths at the midpoint geometry that resulted from this partially constrained geometry optimization are given in Table 2. The data in Table 1 show that the CASSCF and CASPT2 energies at this geometry are, in fact, below those of both **TS**_{1→2} and **TS**_{2→3} but are 9.6 and 9.1 kcal/mol, respectively, above the energy of **2**. When the C₁–C₂–C₃–H dihedral angle constraint at the midpoint geometry was released, the geometry of this intermediate optimized to that of diradical **2**. Following the intrinsic reaction coordinate (IRC) from either **TS**_{1→2} or **TS**_{2→3} does, in fact, also lead to **2**.

Nevertheless, the existence of an LST pathway from **TS**_{1→2} to **TS**_{2→3}, along which the CASSCF energy decreases monotonically, means that molecules of **1** which cross **TS**_{1→2} can also pass over **TS**_{2→3}, without ever developing allylic conjugation. The existence of direct trajectories from reactant (**1**) to product (**3**) that do not pass through intermediate **2** explains the experimental finding that a sizable fraction of the molecules which undergo the allenyl Cope rearrangement apparently do so without forming **2**.^{16,38}

The B3LYP Potential Energy Surface. At the B3LYP level, after correction for $\Delta C_v^{450} \times 450 \text{ K} = -0.5 \text{ kcal/mol}$, $\Delta H^\ddagger = 31.2 \text{ kcal/mol}$ is obtained for the step connecting the reactant to **TS**_{1→2}. Since the allenic moiety, present in **1**, causes the relative energy of the reactant to be underestimated by 4.5 kcal/mol, it is not surprising that B3LYP gives a value of ΔH^\ddagger that is too high by about this amount of energy.

(37) (a) Halgren, T. A.; Lipscomb, W. N. *Chem. Phys. Lett.* **1977**, *49*, 225. (b) The geometries and energies of three of the intermediate points along this LST pathway are available as Supporting Information.

(38) Roth and co-workers found a 0.8 kcal/mol higher activation enthalpy for forming the oxygen-trappable diradical intermediate in the transformation of **1** to **3**¹⁶ than Frey and Lister found for the overall transformation of **1** to **3**.¹⁹ Although the combined uncertainties in the two values of ΔH^\ddagger are large enough to account for the small difference between them, Roth apparently believed that this difference in ΔH^\ddagger is real; and he interpreted it in terms of the existence of two different transition states—one that leads directly from **1** to **3** and one with slightly higher ΔH^\ddagger that passes through **2**. However, this interpretation of the kinetic data was based on the assumption that trapping of **12** by oxygen is diffusion controlled; and it is known experimentally that, at least for singlet diradicals in which the singlet lies well below the triplet in energy, oxygen trapping occurs at rates that are much slower than the diffusion-controlled limit.³⁹ Consistent with both this experimental fact and with the results of our calculations is the interpretation of Roth's kinetic data in terms of a single rate-determining transition state both for direct transformation of **1** to **3** and for formation of **2** and a small but finite activation enthalpy for trapping of **12** by oxygen.

(39) (a) Heath, R. B.; Bush, L. C.; Feng, X.-W.; Berson, J. A.; Scaiano, J. C.; Berinstain, A. B. *J. Phys. Chem.* **1993**, *97*, 13355. (b) Adam, W.; Borden, W. T.; Burda, C.; Foster, H.; Heidenfelder, T.; Heubes, M.; Hrovat, D. A.; Kita, F.; Lewis, S. B.; Scheutzow, D.; Wirz, J. *J. Am. Chem. Soc.* **1998**, *120*, 593.

Starting from what appears to be, at least superficially, the B3LYP geometry for **TS**_{1→2} and following the IRC does not lead to **2**, as in our CASSCF calculations. Instead, the B3LYP IRC leads directly to **3**. The problem is that, since **2** is a diradical, restricted B3LYP calculations, in which orbitals are either doubly occupied or empty, cannot describe this species, in which two orbitals are each singly occupied. For such an orbital occupancy, unrestricted (U)B3LYP calculations are required.

To find a reaction path from **1** to **2**, we tried to locate a UB3LYP transition state that connects the reactant and intermediate. However, all our attempts led to the same transition state geometry that was found by our B3LYP calculations. In this region of the potential surface, a singlet UB3LYP initial guess converges to an $S^2 = 0$ B3LYP solution.

It appears that only in regions of the potential surface beyond **TS**_{1→2} do UB3LYP calculations give a lower energy than RB3LYP calculations and eventually connect this transition state to diradical **2**. To confirm that this was the case, UB3LYP calculations were performed along an LST pathway³⁷ from **TS**_{1→2} to diradical **2**. Although the UB3LYP energy of one of the early points along this *arbitrary* pathway was 2.2 kcal/mol higher in energy than **TS**_{1→2}, beyond that point the energy fell monotonically until the geometry of **2** was reached.

We were able to find a UB3LYP transition state that connects **2** to the product (**3**). As shown in Table 2, the C–C bond lengths in **TS**_{2→3} are very similar to those in the CASSCF transition state.⁴⁰ The UB3LYP value of $S^2 = 0.30$ shows that **TS**_{2→3} has only a modest amount of diradical character, compared to a true UB3LYP “singlet” diradical, which would have $S^2 = 1.00$.²⁰

Inspection of Table 1 reveals that the UB3LYP energy of **TS**_{2→3} is slightly below that of the geometry that appears to serve as both the UB3LYP **TS**_{1→2} and the B3LYP **TS**_{1→3}. Consequently, like our ab initio calculations, (U)B3LYP predicts that, after passage over **TS**_{1→2}, formation of **3** can occur, without the mandatory intermediacy of **2**.

Conclusions

Our UB3LYP and CASPT2//CASSCF calculations provide very similar pictures of the potential energy surface for the Cope rearrangement of **1** to **3**. Both computational methods predict that this rearrangement can occur by two different types of pathways which diverge only after passage over a common transition state.³⁸ One type of pathway leads to formation of diradical **2**; the other leads directly to the product, without formation of this intermediate.

The existence of these two types of pathways on the potential energy surface provides a qualitative explanation for the results of the oxygen-trapping experiments of Roth and co-workers.¹⁶ Since we find that these pathways both involve passage over the same transition state, reaction dynamics calculations would be necessary to compute the partitioning between these two pathways. Such calculations are planned, since the results can be compared with the nearly equal partitioning found by Roth's oxygen-trapping experiments.

For reactions of organic molecules on potential energy surfaces that are qualitatively similar to the surface which we compute for the Cope rearrangement of **1** to **3**, Carpenter's quasiclassical dynamics calculations support the existence of two qualitatively different types of pathways.⁴¹ Carpenter's calculations find short-lived, direct trajectories from the transi-

(40) As in the case of **TS**_{1→2},²⁸ the CASPT2 energy for **TS**_{2→3} is 0.5 kcal/mol lower at the UB3LYP than at the CASSCF geometry for this transition state.

tion state to the product and much longer-lived trajectories, which exhibit the statistical behavior expected from a classical diradical intermediate. Carpenter and Reyes have provided experimental evidence for the existence of these two different types of reactive trajectories.⁴²

Allylic stabilization of the rate-determining transition state does not appear to be responsible for the fact that ΔH^\ddagger for the Cope rearrangement is lower by ca. 6 kcal/mol for **1**¹⁹ than for 1,5-hexadiene⁸ and other more highly unsaturated hydrocarbons.¹¹ Instead, the lowering of the activation enthalpy appears to reside in the strength of the σ bond being formed at C₂ in the transition state. Since C₂ becomes an sp² carbon in **3**, this bond is stronger than the comparable bond, involving two sp³ carbons, that is being formed in the transition state for the Cope rearrangement of 1,5-hexadiene.

In addition, the π bond that is broken at C₂ of **1** is ethylenic and, hence, is ca. 10 kcal/mol weaker than an acetylenic π bond.³⁵ This explains the lower values of both ΔH and ΔH^\ddagger in the rearrangement of **1** to **3** than in Cope rearrangements involving terminal acetylenes.¹¹ We believe that the same factor is also responsible, at least in part,^{33c} for the lower ΔH^\ddagger in the

(41) (a) Carpenter, B. K. *J. Am. Chem. Soc.* **1995**, *117*, 6336. (b) Carpenter, B. K. *J. Am. Chem. Soc.* **1996**, *118*, 10329. See also: (c) Doubleday, C., Jr.; Bolton, K.; Hase, W. L. *J. Am. Chem. Soc.* **1997**, *119*, 5251. (d) Hrovat, D. A.; Fang, S.; Borden, W. T.; Carpenter, B. K. *J. Am. Chem. Soc.* **1997**, *119*, 5253. (e) Doubleday, C., Jr.; Bolton, K.; Hase, W. L. *J. Phys. Chem. A* **1998**, *102*, 3648.

(42) Reyes, M. B.; Carpenter, B. K. *J. Am. Chem. Soc.* **1998**, *120*, 1641.

Myers–Saito cyclization of **8** compared to that in the Bergman cyclization of **6**.^{32,33}

In general, the greater strengths of sp² compared to sp³ σ bonds, combined with the lower BDEs of ethylenic compared to acetylenic π bonds, make formation of a σ bond at the central carbon of an allene more thermodynamically favorable than formation of a σ bond at an ethylenic or acetylenic carbon.³⁵ It is these differences in bond strengths that provide the thermodynamic driving force for reactions such as **1** → **3**, **8** → **9**, and other rearrangements that result in the “decumulation” of an allene.⁴³

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Supporting Information Available: Listings of optimized geometries for all the species whose energies are given in Table 1 and for three of the intermediate points on the LST pathway from **TS**_{1–2} to **TS**_{2–3} (PDF). See any current masthead page for Web access instructions.

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(43) Vedejs, E.; Cammers-Goodwin, A. *J. Org. Chem.* **1994**, *59*, 7541 and references therein.