880 J. Am. Chem. Soc. **1996,** *118,* 880−885

The Dimerization of Cyclobutadiene. An ab Initio CASSCF Theoretical Study

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Received June 8, 1992[⊗]

Abstract: Ab initio molecular orbital calculations have been performed on the dimerization of cyclobutadiene using the 3-21G and 6-31G* basis sets. Complete active space SCF calculations with an 8-electron 8-orbital active space were carried out. The *anti* dimerization occurs by either synchronous concerted or asynchronous concerted pathways with nearly identical activation energies. The *syn* dimerization is highly favored, and this reaction is predicted to have a negative activation energy. There is no synchronous concerted pathway. The stationary points on the *syn* dimerization surface consist of a degenerate stationary point which can collapse directly to the product in four different ways or collapse to the transition state for the Cope rearrangement.

Introduction

Cyclobutadiene (CB) is an extremely reactive species that has only been isolated in an Argon matrix at low temperature[1ab] or recently in molecular container synthesized by Cram and co-workers.[1c] Transient cyclobutadiene generated in the gas phase or in solution undergoes very fast dimerization to form predominantly the syn tricyclooctadiene, **2**. The facile dimerization of cyclobutadiene is thought to be an orbital symmetry allowed [4 + 2] cycloaddition,[1d] while the preference for the syn addition has been attributed to secondary orbital interactions[1b] to less distortions,[2a] or to stabilizing interactions,[2b] occurring upon the "face-to-face" interaction of two antiaromatic π systems.

There have been no mechanistic studies on the dimerization of cyclobutadiene. The small singlet−triplet gap (7 kcal/mol)[3] and high diradical character of CB raise the interesting question whether the concerted [4 + 2] pathway is preferred over a stepwise biradical mechanism. Why should this be a special issue for this species? For the parent [4 + 2] Diels−Alder reaction of butadiene with ethylene, there is a modest (2−7 kcal/mol) advantage of the concerted pathway over the stepwise pathway.[4,5a] CASSCF(3-21G) calculations predict a 6-kcal/mol preference for the concerted pathway and QCISD(T) calculations with the 6-31G* basis set and zero-point energy corrections give a similar value.[5] The [4 + 2] cycloaddition of benzene has a much greater preference for the concerted mechanism, estimated as 23 kcal/mol by Roth *et al.*[4] The concerted mechanism can occur with maintenance of some aromaticity, while the stepwise mechanism involves its destruction.[6] For those two examples, at least, the more stable and closed-shell in nature the reactant, the greater preference it has for the concerted mechanism. Cyclobutadiene is, however, a highly reactive antiaromatic species, essentially a diradical. Is there any advantage at all for cyclobutadiene to react by a concerted mechanism?

Experimental studies of cyclobutadiene have shown that CB generated by oxidation of the cyclobutadiene iron tricarbonyl complex reacts stereoselectively as either a diene or a dienophile.[7] This selectivity is somewhat surprising for such a highly reactive species. CB generated by thermal pyrolysis of α-pyrone at 800 °C reacts readily with radicals and oxygen.[8] Occasionally, stepwise zwitterionic or biradical mechanisms of cycloadditions of CBs have been invoked, as in the cycloaddition of 1,3-di-*tert*-butylcyclobutadiene with tetracyanoethylene[9] and in the dimerization of tri-*tert*-butylcyclobutadiene.[10] However, for the most part, there is no information about the mechanism of dimerization.

In this paper, ab initio molecular orbital calculations on the potential energy surface for the cyclobutadiene dimerization via concerted and biradical pathways to give syn (endo) or anti (exo) dimers are reported.

Computational Methods

The structures of cyclobutadiene, several complexes and saddle points along the reaction path, and the products were initially optimized at the restricted Hartree−Fock (RHF) level, using first the split-valence 3-21G and then the 6-31G* basis sets.[11] The biradical intermediates were optimized with the unrestricted Hartree−Fock (UHF) method and the 3-21G basis set. Beginning from these structures, geometries were

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Table 1. Calculated Relative Energies (kcal/mol) of Stationary Points and Numbers of Imaginary Frequencies [in Brackets]

molecule	HF/3-21G	RHF/6-31G*	RMP2/6-31G* [a]	CASSCF/3-21G	CASSCF/6-31G*
1 (2 cyclobutadienes)	0.0 [0]	0.0	0.0	0.0	0.0
2 (syn adduct)	−104.6 [0]	−94.6	−104.8	−72.9	
3 (anti adduct)	−113.2 [0]	−102.3	−112.0	−80.1	
4 (anti saddle point)	9.3 [1]	16.4	−9.6	12.2 [2]	
5 (second-order saddle)	−10.1 [2]	6.1	−50.1	−4.4 [2]	6.8
6 (Cope TS)	−68.9 [1]	−52.8	−82.4	−43.0 [1]	
7 (anti TS)	−55.1[b]			12.2	15.2
8 (singlet, eclipsed)	−91.4[b]				
8 (triplet, eclipsed)	−87.8[b]			−26.2 [1]	
9 (singlet, anti)	−95.5[b]			−33.1 [0]	
9 (triplet, anti)	−95.5[b]			−33.4 [0]	

[a] Single point on RHF/6-31G* geometries. [b] UHF/3-21G energies.

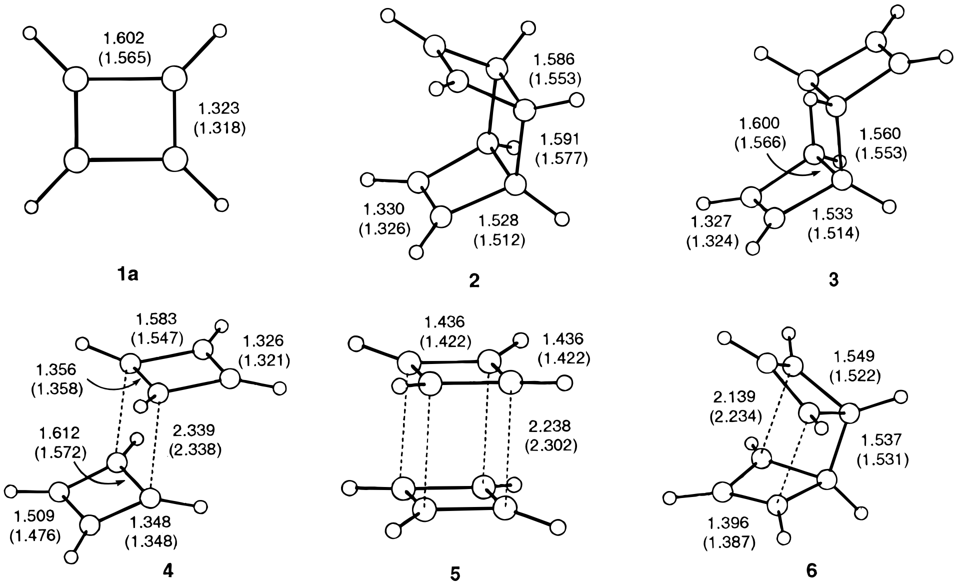

Figure 1. RHF/3-21G (RHF/6-31G*) optimized structures. Bond lengths are in Å.

further refined using the eight-electron eight-orbital complete active space multiconfiguration self-consistent field (CASSCF) method[12] with the 3-21G basis set. The active space includes all π electrons and π orbitals of the two cyclobutadienes. Several species were also studied by CASSCF/6-31G* calculations. During the reaction, two of the π bonds are transformed into two new σ bonds of the product, and these and the other two π bonds are all involved in the active space. Single-point energy calculations with the Moller−Plesset (MP2)[13] correlation energy corrections were also performed with the 6-31G* basis set on the RHF/6-31G* structures. The CASSCF calculations were performed with the GAMESS programs,[14] and the RHF and MP2 calculations were carried out with the GAUSSIAN 90 programs.[15]

A C_s symmetry constraint was used initially to follow the concerted [4 + 2] reaction pathway. Stationary points located in this way were examined by calculating the harmonic vibrational frequencies. If the stationary point has one and only one imaginary vibrational frequency, it is a saddle point and corresponds to a transition structure. A second-order saddle point has two imaginary frequencies corresponding to two directions of negative curvature on the potential surface. When second-order saddle points were found, further searches were carried out without any symmetry constraints in order to find first-order saddle points of lower energy.

Results and Discussion

Table 1 summarizes the calculated relative energies of cyclobutadiene, the saddle points, the biradical intermediates, and the tricyclic products. The total energies (au) are given in the supporting information. The RHF structures are given in Figure 1. The CASSCF optimized structures and energetic profiles are shown in Figures 2 and 3, respectively. The detailed structural features of the saddle points and the reaction energetics are discussed first. Next, the mechanism of the CB dimerization and the theoretical origin of the syn stereoselectivity are described.

Singlet cyclobutadiene, **1a**, is rectangular. It has been found at the highest level of theory to be 7 kcal/mol more stable than the square triplet.[3] At the RHF level, the CB dimerization reaction is calculated to be exothermic by more than 95 kcal/mol. The syn product, **2**, is less stable than the anti adduct, **3**, by about 8 kcal/mol. Nevertheless, the less stable syn dimer is kinetically favored experimentally.[1a,b,7]

For concerted pericyclic reactions, calculations at the RHF/3-21G level have been shown to give reasonable geometries for the transition structures.[6] At this level of theory, concerted transition structures were located for the Diels−Alder reaction of cyclobutadiene with ethylene,[6] and for the anti dimerization of cyclobutadiene. The predicted activation energy is 9 kcal/mol for the CB dimerization via transition structure **4**. Note that this is a Diels−Alder, not [2 + 2], transition state, since

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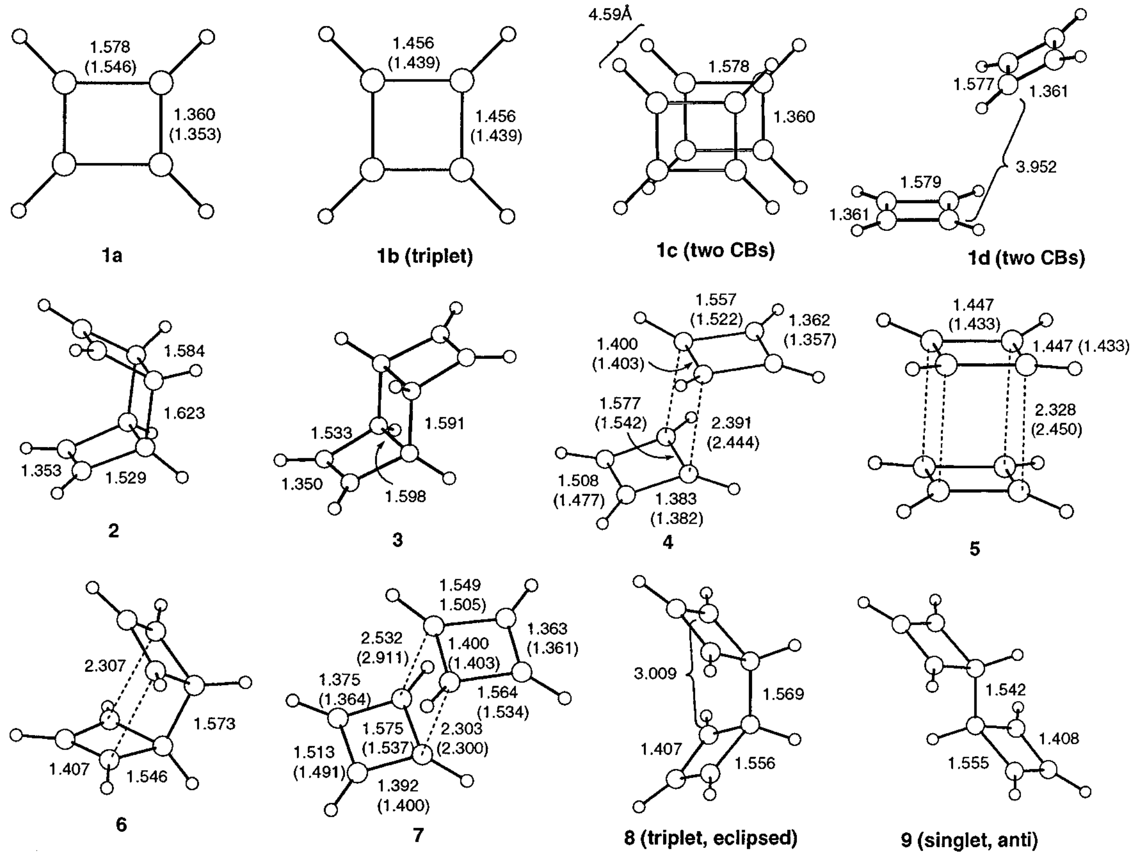

Figure 2. CASSCF/3-21G (CASSCF/6-31G*) optimized structures. Bond lengths are in Å.

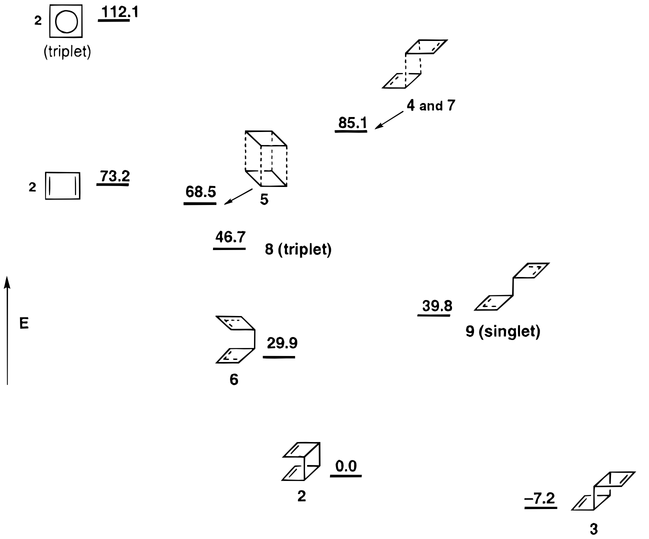

Figure 3. CASSCF/3-21G energetics (kcal/mol) for the stationary points on the cyclobutadiene dimerization potential energy surface.

Table 2. Calculated Entropies (e.u.) and Free Energy Contributions (kcal/mol) at 298 K

molecule	HF/3-21G S (298 K, eu)	CASSCF/3-21G S (298 K, eu)	$-\Delta S^a$ (eu)	$-T\Delta S$ (kcal/mol)
1 (2 cyclobutadienes)	119.2	126.2	0.0	0.0
2 (syn adduct)	73.7		45.5	13.6
3 (anti adduct)	73.4		45.8	13.6
4 (anti saddle point)	81.2	81.4	37.8	11.3
5	74.2	75.8	43.4	12.9
6 (Cope TS)	73.3	75.6	43.6	13.0
7 (anti TS)		85.5	33.7	10.0
8 (triplet, eclipsed)		80.0	46.2	13.8
9 (singlet, anti)		83.5	42.7	12.7
9 (triplet, anti)		83.7	42.5	12.7

[a] Best estimate using RHF/3-21G for the reactants and products and CASSCF/3-21G for the high energy species.

the top cyclobutadiene in **4** acts as a dienophile, while the bottom acts as a diene. For other reactions of this type, the activation energy is overestimated with this basis set or even more so with the 6-31G* basis set.[6] The activation energy is usually underestimated with the MP2 calculations,[6] and this same trend is seen in Table 1. Based on calculations on related reactions, the activation energy for the anti dimerization via **4** is expected to be approximately zero. There will, of course, be a finite activation free energy for this bimolecular reaction, due to the entropy of activation of approximately −40 eu (Table 2), producing $\Delta G^{\ddagger}$ on the order of $-T\Delta S^{\ddagger} \approx 0.04T$ kcal/mol, or 12 kcal/mol at room temperature. It is likely that the reaction will have a negative activation enthalpy, since the free energy maximum is likely to occur at a point where the enthalpy is lower than that of reactants. This has been discussed extensively for carbene cycloadditions and reactions of other reactive intermediates.[16]

Upon attempted location of the syn transition state of CB dimerization, a symmetrical stationary point, **5**, was found. Structure **5** has two imaginary frequencies corresponding to two degenerate synchronous cycloaddition modes (see later). The RHF/6-31G* optimizations give geometries and vibrational normal modes similar to those obtained with RHF/3-21G calculations. The syn stationary point **5** is consistently lower in energy than the anti saddle point **4** by 10−19 kcal/mol with RHF and MCSCF calculations (see later). This indicates that the antiaromaticity of the cyclobutadiene diminishes in the syn stationary point. Indeed, the cyclobutadienes are square in this complex as they are in the triplet state. The structures **4** and **5** have similar forming bond lengths, but **5** is about 20 kcal/mol

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more stable. This is an extreme case of secondary orbital interactions stabilizing the *endo* complex more than the *exo*. As noted above, **5** has two negative force constants. Relaxation of symmetry leads to an authentic transition structure **6**. This can happen in four different ways, and will be discussed in more detail later. Structure **6** is eclipsed like **5**, but has one σ bond completely formed. Structure **6** is the transition structure for the degenerate Cope rearrangement of the syn adduct **2**. Transition structure **6** is much lower in energy than **5,** which is 10 kcal/mol lower in energy than that of two cyclobutadienes at the RHF/3-21G level and 6 kcal/mol above with the 6-31G* basis set. MP2 calculations give a preposterously low energy, because **6** has so much biradical character.[17] For that reason, we turned to CASSCF calculations for a better description of the diradical species.

The MCSCF calculations are summarized in Table 1 and in Figure 2. CASSCF/3-21G calculations on cyclobutadiene and several complexes are shown in structures **1a**−**d**. These calculations check for size consistency and basis set superposition problems. Minimization of two rectangular CB molecules held eclipsed in an orientation corresponding to a forbidden reaction led to a stationary point **1c**. The face-to-face distance in the optimized supermolecule **1c** is 4.6 Å, and the two cyclobutadienes retain their localized rectangular structures. Structure **1c** is 0.5 kcal/mol higher in energy than two isolated cyclobutadienes, indicating that there is no attractive interaction between two CBs in **1c**. There are closed-shell repulsive interactions that keep two singlet cyclobutadienes apart.

When one of the rectangular cyclobutadienes was rotated 90° with respect to the other so that they are set up for the [4 + 2] cycloaddition reaction, minimization led to the cycloadduct with no barrier. Alternatively, the reactive orientation can be achieved if one of the cyclobutadienes undergoes valence isomerization, which is known to have a barrier for the isolated CB of 8−10 kcal/mol.[18] Another optimized edge-to-face supermolecule dimer **1d** has an anti arrangement and is 0.8 kcal/mol lower in energy than **1c**. Although **1c** and **1d** are optimized structures, vibrational frequency calculations indicate that these two supermolecules are not true minima, but have several near-zero frequencies and lie on a very flat region of the potential energy surface, where many dimer configurations are of equal energy.

CASSCF calculations with the 3-21G basis set predict that there are symmetrical stationary points, **4** and **5**, related to the anti and syn dimerizations of cyclobutadiene. Both are second-order saddle points with two negative force constants. The anti structure, **4**, is 12 kcal/mol above the reactants, while the syn structure, **5**, is predicted to be 4 kcal/mol more stable than the reactants. There are obvious structural differences between the syn and anti second-order saddle points. For **4**, the two reacting CB moieties are acting as diene and dienophile, and each has a localized rectangular structure. In contrast to the RHF results, the CASSCF calculations predict that the synchronous concerted anti dimerization pathway no longer is an authentic transition structure. One imaginary frequency of **4** corresponds to motion along the concerted [4 + 2] addition reaction path, and the other (88i cm^{-1}) corresponds to distortion to an asynchronous cycloaddition pathway. Figure 4 shows the two imaginary vibrational modes calculated at the CASSCF level of theory. A transition structure search without any symmetry constraints led to an authentic transition structure, **7**, with one imaginary frequency. This transition structure predicts that CC formation is asynchronous, with one bond lagging behind the other by 0.23 Å and even more at the 6-31G* level (see later). The imaginary frequency mode for **7** (Figure 4) corresponds to the formation of two CC bonds leading to the anti-tricyclic product rather than to a biradical intermediate. However, CASSCF calculations with the 6-31G* basis set give a more asynchronous transition structure most likely leading to a biradical intermediate (Figure 2). It is very unusual to find an asynchronous structure from symmetrical reactants,[19] but here the synchronous and asynchronous structures are of essentially identical energy. This is a manifestation of the reactive biradical nature of cyclobutadiene: there is no advantage to maintenance of a closed-shell structure, in contrast to normal or aromatic dienes. The biradical intermediate is much lower in energy than reactants, and the transition state has much biradical character.

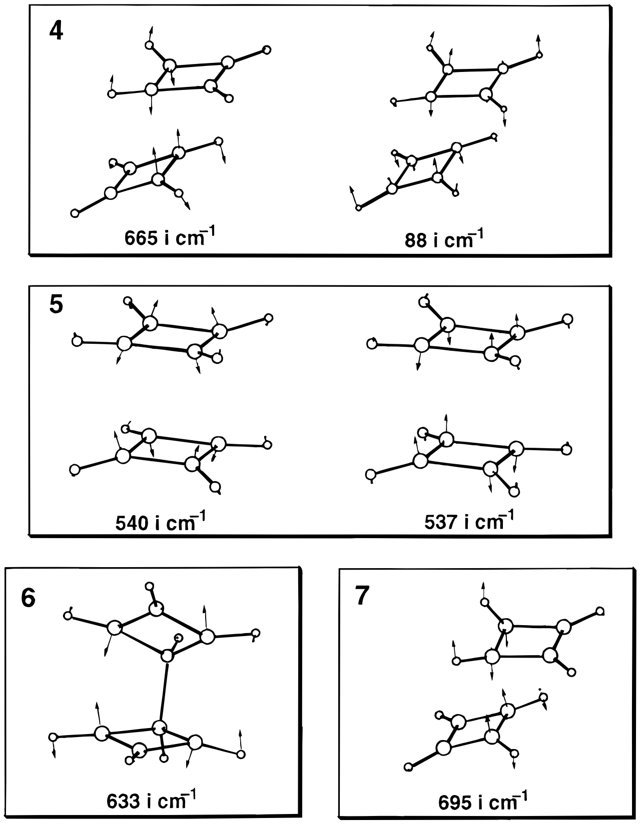

Figure 4. CASSCF/3-21G transition vectors from normal mode analyses for structures **4**−**7**.

At the CASSCF/3-21G level, there is a reaction barrier of only 12 kcal/mol for the anti dimerization through the asynchronous transition structure. The CASSCF method used in our study overestimates reaction barriers of pericyclic reactions. The calculated reaction barrier for the Diels−Alder reaction between butadiene and ethylene is 37 kcal/mol at the CASSCF/3-21G level that includes six π electrons in six orbitals as the active space,[5a] while the experimental activation energy is 27.5 kcal/mol.[19] If the calculated reaction barrier in the cyclobutadiene dimerization is overestimated by 10 kcal/mol, then the

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anti cycloaddition will have a barrier of ~2 kcal/mol. The reported experimental activation enthalpy for the dimerization of tri-*tert*-butylcyclobutadiene is 7 kcal/mol.[10b] This is believed to involve a stepwise mechanism leading to the anti product,[10a] because the syn cycloaddition of tri-*tert*-butylcyclobutadiene is hindered by the steric bulky *tert*-butyl groups.

The syn saddle point has D_{4h} symmetry consisting of two identical CB moieties, which have fully delocalized square geometries. The lower symmetry dimer, **1c**, involving two CBs with rectangular geometries, is of higher energy.

There have been theoretical studies of stacked cyclobutadienes[2] and experimental attempts to construct cyclophanes incorporating such structures.[20] Halevi studied the cyclobutadiene dimerization using his orbital correspondence analysis, and showed that the high-symmetry approach of two stacked cyclobutadienes to form cubane is symmetry forbidden.[2a] According to our calculations, this stacked structure of two cyclobutadienes is not stable with respect to bond formation upon reduction of symmetry. Unless a superstructure is attached which keeps the planes separated and approximately parallel, it will collapse without activation to a dimer or diradical. In the metal complexes of cyclobutadiene superphanes, the interplanar distances are 2.9−3.0 Å. Upon oxidative removal of metals, they all spontaneously cyclize to intramolecular cyclobutadiene dimer products.[20,21] As discussed earlier in the RHF section, **5** has two imaginary vibrational modes (Figure 4) corresponding to two degenerate asynchronous concerted [4 + 2] cycloadditions. A search for the syn dimerization transition structure without any symmetry constraints was carried out starting from this stationary point. This led to the authentic transition structure **6**. The transition vector for **6** (Figure 4) corresponds to the transition structure of the degenerate Cope rearrangement of the syn tricyclic product. The calculated reaction barrier from dimer **2** to **6** is 30 kcal/mol at the CASSCF/3-21G level, and 22 kcal/mol at the MP2/6-31G* level. A degenerate Cope rearrangement has not yet been observed in **2**; indeed, **2** is known to undergo a forbidden electrocyclic ring opening to cyclooctatetraene under thermal conditions.[22]

The syn preference is mentioned in pathways leading to diradicals. As one bond begins to form, attractive interactions between the termini of the two developing allylic radicals provide greater stabilization than occurs upon interaction of one pair of termini in the anti geometry. The second-order saddle point, **5**, has two degenerate imaginary vibrational modes, which lead downhill to the syn dimer in four possible ways, represented with the heavy arrows in Figure 5. Any linear combination of these two degenerate modes is also a correct representation of these normal modes. For example, downhill passage to **6** is also possible in four different ways, as indicated by the dotted arrows in Figure 5. Subsequently, **6** may collapse to **2** in two different ways. Indeed, from **5** to any other point on the surface around the perimeter of the diagram in Figure 5 is a downhill process, although the curvature in the direction of **2** is steepest. The Murrell−Laidler theorem[23a] and McIver−Stanton rules[23b] forbid a second-order saddle point from being simultaneously the transition state for two different reactions. Wales and Berry have shown that these rules can break down in cases of high symmetry.[24] This surface does not really violate the symmetry rules, in that two cyclobutadienes may come together to form product, without passing through structure **5** or **6** at all. This reaction constitutes a special case where the attractive interactions between two cyclobutadienes are so large that they combine without activation and are deposited on the ground state surface for the degenerate Cope rearrangement. The energy of concert is zero for this reaction.

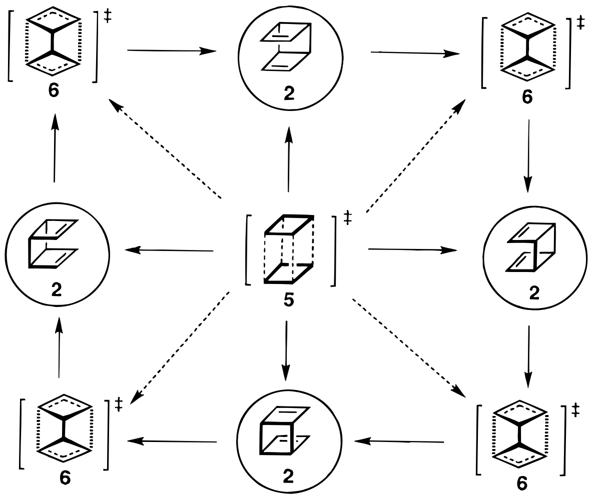

Figure 5. Modes of interconversion of stationary points on the potential energy surface in the syn dimer region.

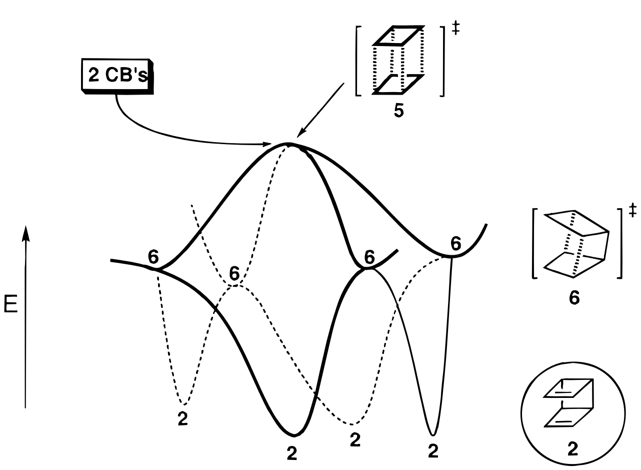

Figure 6. Potential surface features in the region of syn dimerization. Structure **5** has degenerate negative force constants, and the four Cope rearrangement transition structures (**6**) and four stable syn dimers (**2**) are all lower energy.

The high biradical character of cyclobutadiene itself permits facile formation of biradical intermediates. Formation of both singlet and triplet biradicals from two cyclobutadienes is very exothermic. For the eclipsed syn biradical, optimizations of the singlet state led to the syn tricyclic product **2**. The syn diradicals may be considered to be non-stationary points on the side of the hills in Figure 6. The corresponding eclipsed triplet biradical **8** is 7 kcal/mol higher in energy than the triplet biradical of anti conformation **9**. The eclipsed triplet diradical is 17 kcal/mol higher in energy than the concerted Cope rearrangement transition structure **6**, indicating that there are considerable bonding interactions in the transition structure of the Cope rearrangement. This is also found for the prototypical

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Cope rearrangement of 1,5-hexadiene, for which the boat-like transition structure is, depending upon the levels of theory, 2−13 kcal/mol lower in energy than two allyl radicals.[25]

In summary, our attempts to locate an asynchronous saddle point for the syn addition led either to the syn saddle point, **5**, or to the Cope transition structure **6**. The failure to locate either an asynchronous saddle point or a singlet biradical intermediate for the syn addition suggests that the syn dimerization is spontaneous without any reaction barrier when two cyclobutadienes approach each other in a staggered face-to-face orientation. The syn dimerization will have a negative activation energy and a small free energy of activation on the order of $0.04T$ kcal/mol due to the large negative entropy of activation. The reaction should be faster at low temperature than at high temperature. The anti dimerization can occur by an asynchronous pathway with a small activation energy. The syn preference for the dimerization can be overturned, however, by steric effects as in the case of tri-*tert*-butylcyclobutadiene dimerization.

Conclusion

These calculations predict that two cyclobutadienes will react with no potential energy barrier. The energy lowering upon interaction is greatest in a concerted syn geometry, but the passage through syn diradical geometries is also a highly stabilized pathway. To obtain more quantitative predictions about activation energies, quantum mechanical calculations which include dynamic correlation energy corrections beyond that in the active space (MR-CI or CASSCF-MP2) are necessary. This simple reaction proves to have a very interesting potential energy surface. Studies of the dynamics of motion[26] along this surface will be required to understand this reaction.

Acknowledgment. We thank Professors W. T. Borden and R. S. Berry for helpful discussions. We are grateful to the National Science Foundation for financial support and to the Office of Academic Computing at UCLA for computer resources.

Supporting Information Available: Absolute energies of all structures reported (1 page). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm edition of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

JA921663M

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