5622 *J. Am. Chem. Soc.* **1998,** *120,* 5622−5627

Alkynes, Allenes, and Alkenes in [3,3]-Sigmatropy: Functional Diversity and Kinetic Monotony. A Theoretical Analysis

Kersey A. Black,[‡] Sarah Wilsey,[†] and K. N. Houk*,[†]

Contribution from the Department of Chemistry and Biochemistry, University of California, Los Angeles, California 90095-1569, and Claremont Colleges, Claremont, California 91711-5916

Received August 12, 1997. Revised Manuscript Received March 29, 1998

Abstract: The [3,3]-sigmatropic shifts of 1,5-hexadiyne, 1,2-hexadien-5-yne, 1,2,5-hexatriene, 1,2,4,5-hexatetraene, and 1-hexen-5-yne were studied, using a hierarchy of methods (RHF/6-31G*, MP2//RHF/6-31G*, BLYP/6-31G*, Becke3LYP/6-31G*, and CASSCF/6-31G*). Hartree−Fock, MP2, and density functional methods predict the mechanisms to be concerted, involving aromatic transition structures, whereas CASSCF/6-31G* favors the stepwise pathways via diradical intermediates. Both MP2//RHF/6-31G* and Becke3LYP/6-31G* give activation energies in good agreement with the experimental values. Becke3LYP is a reliable tool for predicting the activation energies of such reactions, although it has a tendency to overstabilize allene systems. The activation energies for the series of reactions are remarkably constant at 31−35 kcal/mol, consistent with the aromatic character of their transition states. The origin of this kinetic monotony even in the face of structural diversity is analyzed.

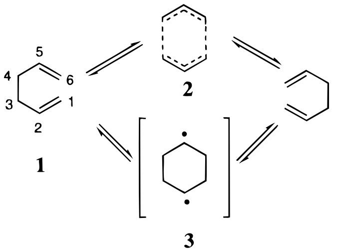
Introduction

Cope rearrangements of dienes (Scheme 1) are highly useful processes which have attracted extraordinary mechanistic interest. After decades of experimental[1] and computational[2] investigation, consensus has arrived at a concerted mechanism, with an aromatic transition state[3] slightly favored over a diradical transition state or intermediate.[2]

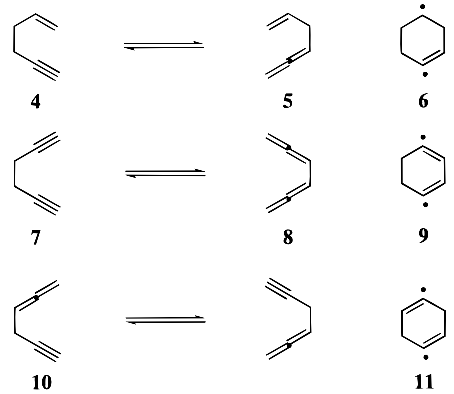
The remaining members of the family of related [3,3]-sigmatropic shifts (Scheme 2) have garnered much less critical attention. The replacement of an alkene functionality with an allene or acetylene would be expected to have a significant effect on rate and mechanism, by altering the relative energies of the diradicals shown; they may be intermediates or resonance contributors to the transition state. Addition of H_2 to acetylene is 9 kcal/mol more exothermic than to ethylene, and H_2 addition to allene is even more exothermic. Radical addition thermochemistry is similar for alkenes and acetylene but might be expected to differ for allenes. Nevertheless, this thermochemical factor is not manifested in rate differences: simple examples of the rearrangements in Scheme 2 have nearly the same activation energies as **1**, and experimental studies outlined below have given no evidence for a change in mechanism.

How can molecules with such diverse functionality exhibit such monotonic kinetic and mechanistic behavior? We have explored these reactions theoretically and provide answers to these questions, as well as additional insights into the performance of various computational methods for the investigations of such reactions. Preliminary results on these systems were presented in a recent report of our work on pericyclic reactions.[4]

Scheme 1



Scheme 2



Background

Ever since the discovery of the reaction by Cope,[5] the rearrangement of **1** has been assumed to be a concerted "no-

---

* To whom correspondence should be addressed.

[†] University of California, Los Angeles.

[‡] Claremont Colleges.

(1) For reviews see: (a) Viola, A.; Collins, J. J.; Fillip, N. *Tetrahedron* **1981**, *37*, 3765. (b) Gajewski, J. J. *Hydrocarbon Thermal Isomerizations*; Academic Press: New York, 1981; p 120. (c) Huntsman, W. D. *Chemistry of Ketenes, Allenes and Related Compounds, Part 2*; Patai, S., Ed.; Wiley: New York, 1980; Chapter 15, p 522.

(2) For reviews see: (a) Houk, K. N.; Gonzalez, J.; Li, Y. *Acc. Chem. Res.* **1995**, *28*, 81. (b) Houk, K. N.; Li, Y.; Evanseck, J. D. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 682. (c) Dewar, M. J. S.; Jie, C. *Acc. Chem. Res.* **1992**, *25*, 537.

(3) (a) Schleyer, P. v. R.; Jiao, H. *Pure Appl. Chem.* **1996**, *68*, 209. (b) Evans, M. G.; Polanyi, M. *Trans. Faraday Soc.* **1938**, *34*, 11.

(4) Houk, K. N.; Beno, B. R.; Nendel, M.; Black, K.; Yoo, H. Y.; Wilsey, S.; Lee, J. K. *J. Mol. Struct.* (THEOCHEM) **1997**, *398*, 169.

(5) (a) Cope, A. C.; Hardy, E. M. *J. Am. Chem. Soc.* **1940**, *62*, 441.

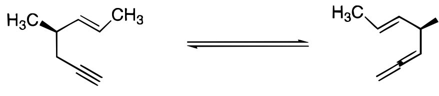
S0002-7863(97)02826-6 CCC: $15.00

mechanism" reaction. Woodward and Hoffmann defined this as a typical pericyclic reaction, occurring via a cyclic aromatic transition structure, **2**, with six electrons delocalized over the molecule.[6] However, in a later study by Doering and co-workers, it was suggested that the transition structure for the reaction has more cyclohexan-1,4-diyl diradicaloid character, with short forming and breaking C−C bond lengths.[7] The alternative stepwise mechanism involving cleavage to two allyl radicals was shown to be energetically inaccessible. Dewar proposed that a diyl diradical, **3**, must be a stable intermediate on the potential surface in a stepwise pathway, on the basis of kinetic studies of phenyl- and naphthyl-substituted 1,5-hexadienes.[8]

While the experimental results tend to suggest a concerted pathway, the preference for one particular pathway is somewhat difficult to reproduce theoretically. To describe these types of reactions realistically, a method including both nondynamical and dynamical electron correlation is essential. Semiempirical calculations predict the stepwise pathway should be favored.[9,10] CASSCF studies with a 6-31G* basis set find *both* stepwise and concerted pathways.[11] The concerted transition state is slightly higher in energy than the stepwise transition state, with a second-order saddle point (SOSP) connecting the concerted transition structure and the 1,4-diyl diradical intermediate. When these calculations are corrected[12] using Roos' CASPT2N method[13] or the CASMP2 method of Kozlowski, Dupuis, and Davidson,[14] only one transition state is found for the reaction; it is aromatic, with bond-forming and bond-breaking C−C distances of around 1.885 Å. Similar results were obtained by using the more hybrid density functional method, Becke3LYP.[15]

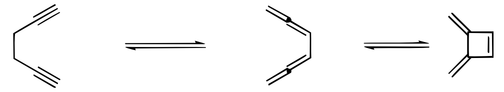
Less work has been carried out computationally on other [3,3]-sigmatropic shifts. This is no doubt related to the need for multireference methods incorporating both dynamical and nondynamical electron correlation to describe these systems. While multireference MP2 calculations are expensive for the parent system, they become almost unfeasible for a system that needs more than six electrons and six orbitals to describe the active space. However, we were encouraged by the results obtained using the hybrid DFT method, Becke3LYP, for the parent system. These computations are considerably cheaper than multireference methods, they correctly predict the concerted pathway, and the hybrid functional gives energies in very good agreement with those obtained experimentally. This idea has been further reinforced by recent results of Davidson,[16] who has shown that in systems such as the Cope rearrangement, where the leading configuration does not change during the reaction, DFT (Becke3LYP) gives more reliable results than CASSCF.

Scheme 3



12

Scheme 4



7 **8** **13**

From an experimental point of view, the hydrocarbon rearrangements shown in Scheme 2 are often considered to be concerted reactions by analogy with the parent system and on the basis of their negative activation entropies. For the parent Cope rearrangement, the activation energy for the reaction is 33.5 kcal/mol, and the entropy of activation is −13.8 eu.[17]

The thermal rearrangement of 1-hexen-5-yne, **4**, was first observed by Huntsman and co-workers.[18] At 340 °C, a reversible isomerization between 1-hexen-5-yne and 1,2,5-hexatriene, **5**, was observed, while at higher temperatures the hexatriene rearranged irreversibly to form a mixture of methylcyclopentenes. They also demonstrated that the thermolysis of 1-hepten-5-yne and 2-methyl-1-hexen-5-yne gave similar rearrangements, forming 3-methyl-1,2,5-hexatriene and 5-methyl-1,2,5-hexatriene, respectively, which then went on to cyclize. The methyl group in 1-hepten-5-yne hinders the rate of formation of the hexatriene due to steric effects and some stabilization of the ground state, whereas that in 2-methyl-1-hepten-5-yne was shown to have little effect on the rate of isomerization. Kinetic and thermodynamic studies showed that the activation energy for the rearrangement of the unmethylated system was 32.7 kcal/mol, with an activation entropy of −11.6 eu.[1c,19] These mechanistic results were later reinforced by Owens and Berson,[20] who showed that the rearrangement of 1,3-dimethyl-1-hexen-5-yne, **12** (Scheme 3), to the corresponding 1,2,5-hexatriene was almost 100% stereospecific and that the methyl substituents had no effect on the rate of reaction. They concluded that the reaction must therefore be concerted, and no true diradical intermediate exists along the reaction path.

In 1963, Huntsman and Wristers reported that when 1,5-hexadiyne (**7**) is heated to 350 °C, 3,4-dimethylenecyclobutene (**13**) is formed in high yield (Scheme 4).[21] The activation parameters were determined over the temperature range 210−297 °C; the activation enthalpy and entropy of this process are 34.4 kcal/mol and −9.4 eu, respectively. This again suggested a concerted pathway through a closed transition structure. Other substituted 1,5-hexadiynes were reported to behave in an analogous manner. Hopf later isolated both 1,5-hexadiyne, **7**, and 1,2,4,5-hexatetraene, **8**, upon coupling of propargyl bromide with magnesium.[22] On the basis of these results, the mechanism for the interconversion of **7** to **13** was deduced to occur via **8**, where the rearrangement of **7** to **8** is the rate determining step.

---

(6) Woodward, R. B.; Hoffmann, R. *The Conservation of Orbital Symmetry*; Verlag Chemie GmbH: Weinheim, Germany, 1970; p 114.

(7) (a) Doering, W. von. E. *Proc. Natl. Acad. Sci. U.S.A.* **1981**, *78*, 5279. (b) Doering, W. von. E.; Toscano, V. G.; Beasley, G. H. *Tetrahedron* **1962**, *18*, 67.

(8) Dewar, M. J. S.; Wade, L. E., Jr. *J. Am. Chem. Soc.* **1977**, *99*, 4417.

(9) Komornicki, A.; McIver, J. W. *J. Am. Chem. Soc.* **1976**, *98*, 4553.

(10) Dewar, M. J. S.; Ford, G. P.; McKee, M. L.; Rzepa, H. S.; Wade, L. E. *J. Am. Chem. Soc.* **1977**, *99*, 5069.

(11) Dupuis, M.; Murray, C.; Davidson, E. R. *J. Am. Chem. Soc.* **1991**, *113*, 9756.

(12) Hrovat, D. A.; Morokuma, K.; Borden, W. T. *J. Am. Chem. Soc.* **1994**, *116*, 1072.

(13) Andersson, K.; Malmqvist, P.-Å.; Roos, B. O. *J. Am. Chem. Soc.* **1992**, *96*, 1218.

(14) Kozlowski, P. M.; Dupuis, M.; Davidson, E. R. *J. Am. Chem. Soc.* **1995**, *117*, 774.

(15) Wiest, O.; Black, K. A.; Houk, K. N. *J. Am. Chem. Soc.* **1994**, *116*, 10336.

(16) (a) Davidson, E. R. *Chem. Phys. Lett.* In press. (b) Davidson, E. R. *J. Phys. Chem.* **1996**, *100*, 6161.

(17) Doering, W. von E.; Toscano, V. G.; Beasley, G. H. *Tetrahedron* **1971**, *27*, 5299.

(18) Huntsman, W. D.; De Boer, J. A.; Woosely, M. H. *J. Am. Chem. Soc.* **1966**, *88*, 5846.

(19) Huntsman, W. D.; Dykstra, K. A. Unpublished results. Dykstra, K. A. Ph.D Dissertation, Ohio University, 1972.

(20) Owens, K. A.; Berson, J. A. *J. Am. Chem. Soc.* **1988**, *110*, 627.

(21) (a) Huntsman, W. D.; Wristers, H. J. *J. Am. Chem. Soc.* **1963**, *85*, 3308. (b) Huntsman, W. D.; Wristers, H. J. *J. Am. Chem. Soc.* **1967**, *89*, 342.

(22) Hopf, H. *Angew. Chem., Int. Ed. Engl.* **1970**, 732.

Table 1. Activation Enthalpies at 0 K in kcal/mol with Activation Entropies in eu in Parentheses, Computed for the Concerted Reactions at RHF/6-31G*, MP2/6-31G*//RHF/6-31G*, BLYP/6-31G*, and B3LYP/6-31G* Levels of Theory, with Experimental Values for Comparison

system	RHF	MP2//RHF	BLYP	B3LYP	expt value[a]
1,5-hexadiene	56.0 (−1.7)	30.8	29.7 (−9.7)	34.2 (−10.2)	33.5 (−13.8)[b]
1-hexen-5-yne	59.5 (−6.4)	30.7	27.8 (−7.6)	33.0 (−8.0)	32.7 (−11.6)[c]
1,5-hexadiyne	63.4 (−4.3)	31.6	26.5 (−5.3)	32.7 (−5.1)	34.4 (−9.4)[d]
1,2-hexadien-5-yne	60.3 (−7.1)	26.7	28.4 (−6.0)	33.7 (−8.8)	30.8 (−11.7)[e]

[a] E_a values measured experimentally at temperatures given in the text. [b] See ref 17. [c] See ref 1c. [d] See ref 21b. [e] Experimental results given for 3-methyl-1,2-hexadien-5-yne—see ref 23.

Hopf also studied the [3,3]-sigmatropic rearrangements of several 1,2-hexadien-5-ynes.[23] He found that at temperatures of 150−210 °C, 3-methyl-1,2-hexadien-5-yne undergoes a Cope-type rearrangement with an activation energy of 30.8 kcal/mol and an observed entropy of activation of −11.7 eu, again indicative of a cyclic transition state.

All of these reactions, whether involving alkene, alkyne, or allene, have remarkably similar activation energies of 31−34 kcal/mol. This is in the range of activation energies noted earlier for a wide variety of hydrocarbon pericyclic reactions.[2b] In addition, the activation entropies range from −9 to −12 eu, consistent with significant restriction of conformation in either an aromatic or a 1,4-diyl diradicaloid transition state.

Computational Methods

All the calculations were carried out with the methods and standard 6-31G* basis set implemented in the Gaussian suite of programs.[24] The reactants, products, and transition structures were fully optimized for each of the reactions shown in Scheme 2. Frequency calculations were then carried out at each of the structures located, both to verify the nature of the point and to evaluate zero-point energy (ZPE) corrections. The ZPEs were scaled by 1.0126, 0.96, and 0.8929 for the BLYP/6-31G*, B3LYP/6-31G*, and RHF/6-31G* calculations, respectively, according to the recommended values by Scott and Radom[25] for the BLYP/6-31G* results, and the more recent values of Curtiss, Raghavachari, Redfern, and Pople for the RHF/6-31G* and B3LYP/6-31G* results.[26]

An appropriate choice of active space was used for the CASSCF calculations in each case. The parent Cope rearrangement requires only six electrons in six orbitals (the four π orbitals and the σ orbitals in the bond that is broken) to fully describe it. For the 1-hexen-5-yne system, an active space of eight electrons in eight orbitals (six π orbitals and two σ orbitals) was used. The two additional out-of-plane π orbitals were added for the other two systems, such that the calculations in these cases used active spaces of 10 electrons in 10 orbitals. The concerted transition structures could not be fully optimized at this level of theory, and therefore, constrained optimizations were carried out with the optimized RHF bond-making and bond-breaking distances. These energies were then ZPE corrected by using the scaled RHF values to compare them with the other computed enthalpies.

Results and Discussion

The barriers for each of the rearrangements shown in Scheme 2 were computed using a hierarchy of methods. The results are given in Tables 1 and 2 and illustrated in Figure 1. Except for the CASSCF results, each method predicts a concerted pathway through an aromatic transition structure. The bond-forming and bond-breaking distances are given in Figure 2; the fully optimized geometries can be obtained as Supporting Information.

Table 2. Relative Energies in kcal/mol of Optimized Structures Along Stepwise and Concerted Pathways Computed at the CASSCF/6-31G* Level

system	1,5-hexadiene	1-hexen-5-yne	1,5-hexadiyne	1,2-hexadien-5-yne
reactant	0.0[a]	0.0	0.0	0.0
diradical	46.8[c]	47.5	45.9	39.4
product	0.0	6.6	8.6	0.0
react/dirad TS	48.0[d]	48.2	48.1	39.6
dirad/prod TS	48.0	49.1	47.3	39.6
concerted TS	48.7[c,d]	50.7[b]	51.2[b]	42.6[b]
concerted TS (+ZPE)	46.9[c,d]	49.5[b]	49.3[b]	41.1[b]

[a] This value differs from that computed by Dupuis, Murray, and Davidson (see ref 11) by 1 kcal/mol. [b] Optimized with use of constrained RHF bond-forming and bond-breaking distances. [c] Absolute energies in agreement (±0.1 kcal/mol) with those computed by Hrovat, Morokuma, and Thatcher Borden (see ref 12). [d] Absolute energies in agreement (±0.1 kcal/mol) with those computed by Dupuis, Murray, and Davidson (see ref 11).

In accord with the results on the parent system,[11] the CASSCF/6-31G* results predict a stepwise mechanism, although the computed energy difference between the two pathways is less than 2 kcal/mol in each case. A diradical intermediate and transition structures (Dewar structures) leading to and from the intermediate were located for each system at this level of theory. The results are given in Table 2. As in the case of the parent system, a second-order saddle point (SOSP) appears to exist on the CASSCF potential energy surfaces of each of these systems. These led to problems in optimizing the geometries of the concerted transition structures; therefore, these transition structures were optimized with constrained C−C bond-forming and bond-breaking distances taken from the relevant RHF/6-31G* transition structures. The resulting energies, with scaled RHF ZPE corrections, are given in Table 2.

Figure 1 shows that while the trend of activation enthalpies for the RHF results is in good agreement with the experimental data, they are overestimated by some 20−30 kcal/mol. These energies are dramatically improved when they are corrected with MP2 single points, indicating the importance of electron correlation in computing the barriers for such rearrangements. It is interesting to note that the correlation correction increases with the number of π bonds in the system, ranging from 25 kcal/mol for the parent system to some 34 kcal/mol for the 1,2-hexadien-5-yne system. This arises since the stretching of a π bond from the short acetylenic bond to the alkene π bond occurs with an increase in the correlation energy. Neglect of this correlation energy causes an unrealistic increase in activation energy. Some of this electron correlation shows up in the CASSCF/6-31G* results for the concerted pathway (see Table 2 and Figure 1). However, these barriers are still overestimated by some 15−20 kcal/mol.

---

(23) Hopf, H. *Tetrahedron Lett.* **1972**, 3571.

(24) *Gaussian'94 (Revision B2)*; Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T. A.; Peterson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Oriz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A.; Gaussian, Inc.: Pittsburgh, PA, 1995.

(25) Scott, A. P.; Radom, L. *J. Phys. Chem.* **1996**, *100*, 16502.

(26) Curtiss, L. A.; Raghavachari, K.; Redfern, P. C.; Pople, J. A. *Chem. Phys. Lett.* **1997**, *270*, 419.

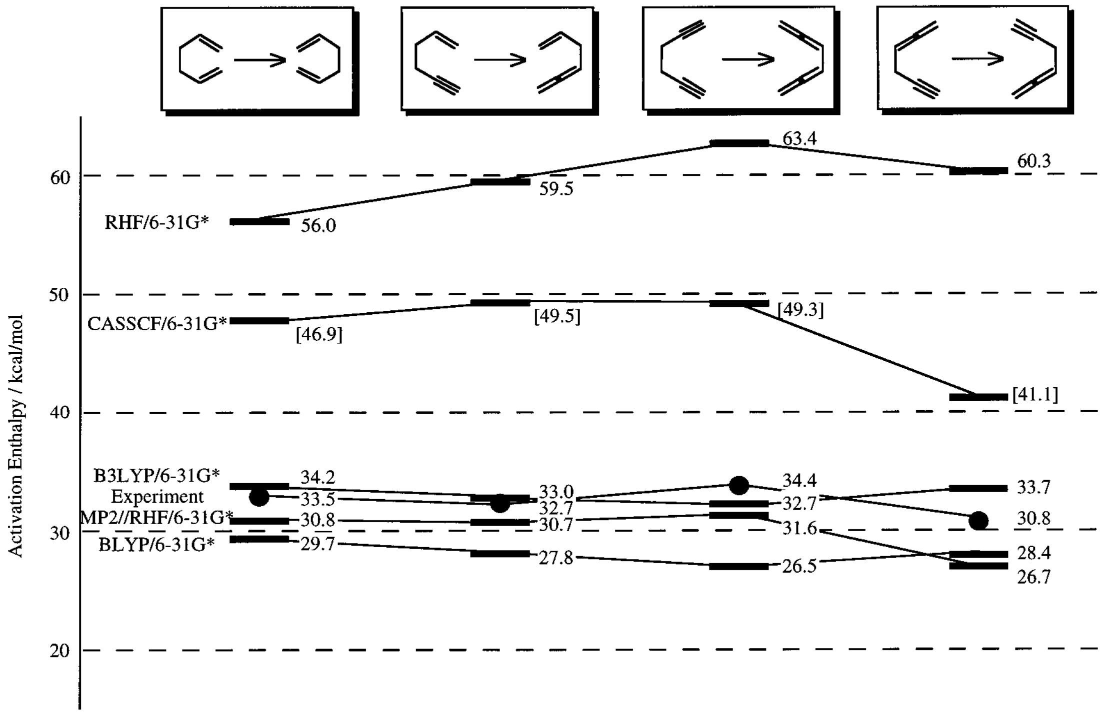
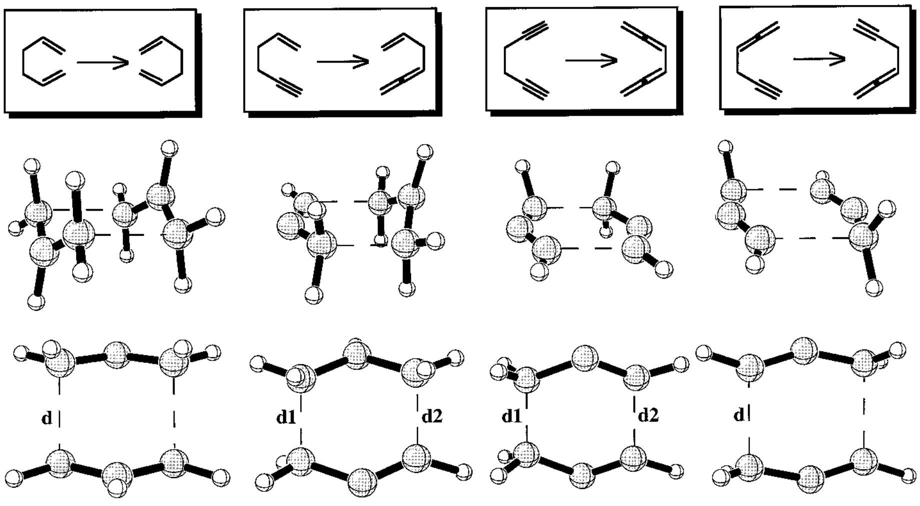


Figure 1. Activation energies for [3,3]-sigmatropic shifts obtained by different computational methods, compared with experimental values. (Values in square brackets are activation energies from geometries optimized with constrained C−C distances.)



METHOD	d	d1	d2	d1	d2	d
RHF/6-31G*	2.046	1.987	1.959	1.964	1.915	1.903
BLYP/6-31G*	2.034	1.828	1.898	1.769	2.008	1.755
B3LYP/6-31G*	1.969	1.826	1.863	1.770	1.927	1.762

Figure 2. Forming and breaking C−C bond lengths according to RHF/6-31G*, BLYP/6-31G*, and B3LYP/6-31G* methods.

DFT methods describe these systems very well. The BLYP activation energies are a considerable improvement over the RHF and CASSCF results, although they are underestimated by 3−7 kcal/mol, and the trend is not well-reproduced. The hybrid DFT method, Becke3LYP/6-31G*, gives much better agreement with experiment. Calculations at this level of theory predict that all the activation energies are 33−34 kcal/mol, and vary from the experimental results by a maximum of 3 kcal/mol, in the case of the 1,2-hexadien-5-yne system.

The open-shell method, UB3LYP, predicted the same energies and geometries as the corresponding closed-shell method, indicating that the structures located are not artifacts of the computational method used. Furthermore, the coefficients of the leading configurations in the CASSCF wave functions lie between 0.89 and 0.93, suggesting that closed-shell methods are suitable for describing these systems.

The energies of reaction were calculated for the two nondegenerate reactions **A** (1-hexen-5-yne, **4**, to 1,2,5-hexatriene, **5**) and **B** (1,5-hexadiyne, **7**, to 1,2,4,5-hexatetraene, **8**). Both of the reactions are expected to be exothermic, as experimental heats of formation indicate that 1,2-butadiene is 0.7 kcal/mol more stable than 1-butyne.[27] The experimental activation energies for **A** and **B** are not reported in the literature, although the equilibrium constant for **A** is known to be 2.73 at 500 K.[1c]

Table 3. Computed and Experimental Energies of Reaction in kcal/mol for Conversion of Butyne to 1,2-Butadiene and for the Nondegenerate Cope Rearrangements

system	CASSCF	RHF	MP2//RHF	BLYP	B3LYP	expt value
1-butyne to 1,2-butadiene	+8.4	−0.2	+1.5	−7.0	−5.6	−0.7
A (**4** to **5**)	+6.6^b	−0.5	+1.0	−6.9	−5.6	−1.0^a
B (**7** to **8**)	+8.6^b	−3.8	−1.5	−18.4	−9.5	

^{a} Computed from K_{eq} given in ref 1c. ^{b} Not ZPE corrected.

If we assume that $\Delta S = 0$, then the reaction can be estimated to be exothermic by around 1 kcal/mol. Based on the fact that conversion of one monosubstituted alkyne group to a monoalkyl-substituted allene group is exothermic, then the equilibrium for **B** is expected to lie even further to the right. Additionally, conjugation should further stabilize the tetraene relative to the dialkyne, such that the reaction can be estimated to be exothermic by around 3−4 kcal/mol.

The computed energies of reaction for **A** and **B** are given in Table 3. The energies range from −6.9 (BLYP) to +6.6 kcal/mol (CASSCF) for **A**, and from −18.4 (BLYP) to +8.6 kcal/mol (CASSCF) for **B**. It is apparent that CASSCF describes the relative energies of the reactants and products poorly, as the products in both cases are predicted to be considerably less stable than the reactants. RHF predicts an energy of reaction (−0.5 kcal/mol) closest to the experimental value for **A**. The MP2 energies are close, although **A** is predicted to be slightly endothermic. Both RHF and MP2 predict that **B** is more exothermic than **A** by around 3 kcal/mol. The DFT methods, BLYP and B3LYP, predict the correct relative stabilities of the reactants and products, but these methods overestimate the product stabilization for both **A** and **B**. The computed errors in exothermicity for system **A** are 6 (BLYP) and 5 kcal/mol (B3LYP) when compared with experiment. This is not too surprising, as it has been noted previously that DFT methods erroneously predict allene to be more stable than propyne.[28] This may be attributed to the self-interaction problem that has been observed in DFT methods.[29] The same trends are observed in the computed energy of reaction for conversion of 1-butyne to 1,2-butadiene also given in Table 3. RHF predicts an energy of reaction closest to the experimental value, MP2 predicts the reaction is slightly endothermic, both DFT methods considerably overestimate the reaction exothermicity, while CASSCF predicts the reaction is endothermic by some 8 kcal/mol. Nondynamical correlation appears to bias the equilibrium toward the alkyne, where the correlated orbitals are in close proximity, while DFT favors the allenic system.

The bond lengths in the transition structures of the Cope-type rearrangements are given in Figure 2. Full geometrical information is given as Supporting Information. The values of the forming and breaking bond lengths vary considerably depending on the method used. The DFT bond lengths are shorter than the RHF bond lengths in every case (by 0.1−0.16 Å), i.e., the transition structures are much tighter. The effect of the out-of-plane π systems on the asynchronicity of the transition structures of the 1-hexen-5-yne and 1,5-hexadiyne isomerizations also varies. The DFT transition structures are much more asynchronous than those optimized at the RHF level, and while the out-of-plane π orbitals cause the C−C bond forming distance to be shorter in the RHF geometry (i.e., d2 is shorter than d1), the asynchronicity is reversed in the DFT transition structures (i.e., d1 is shorter than d2). This asynchronicity is consistent with the observed reaction energies; DFT predicts the reactions to be more exothermic and therefore the transition structures occur earlier on along the reaction paths.

Finally, we comment on the relative activation energies of the reactions. As noted previously,[2b] many pericyclic reactions have very similar barriers of around 32−34 kcal/mol and the rearrangements studied here also fall into this category of reactions. Surprisingly, the degree of unsaturation in the molecule does not have a significant effect on the energy of the transition state. Instead, it is the degree of bond-breaking and bond-forming character in the transition state that controls the barrier height. In each of these reactions, we may consider one single bond (C_3−C_4) and a nonbond (C_1−C_6) to be converted into two half (or partial) bonds in the transition state. The energy required to do this is approximately constant for these rearrangements, and in fact is remarkably similar for many other pericyclic processes.[2b]

By contrast, if the reactions involved diradical intermediates such as shown in Scheme 2, or if these diradicals were significant contributors to the transition structure, then a much wider variation of activation energies would be expected. The 9 kcal/mol difference in activation energy (Table 2) predicted by the CASSCF method, which forms a stepwise mechanism, is a manifestation of this. In fact, the concerted nature of the transition states, and their aromatic character, leads to the activation energy monotony, even in the presence of structural diversity.

Conclusions

The results for the three new Cope-type transformations documented here are directly analogous to those obtained for the parent Cope reaction. The mechanism in each case is predicted to be concerted through an aromatic transition structure. However, the most striking observation is the similarity in activation energies, which appear to be independent of the degree of unsaturation in each of the systems.

As in the case of the parent system, we have shown here that the incorporation of electron correlation is essential for studying these types of rearrangements. Without the additional dynamical correlation, RHF overestimates the activation energies by some 20 kcal/mol, while CASSCF both overestimates the activation energy and finds the stepwise pathway to be the lowest in energy. This overstabilization of diradical species is a common artifact of CASSCF calculations, resulting from the limited active space used. However, it can be corrected for using second-order perturbation methods; a CASPT2N investigation is planned.

The best results are obtained with MP2 and DFT methods. MP2 single points at RHF geometries predict energies to within 4 kcal/mol of the experimental values. Pure DFT methods, such as BLYP, underestimate the activation energies for these isomerizations somewhat; but the hybrid DFT method, Becke3LYP, gives activation energies in excellent agreement with experiment. However, both DFT methods have a tendency to overestimate the stability of allenes.

Acknowledgment. We are grateful to the National Science Foundation for financial support of this research and to the National Center for Supercomputing Applications, University of Illinois at Urbana-Champaign and the Office of Academic Computing at UCLA for computational resources. S. Wilsey

---

(27) Prosen, E. J.; Maron, F. W.; Rossini, F. D. *J. Res. Natl. Bur. Stand.* **1951**, *46*, 106.

(28) Plattner, D. A.; Houk, K. N. *J. Am. Chem. Soc.* **1995**, *117*, 4405.

(29) Johnson, B. G.; Gonzales, C. A.; Gill, P. M. W.; Pople, J. A. *Chem. Phys. Lett.* **1994**, *221*, 100.

thanks the Royal Society for a NATO Fellowship and the Fulbright Commission for a scholarship.

Supporting Information Available: Three figures are available containing (i) fully optimized geometries of reactants, transition structures, and products optimized at the RHF/6-31G*, BLYP/6-31G*, and B3LYP/6-31G* levels of theory; (ii) fully optimized geometries of reactants and products and geometries from constrained optimizations of concerted transition structures obtained at the CASSCF/6-31G* level of theory; and (iii) fully optimized geometries of stepwise transition structures and diradical intermediates obtained at the CASSCF/6-31G* level of theory (4 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

JA972826F