

Transition Structures of the Ene Reactions of Cyclopropene

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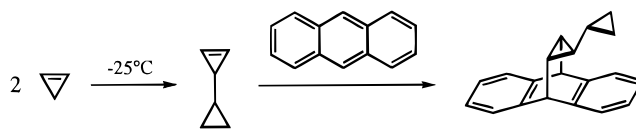
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Abstract: The transition structures for the ene reactions of cyclopropene with ethylene, propene, and cyclopropene have been located with ab initio molecular orbital calculations and the 6-31G* basis set and by DFT calculations with the Becke3LYP functional and the 6-31G* basis set. Several of the transition structures have also been located with CASSCF calculations. Energies of all stationary points were also evaluated with second-order Møller–Plesset theory using the RHF/6-31G* optimized geometry. The geometries of each transition structure and the energetics of each reaction are discussed and compared to the ene reaction of propene with ethylene. Calculations show that the cyclopropene ene reactions have much lower activation barriers than the propene–ethylene ene reaction, in agreement with experimental results. The transition structures have varying degrees of asynchronicity. The stabilities of the possible radical intermediates for each reaction are reflected in the geometries of the transition structures. The relief of strain in a cyclopropene, when acting as the enophile, accounts for the energetic differences in these reactions. The *endo* transition structure for the dimerization is lower in energy than the *exo* transition structure by 2.7 kcal/mol at the Becke3LYP/6-31G* + ZPE level of theory. Secondary orbital overlap of a CH bond of the enophile with the π -system at the central carbon of the ene is proposed to account for the preference for the *endo* transition structure. Barely stable diradical intermediates have been found for both *endo* and *exo* cyclopropene dimerization reactions, but it is likely that they are artifacts of the current level of theory.

Introduction

Cyclopropene is known to dimerize and to polymerize at room temperature.^{1–3} Substituted cyclopropenes are generally more stable and dimerize at higher temperatures.^{4–9} The products of some of these dimerizations are consistent with that of an Alder-ene reaction. In this paper we present the results of an ab initio molecular orbital study of the dimerization of cyclopropene, as well as other ene reactions of cyclopropene.

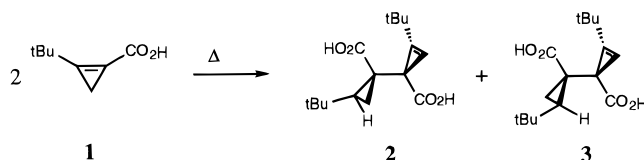
Since the ene reactions of cyclopropene have been reviewed by Baird,¹⁰ only a summary of the most pertinent examples of these reactions is presented. In 1963, Breslow and Dowd reported the thermal dimerization of 1,2,3-triphenylcyclopropene to form 3-(1,2,3-triphenylcyclopropyl)-1,2,3-triphenylcyclopropene.⁴ The addition of di-*tert*-butyl peroxide had no effect on the rate of reaction, and both deuteriums from the dimerization of 1-deuterio-1,2,3-triphenylcyclopropene were conserved in the product.⁴ On the basis of these experiments, Breslow and Dowd proposed a concerted mechanism for this reaction. In 1969, Dowd and Gold trapped the cyclopropene dimer with anthracene.³ They proposed that the mechanism of the dimerization was that of an Alder-ene reaction. Radical mechanisms



were dismissed after observing that the addition of radical traps failed to reduce the dimerization rate.

The dimerizations of 1,3-diarylcyclopropenes have been investigated by Komatsu et al.⁷ The products are those expected from ene reactions. The activation energy for the dimerization of 1,3-diphenylcyclopropene was determined to be 9.7 kcal/mol, and ΔS^\ddagger was found to be -32.8 eu. The primary kinetic isotope effect for the dimerization of 3-deuterio-1,3-diphenylcyclopropene is $k_H/k_D = 3.1$. This is similar to k_H/k_D for transferring hydrogens in other ene reactions.⁸

Baird et al. studied the dimerization of 2-*tert*-butylcyclopropenecarboxylic acid (**1**) at 20 °C. Products **2** and **3** were formed in a 1.5:1 ratio in CDCl₃ or neat and in a 1:1 ratio in ether.⁹ The two products are proposed to be formed from *endo* and

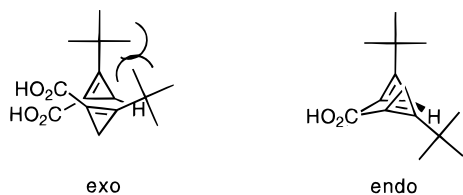


exo transition structures. Baird noted that the *tert*-butyl groups would interact unfavorably in the *exo* transition structure, causing the *endo* transition structure to be preferred.⁹ Baird et al. also studied the ene reaction of **1** with 3,3-dimethylcyclopropenecarboxylic acid. The latter reacted as the enophile. The *exo* product is formed exclusively, perhaps due to the steric repulsion between a methyl group of the enophile and the ene in the *endo* transition structure.

Recently, Apeloig and Matzner have reported theoretical studies of Diels–Alder reaction of cyclopentadiene with cy-

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clopropene and have rationalized the stereoselectivity based upon attractive orbital interactions with CH.¹¹ A similar theme will be developed later in this paper.

Computational Methods

Ab initio molecular orbital calculations were performed with the GAUSSIAN 88 and GAUSSIAN 94 series of programs.¹² All geometries of the reactants, transition structures, and products were optimized with Hartree–Fock (HF) or Kohn–Sham (KS) theory with the Becke3LYP functional and the 6-31G* basis set.¹³ Because of possible diradical character in the reaction, both restricted (R) and unrestricted (U) DFT calculations were performed. The UKS results are lower in energy than the RKS results only for the cyclopropene dimerization. CASSCF calculations were performed on transition states for the reactions of cyclopropene with ethylene and for the cyclopropene dimerization. Harmonic vibrational frequency calculations were performed to confirm the nature of all stationary points. Zero-point energy corrections were obtained from harmonic vibrational frequencies with the 6-31G* basis set. Energies of each RHF/6-31G* stationary point were calculated with inclusion of electron correlation by using second-order Møller–Plesset theory¹⁴ and the 6-31G* basis set. Preliminary calculations were performed with use of the AM1 semiempirical method.¹⁵

Results and Discussion

Three ene reactions of cyclopropene, shown along with the parent reaction in Figure 1, have been studied with ab initio molecular orbital theory. The total and zero-point energies of the reactants, transition structures, and products are given in Table 1, which appears in the Supporting Information. Table 2 gives the relative energies. The RHF/3-21G transition structure for the parent ene reaction of propene with ethylene has been reported earlier.¹⁹ It is similar in structure to the Becke3LYP/6-31G* transition structure, which is shown in Figure 2. The forming CC bond length is 2.112 Å. The breaking CH bond is 1.316 Å, while the forming CH bond is 1.483 Å. The activation energy is calculated to be 33.3 kcal/

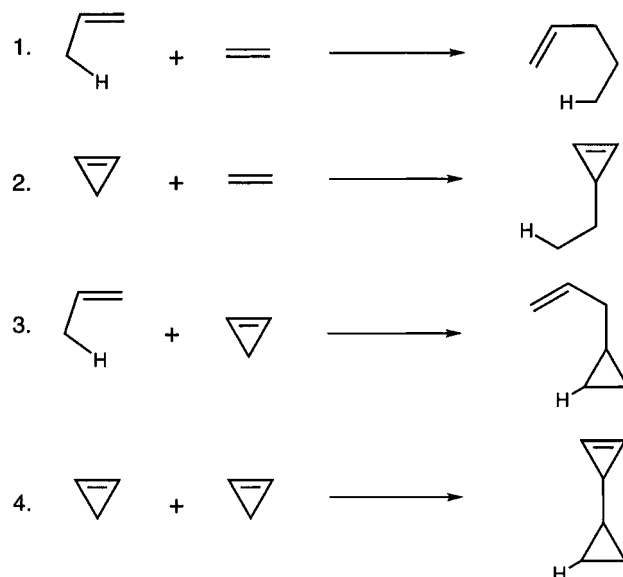


Figure 1. The ene reactions studied theoretically.

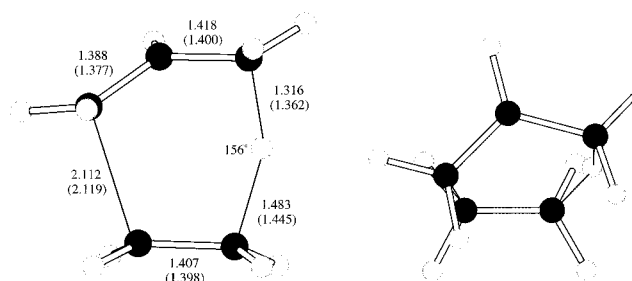


Figure 2. Two views of the Becke3LYP/6-31G* transition structure for the ene reaction of propene with ethylene. Bond lengths in parentheses are the results from RHF/6-31G* calculations. Bond lengths are in angstroms and angles are in degrees.

mol. This is similar to the experimental activation energy of 37 kcal/mol.²⁰

A CASSCF structure was also located for the parent reaction, with a six-orbital, six-electron active space. There is very little change in the CASSCF structure as compared to the RHF structure. The bond lengths are slightly longer, except the forming CH bond length is slightly decreased at the CASSCF/6-31G* level. The calculated activation barrier is 35.0 kcal/mol by 6-31G* CASSCF calculations. A natural orbital analysis of the results gives occupation numbers of 1.971, 1.915, 1.890, 0.123, 0.085, and 0.027, so the transition structure has little diradical character. A pure diradical would have occupations of 2.0, 2.0, 1.0, 1.0, 0.0, and 0.0.

In the remaining discussion, the Becke3LYP results will be emphasized, but the RHF and MP2 results given in the tables lead to the same conclusions about mechanisms and transition state geometries as deduced from the DFT results.

The ene reaction of propene with cyclopropene, where cyclopropene is the enophile, has both *exo* and *endo* transition structures. The Becke3LYP/6-31G* transition structures are shown in Figure 3. The forming CC bond lengths in the *exo* and *endo* transition structures are 2.108 and 2.075 Å, respectively, somewhat shorter than in the parent ene reaction. At the same time, the hydrogen transfer is less advanced in the cyclopropene reactions. The lengths of the breaking CH bonds (*exo*, 1.216 Å; *endo*, 1.204 Å) are shorter, while the lengths of the forming CH bonds (*exo*, 1.662 Å; *endo*, 1.690 Å) are longer. These transition structures are slightly more asynchronous than

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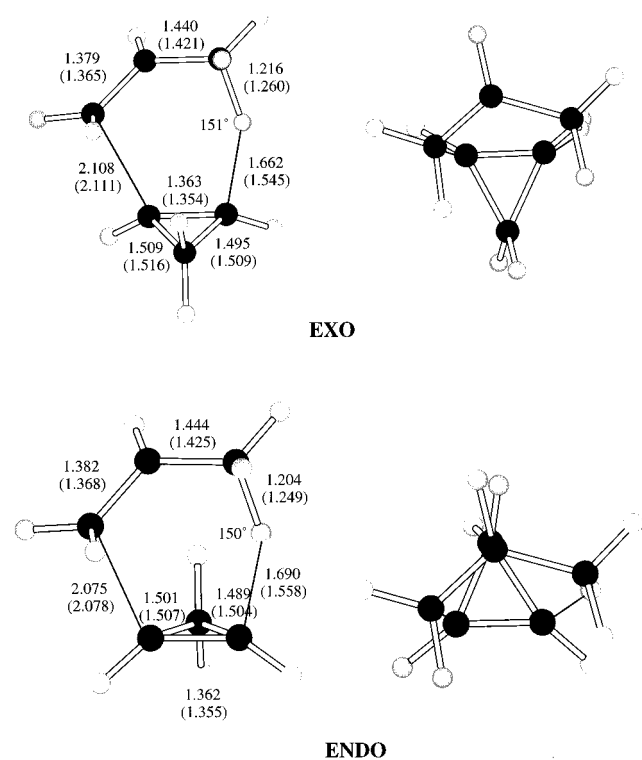
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Table 2. Relative Energies (kcal/mol) of the Reactant, the Transition Structure(s), and the Product for the Ene Reactions of Propene with Ethylene and Cyclopropene with Ethylene, Propene, and Cyclopropene

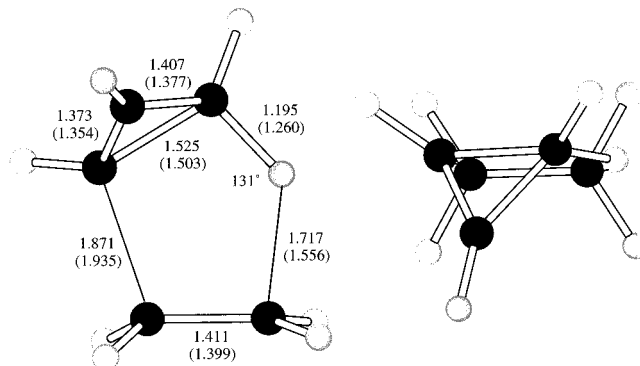
structure	RHF/6-31G*	MP2/6-31G* ^a	MP2/6-31G* ^a + ZPE ^b	B3LYP/6-31G*	B3LYP/6-31G* + ZPE ^c
propene + ethylene	0.0	0.0	0.0	0.0	0.0
TS1	61.0	31.4	31.5	33.0	33.3
1-pentene	-22.7	-28.8	-24.5	-25.1	-21.0
propene + cyclopropene	0.0	0.0	0.0	0.0	0.0
TS2 <i>exo</i>	50.4	18.2	16.1	23.4	23.7
TS3 <i>endo</i>	48.5	15.6	13.6	21.6	22.1
3-cyclopropylpropene	-49.5	-53.3	-50.5	-47.9	-43.3
cyclopropene + ethylene	0.0	0.0	0.0	0.0	0.0
TS4	57.9	26.1	23.9	28.5	28.9
3-ethylcyclopropene	-25.6	-32.1	-30.5	-27.4	-23.8
cyclopropene	0.0	0.0	0.0	0.0	0.0
TS5 <i>exo</i>	45.8	10.9	6.6	17.5	18.1
TS6 <i>endo</i>	44.5	7.2	2.9	14.9	15.4
3-cyclopropylcyclopropene	-51.6	-55.9	-55.7	-50.8	-46.7

^a Single-point energy evaluation with RHF/6-31G* optimized geometry. ^b Zero-point energy correction obtained from unscaled RHF/6-31G* frequency calculations. ^c Zero-point energy correction obtained from unscaled Becke3LYP/6-31G* frequency calculations.

**Figure 3.** Two views of the Becke3LYP/6-31G* transition structures for the ene reaction of propene with cyclopropene. RHF values are in parentheses.

the parent transition structure. The Becke3LYP activation energies for these ene reactions are 22.1 (*endo*) and 23.7 kcal/mol (*exo*), respectively, 9–11 kcal/mol lower than for the parent ene reaction. This reflects the high reactivity of cyclopropene in reactions involving additions to the highly strained double bond.

The transition structure of the ene reaction of cyclopropene with ethylene is shown in Figure 4. Its geometry is also significantly distorted from that of the parent ene reaction. The forming CC bond length is only 1.871 Å, which is much shorter than in the parent transition structure or in the propene–cyclopropene transition structures. The breaking CH bond length is 1.195 Å, while the forming CH bond length is 1.717 Å. The Becke3LYP activation energy is 28.9 kcal/mol. The transition structure for this ene reaction is significantly distorted from the parent transition structure toward a more diradical transition structure, which will be discussed in more detail later.

**Figure 4.** Two views of the Becke3LYP/6-31G* transition structure for the ene reaction of cyclopropene with ethylene. RHF values are in parentheses.

The calculated activation energy is only 4.4 kcal/mol less than that of the parent reaction, and 7 kcal/mol above that of the reaction with cyclopropene as the enophile.

The transition structures for the dimerization of cyclopropene are shown in Figure 5. Both the *exo* and *endo* transition structures are very asynchronous. The forming CC bond lengths are 1.926 and 1.939 Å, in the *exo* and *endo* transition structures, respectively. The breaking CH bond lengths are 1.133 and 1.118 Å, while the forming CH bond lengths are 2.035 and 2.201 Å, respectively. These transition structures are the most asynchronous and the earliest transition structures of those studied. The calculated activation energies are only 15.4 (*endo*) and 18.1 kcal/mol (*exo*).

The low calculated activation energies are consistent with the rapid dimerization observed for cyclopropene, and the preference for the *endo* transition state is quite striking. The transition structures with both RHF and DFT methods suggest that the reaction could involve diradical intermediates. We further explored the reaction surface with unrestricted DFT methods, which give a reasonably balanced description of concerted and diradical pathways.²¹

Intrinsic reaction coordinates (IRC) calculations have been carried out for the cyclopropene dimerization reaction at the UB3LYP/6-31G* level. Starting from either the *endo* or the *exo* transition structure, an intermediate can be found with UB3LYP. The energies of these intermediates are listed in Table 3 and shown in Figure 6. Figure 7 shows the UB3LYP

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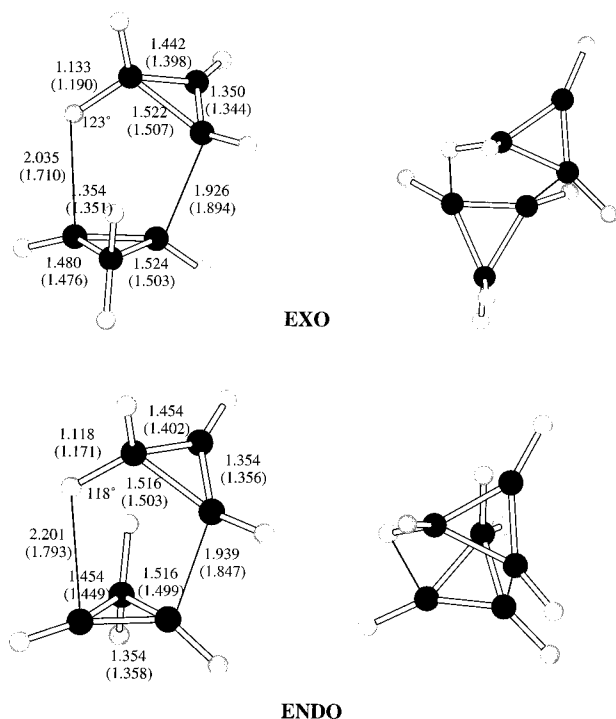


Figure 5. Two views of the Becke3LYP/6-31G* transition structures for the ene dimerization of cyclopropene. RHF values are in parentheses.

Table 3. Relative Energies of the Reactant, the Transition Structure(s), Intermediate, and the Product for the Ene Reactions of Cyclopropene Dimerization

	structure	rel energies (kcal/mol)	rel energies + ZPE ^a (kcal/mol)
reactant	cyclopropene	0.0	0.0
<i>exo</i>	TS5	17.5	18.1
	intermediate	3.4 (1.4) ^b	5.4 (3.4)
<i>endo</i>	TS6	14.9	15.4
	intermediate	6.2 (3.2)	7.9 (4.9)
	TS6'	9.1 (4.3)	8.9 (4.1)
	TS6''	6.7	5.4
product	3-cyclopropyl-cyclopropene	-50.8	-46.7

^a Zero-point energy correction obtained from unscaled UBecke3LYP/6-31G* frequency calculations. ^b Energies in parentheses are after spin correction.

intermediate structures. Both intermediates are 1,4-diyls, with the new CC bond completely formed and no hydrogen transfer. The lengths of the newly formed CC bonds are 1.537 and 1.518 Å, respectively. These values are in the standard single CC bond length range. The lengths of the breaking CH bonds are 1.096 and 1.093 Å, a little longer than the standard CH bond lengths; the forming CH bond lengths are 2.590 and 2.646 Å, respectively. The energies of the intermediates are 5.4 (*exo*) and 7.9 (*endo*) kcal/mol. The S^2 value for the intermediate is 0.92 for *endo* and 0.95 for *exo*. This means that the intermediates are typical non-interacting diradicals, and are mixtures of singlet and triplet states, since unrestricted calculations do not necessarily give pure spin states. Spin correction using a procedure described recently,²¹ gives a prediction of the energies shown in Table 3 in parentheses.

UBecke3LYP/6-31G* calculations were used to search for the second transition structure for the reaction. For the *exo*, no transition structure has been located as yet, because the surface is very flat in the region. For the *endo*, two transition structures were obtained starting with different initial guesses (Figure 8). An IRC calculation verified that TS6' in Figure 8 led to the intermediate and the product in the two reaction coordinate

directions. This is the transition structure for hydrogen transfer from the diradical intermediate to product. A second transition structure (TS6''), also shown in Figure 8, led to the cyclopropylcyclopropene product in both directions. It is the transition structure for the dyotropic hydrogen shift of cyclopropylcyclopropene. Such dyotropic shifts have been studied extensively in sesquiorbornene-derived systems,²² but have not previously been observed or suggested for cyclopropene dimers.

Figure 6 shows the reaction path and relative activation energies for the stepwise *endo* cyclopropene dimerization. TS6 has a 6.5 kcal/mol higher activation energy than TS6', while the intermediate and TS6' have similar energies (Table 3). Spin correction²¹ of the energies of the *endo* intermediate and transition state leads to the prediction that TS6' is actually slightly below the intermediate (Table 3). Both spin-contaminated and spin-corrected results indicate the second barrier is very low or non-existent. Thus dimerization involves a rate-determining transition state mainly involving CC bond formation. It is highly unlikely that an intermediate, if formed, could be trapped, since the barrier to hydrogen transfer is negligible. Tunneling could make H transfer even faster.^{22,36}

We also studied the dimerization reaction with the 60/66 CASSCF/6-31G* method. The transition structure obtained for the first step is similar to that obtained with the DFT method. The CH bond being transferred is only slightly perturbed from its value in cyclopropene; the CH bond formation has hardly begun and has a distance of 2.48 Å. The activation energy calculated at the 6-31G* CASSCF level is 25.7 kcal/mol. The natural orbital populations of 1.983, 1.938, 1.700, 0.309, 0.061, and 0.018 electrons are indicative of greater diradical character than in the parent ene reaction. The transition state is very early with mainly CC bonding, as in the DFT calculation.

There is a wide variation of transition states for these reactions, varying from nearly synchronous for propene plus ethylene to extremely asynchronous or even stepwise in the cyclopropene dimerization. More O'Ferrall and Jencks have used bond-order diagrams to show the effect of substitution on the geometry of transition structures.²³ This type of diagram is shown in Figure 9 for the ene reactions studied. The reactants are in the lower left-hand corner and the product is in the upper right-hand corner. In the upper left-hand corner is a 1,4-diyl, the diradical intermediate that would be formed upon complete CC bond formation without the transfer of hydrogen. The lower right hand corner locates the allyl radical and an ethyl radical, the two radicals that would be formed upon hydrogen transfer without CC bond formation. The six calculated transition structures are located on this diagram, where the vertical axis corresponds to the extent of CC bond formation and the horizontal axis corresponds to the extent of CH bond breaking. The use of CH bond formation instead of CH bond breakage gives a different MOJ diagram (not shown) that reveals the same trends as Figure 9. The equation used to calculate the Pauling bond order is $n_p = n_o \exp((R_o - R)/0.6)$, where n_p is the calculated bond order, n_o is the bond order of the fully formed bond of length R_o , and R is the bond length of a bond with a bond order of n_p .²⁴ The use of 0.6, rather than Pauling's 0.3, in this equation is recommended for partial single bonds by the Indiana group.^{25,26}

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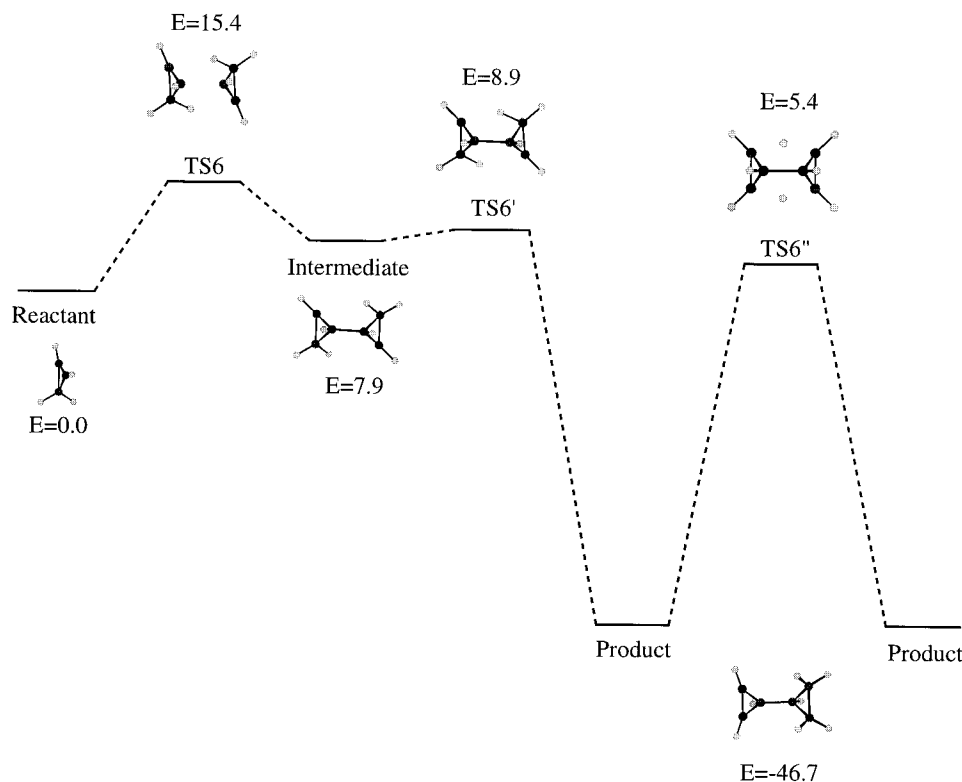


Figure 6. Reaction path and activation energies for the cyclopropene dimerization reaction and the dyotropic hydrogen shift of the dimer (energies in kcal/mol).

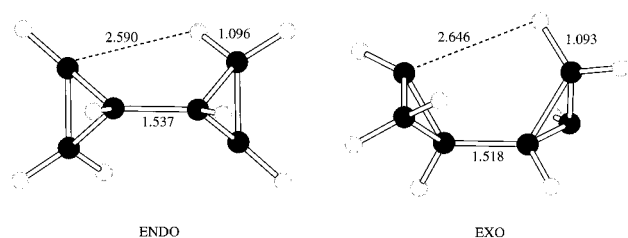


Figure 7. The UB3LYP intermediates for the cyclopropene dimerization.

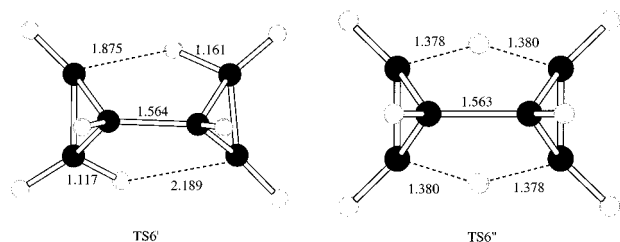


Figure 8. The transition structures (left) for hydrogen transfer from the diradical intermediate in Figure 7 and (right) for the dyotropic hydrogen shift of cyclopropylpropene.

Unlike the Diels–Alder reaction, it is difficult to discuss absolute synchronicity of ene reactions based on the bond lengths or bond orders of the forming and breaking bonds because there is no symmetry, even in the parent transition structure. The parent transition structure may be considered to be synchronous, because the forming CC bond and the breaking CH bond orders are similar in value. There is a third important bonding change, that of CH bond making. This is strongly coupled to CH bond breaking in the whole series. The sum of breaking CH and forming CH bond lengths is 2.8–2.9 Å for the propene–ethylene, propene–cyclopropene, and cyclopro-

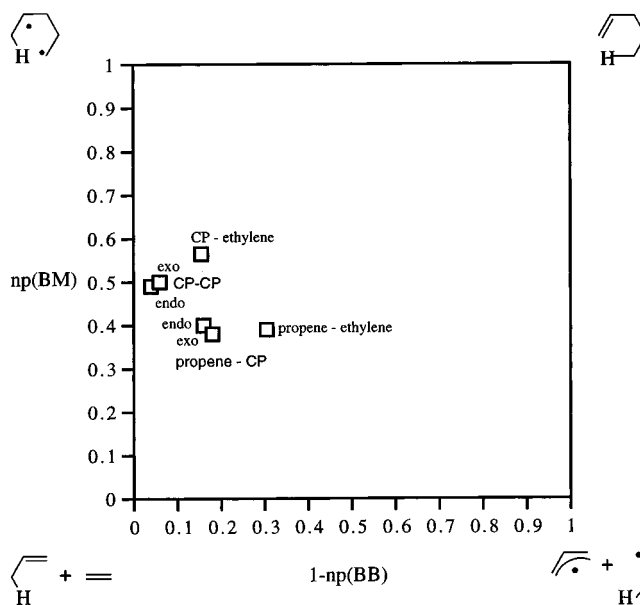


Figure 9. More O'Ferrall–Jencks diagram for the ene reactions studied. CP is cyclopropene.

prene–ethylene reactions and becomes larger, 3.2–3.3 Å, for the cyclopropene dimerizations. The five cyclopropene ene transition structures are all located toward the upper left-hand corner of the MOJ diagram relative to the parent ene transition structure. These transition structures all have diradical character, resulting from more CC bond formation and less hydrogen transfer than the parent system.

Understanding the change in geometries of the transition structures is facilitated by examining the possible radical intermediates for each of the ene reactions studied. These intermediates are shown in Figure 10, along with their heats of formation. The heats of formation for the radical intermediates were estimated by using Benson's group equivalents and

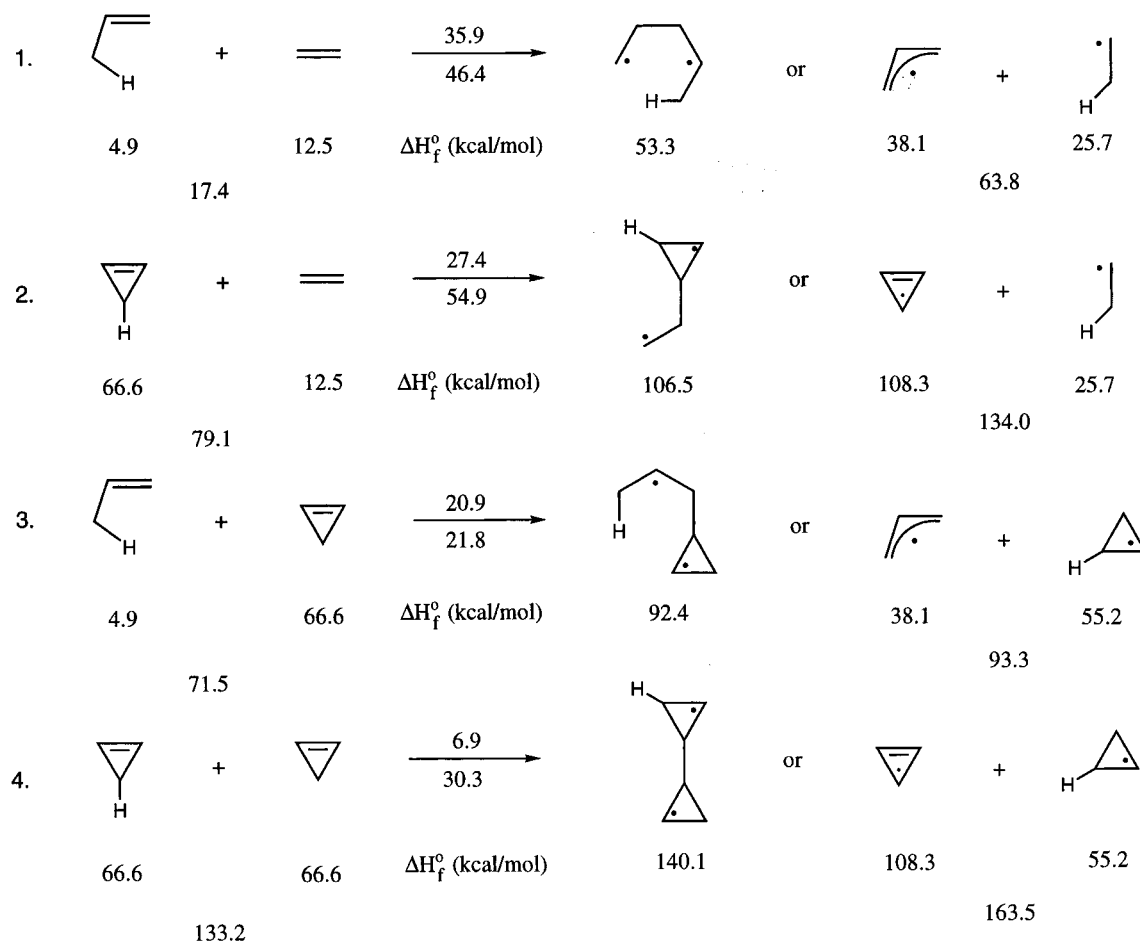


Figure 10. Possible radical intermediates for each ene reaction and their heat of formation as determined by using the Benson rules of group additivity.^{27,28} Heats of reaction are given above the arrow (CC formation) and below the arrow (hydrogen transfer).

cycloalkene heats of formation.^{27–31} To the sum of standard group increments, strain corrections were added for cyclic species. For the parent reaction 1, the heats of formation for the possible radical intermediates show that the 1,4-diyli is more stable than the radicals produced by hydrogen transfer by 10.5 kcal/mol. By using these heats of formation as a guide, the transition structure should be fairly synchronous, but with somewhat more CC bond formation than hydrogen transfer. This is what is found (Figure 9). For the propene–cyclopropene reaction, two processes have similar energies. The transition structures for the propene–cyclopropene reaction have similar geometries to that of the parent transition structure, but are shifted toward less hydrogen transfer and earlier (Figure 9). For the cyclopropene–ethylene reaction, the 1,4-diyli is favored substantially. The geometry of the cyclopropene–ethylene transition structure is significantly distorted toward the 1,4-diyli, with significantly more CC bond formation than hydrogen transfer. A similar situation is encountered with the dimerization of cyclopropene, where the 1,4-diyli is more stable than the radical pair by over 20 kcal/mol. The cyclopropene dimerization transition structures have the least hydrogen transfer. The

diradical energy from the Benson estimates is, essentially identical with the Becke3LYP value.

The diradical character of the transition structure for the ene dimerization of cyclopropene is reflected in the ease in which some substituted cyclopropenes undergo thermal [2 + 2] dimerizations, which may proceed through diradical intermediates.^{32–34} An example of this is the [2 + 2] dimerization of 1-vinylcyclopropene, which proceeds readily at -60°C .³⁴

While the geometries of the transition structures are dictated by the stabilities of the possible radical intermediates and the strain relieved in these radical intermediates, the exothermicity of these cyclopropene ene reactions is dictated by whether or not a cyclopropene is converted to a cyclopropane. The ene reaction of cyclopropene with ethylene is calculated to be exothermic by 23.8 kcal/mol, similar to the parent ene reaction (21.0 kcal/mol). A cyclopropene moiety is still present in the product. The ene reaction of propene with cyclopropene is exothermic by 43.3 kcal/mol, while the ene dimerization of cyclopropene is exothermic by 46.7 kcal/mol. A cyclopropene is converted to a cyclopropane in each of these reactions. The difference between the energy of reaction for these ene reactions and the parent ene reaction is close to approximately 26 kcal/mol of strain energy gained by converting a cyclopropene to a cyclopropane. The more exothermic reactions are expected to have the earlier transition structures and have lower activation barriers, in agreement with the Hammond postulate.³⁵ Exami-

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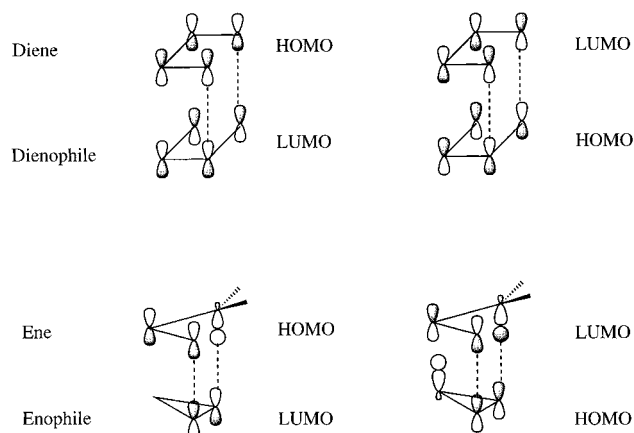


Figure 11. The HOMO-LUMO combinations for the *endo* transition structures of the Diels-Alder reaction of butadiene with butadiene and the Alder-ene reaction of propene with cyclopropene.

nation of Table 2 shows this to be true for the ene reactions studied.

Substituted enophiles may react via *exo* and *endo* transition structures. The *exo* transition structure should be preferred on steric grounds, but calculations predict that the *endo* transition structure is preferred in the ene reactions where cyclopropene acts as the enophile. At the Becke3LYP level, the *endo* preference is 2.7 kcal/mol for the dimerization of cyclopropene and 1.6 kcal/mol for the ene reaction of cyclopropene with propene. To make sure that the difference did not arise from basis set superposition errors, we performed a counterpoise correction on the *exo* and *endo* transition states. The *exo* is lowered by 2.5 kcal/mol, and the *endo* by 2.6 kcal/mol by this, so there is an insignificant difference in BSSE for *exo* and *endo* structures. We postulate that the preference is caused, in part, by the overlap of a CH bond from the enophile with the π -system at the central carbon of the ene. This secondary orbital interaction involving a CH σ bond is an effect similar to that postulated for the Diels-Alder reactions of dienes with cyclopropene.¹¹ The frontier molecular orbitals for the Diels-Alder reaction of butadiene with butadiene and the Alder-ene reaction of propene with cyclopropene are shown in Figure 11. Woodward and Hoffmann first proposed this type of interaction to explain the preference for *endo* addition of unsaturated dienophiles in Diels-Alder reactions.⁴⁰ In the example of the Diels-Alder reaction, either combination of HOMO and LUMO yields a stabilizing secondary orbital interaction. In the propene-cyclopropene ene reaction, only one combination of HOMO and LUMO provides a secondary orbital interaction. It would be expected that the *endo* preference would be less in the ene reactions than in the Diels-Alder reaction. In the cyclopropene dimerization, neither HOMO-LUMO combination yields a secondary orbital interaction due to the symmetry of cyclopropene. Upon reaching the transition structure, symmetry has been broken and mixing of the cyclopropene orbitals is expected to yield the proper combination for secondary orbital overlap. Alternatively, the *endo* preference could be due to an attractive van der Waals or electrostatic interaction.

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This type of secondary orbital interaction involving a CH bond has been proposed previously. Sustmann et al. used SCF perturbation calculations to investigate the Diels-Alder reaction of cyclopentadiene with cyclopropene.⁴¹ While steric effects were found to cause the *endo* preference of this reaction, an interaction between the CH bond of the dienophile and the central carbons of the diene was detected. Indeed, the attractive secondary intermediate was confirmed by experimental studies. Baldwin et al. found that the Diels-Alder reaction of butadiene with cyclopropene gives the *endo* product stereoselectively at 0 °C.⁴² No steric interactions are present to disfavor *exo* addition. The attractive interaction of a CH bond of the dienophile with the central carbons of the diene was proposed to explain the *endo* preference in the Diels-Alder reaction of butadiene with cyclopropene.¹¹

In our work, the interaction of the CH bond of the enophile with the ene manifests itself in the geometry of the transition structures. In the *exo* transition structure, where no overlap occurs, the lengths of both CH bonds at the 3-position of the enophile are 1.095 Å. In the *endo* transition structure, the bond length of the CH bond close to the ene is elongated to 1.118 Å, while the other CH bond is shortened to 1.093 Å. We propose that electron density from the CH bond is donated to the ene, resulting in the lengthening of the CH bond. This seems reasonable when considering that the central carbon of the ene acquires a small positive charge in every ene transition structure calculated.^{19,43} The lengthening of the interacting CH bond is also observed in the *endo* transition structure for the ene reaction of cyclopropene with propene. In the *exo* transition structure the bond lengths of the CH bonds are 1.095 Å. In the *endo* transition structure, the bond length of the CH bond close to the ene is elongated to 1.100 Å, while the other CH bond is shortened to 1.093 Å. The effect is not as dramatic, but it is consistent with the smaller *endo* preference in this system.

Conclusion

The transition structures for the ene reactions of cyclopropene with ethylene, propene, and cyclopropene have been located with several quantum mechanical methods. The geometries of the transition structures vary from somewhat synchronous (propene-cyclopropene) to very asynchronous, perhaps stepwise (cyclopropene dimerization). A preference for the *endo* transition structure is found for the ene reactions in which a cyclopropene is the enophile. The preference is proposed to be the result of an attractive interaction of a CH bond of the enophile with the central carbon of the ene.

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Supporting Information Available: Table 1, containing total energies in hartrees and zero-point energies for all species (1 page). See any current masthead page for ordering and Internet access instructions.

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