

# Cycloaddition Reactions between Cyclopentadiene and Ketene. Ab Initio Examination of [2 + 2] and [4 + 2] Pathways

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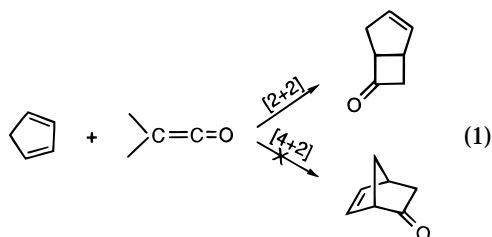
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The Diels–Alder [4 + 2] and Staudinger [2 + 2] reactions between ketene and cyclopentadiene were examined at the MP4/6-31G\*/MP2/6-31G\* and CCSD(T)/6-31G\*/MP2/6-31G\* levels. Both reactions are exothermic, 29 kcal mol<sup>-1</sup> (Diels–Alder) and 23 kcal mol<sup>-1</sup> (Staudinger). The activation energies are 31 kcal mol<sup>-1</sup> (Diels–Alder) and 20 kcal mol<sup>-1</sup> (Staudinger). The reaction is therefore kinetically controlled, consistent with experiments. The Diels–Alder reaction is concerted and synchronous, while the Staudinger reaction occurs in two stages, with partial formation of a C–C bond to the carbonyl carbon of ketene. The relative activation energies, regiocontrol, and mechanism are discussed in terms of frontier molecular orbital theory, natural population analysis, and topological electron density analysis.

## Introduction

Ketenes add to cyclopentadiene (CP) in a [2 + 2] fashion forming cyclobutanones (the Staudinger reaction) rather than in a [4 + 2] fashion leading to norbornenones (eq 1).<sup>1–3</sup> The outcome of the Staudinger reaction is in sharp contrast to that of the addition of alkenes to CP, which yields exclusively [4 + 2] (Diels–Alder) adducts. Otto and Huisgen<sup>1</sup> examined the Staudinger reaction between diphenylketene and various dienes with special attention to the possibility that small amounts of [4 + 2] product may have been overlooked in the early studies. No indication of any Diels–Alder adduct formation was found.



According to the Woodward–Hoffmann rules,<sup>2</sup> the preference of ketenes for the [2 + 2] over the [4 + 2] reaction pathway is due to the low lying C=O antibonding orbital. This orbital was assumed to stabilize the [ $\pi^2s + \pi^2a$ ] transition state by interacting with the  $\pi$ -system of the alkene component (Chart 1).

Ketene plus alkene<sup>3–9</sup> cycloadditions and the ketene dimerization<sup>10,11</sup> have been examined using theoretical methods. These investigations show unambiguously that [ $\pi^2s + \pi^2a$ ] structures as shown in Chart 1 are second-order saddle points. In agreement with experiment,<sup>12</sup> the proper transition state for the ketene dimerization is unsymmetrical and biradicaloid with partial charge separation (Chart 2). Formation of diketene and 1,3-cyclobutanedione via ketene dimerization occurs through concerted but not synchronous transition states.

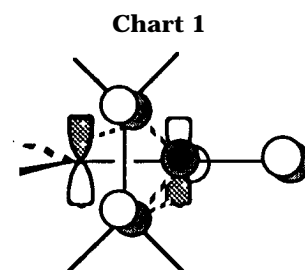
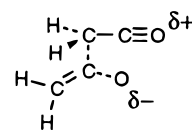


Chart 2



Since the [ $\pi^2s + \pi^2a$ ] pathway does not occur, it is still not clear why ketenes prefer the [2 + 2] over the [4 + 2] mechanism. Are Diels–Alder reactions disfavored or is the [2 + 2] pathway lowered in energy compared to cycloadditions involving alkenes? In the present study we employ high-level ab initio calculations to examine the reaction and activation energies for the Staudinger and Diels–Alder reactions between ketene and CP and compare the results to the parent Diels–Alder reaction between ethene and CP.

## Computational Method

Geometries of reactants, products, and transition states were optimized at the HF and MP2 levels of theory. The nature of the stationary points was characterized at the

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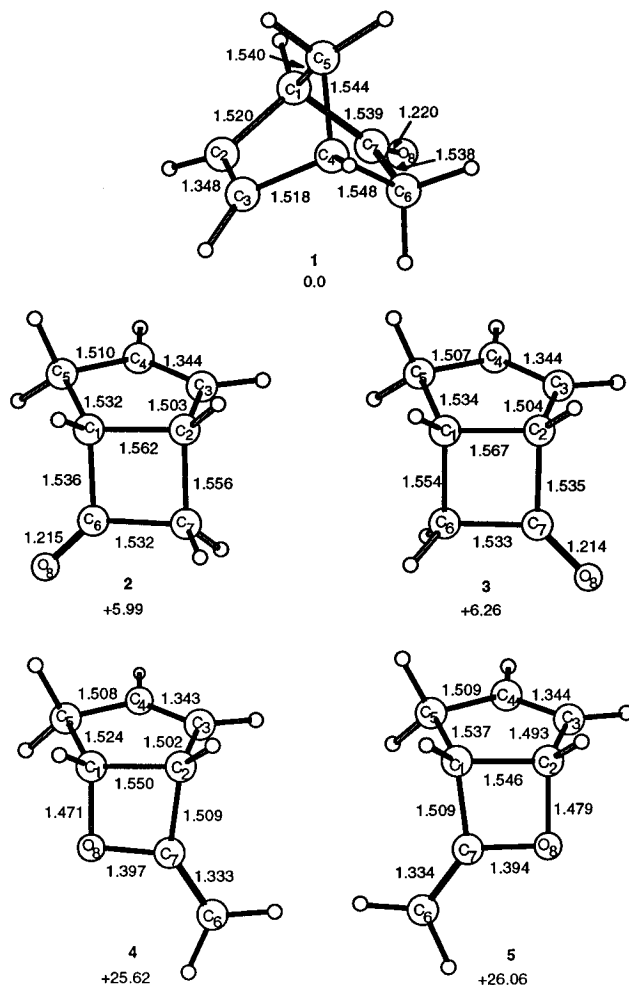
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HF level using analytical frequencies. All reactants and products are minima. All transition states were confirmed to have one and only one imaginary frequency. HF zero-point vibrational energies (ZPE) have been scaled by 0.89. Since transition states for the Staudinger reaction have considerable diradical character, we also computed the frequencies for structure **II** (Figure 2) at the MP2 level. Structure **II** proved to be a genuine transition state at both the HF and MP2 levels. To better account for the effects of electron correlation, reaction and activation energies were obtained at MP4SDQ using the MP2 geometries. The activation energies for the low-lying transition states **I**, **II**, and **X** were also evaluated at MP4SDTQ and CCSD(T), again using the MP2 geometries. The 6-31G\* basis set was used throughout. All calculations were performed using GAUSSIAN92.<sup>13</sup>

Some comments concerning the choice of methods employed are warranted. The [2 + 2] reaction may be biradical or biradicaloid in nature; perhaps a multiconfiguration wave function might be more appropriate than the single-reference methods we have used. We opted not to use a multiconfiguration method for a number of reasons. First, recent detailed studies of the Cope rearrangement<sup>14</sup> have shown that correlated wave functions built from a single configuration are in close agreement with the multireference MP2 results. On the other hand, CASSCF and MCSCF wave functions produce spurious biradicaloid TSs and intermediates. Second, we need to compare the [2 + 2] and [4 + 2] TSs on equal footing. This is nearly impossible employing CASSCF wave functions, since the [2 + 2] reaction requires (at least) a four-electron, four-orbital space while the [4 + 2] reaction requires a six-electron, six-orbital space.

The results we have obtained further justify this choice. The relative energies of the [2 + 2] and [4 + 2] TSs hardly change in going from MP4SDQ to CCSD(T), even though the latter accounts for considerably more nondynamical correlation energy than the former, indicating that more inclusive correlation treatments are unlikely to alter the energies significantly. Improvement of the treatment of nondynamical correlation effects (by, for example, using a multiconfiguration reference) would preferentially stabilize biradical (or biradicaloid) states, therefore lowering the energy of the [2+2] TS relative to the [4+2] TS. Since the single-reference methods indicate that the [2 + 2] TS is lower than the [4 + 2] TS, no qualitative change would result from going to a multiconfiguration reference. Finally, we have obtained the T1 diagnostic<sup>15</sup> for the CCSD wave function. The T1 diagnostic is 0.011 for the [4 + 2] TS and 0.026 for the [2 + 2] TS. This suggests that the [2 + 2] may be susceptible to problems, but keep in mind that we have actually used the CCSD(T) energy, and furthermore, the multiconfiguration approach will favor the [2 + 2] TS, which we already find is the lowest-energy pathway.

Electronic structures of ground and transition states were analyzed with Bader's topological analysis<sup>16</sup> and



**Figure 1.** Products of Diels–Alder and Staudinger reactions between cyclopentadiene and ketene. Reaction energies (kcal mol<sup>-1</sup>) are given at MP4SDQ/6-31G\*/MP2/6-31G\*+ZPE.

with the NBO method.<sup>17–19</sup> Charge densities at bond critical points were obtained employing a locally modified version of EXTREM.<sup>20</sup> Bond orders  $n$  were calculated using the empirical relationship in eq 2,<sup>21</sup> where  $\rho$  is the value of the electron density at the bond critical point.

$$n(X-Y) = \exp[6.458[\rho(\mathbf{r}_c) - 0.252]] \quad (2)$$

## Results

**Products.** The structures of the product of the Diels–Alder reaction (**1**) between ketene and CP and four [2 + 2] addition products (**2–5**) are depicted in Figure 1. Reaction energies at various levels of theory are summarized in Table 1. All five reactions are exothermic. Lactone formation, however, is very unfavorable compared to cyclobutanone and norbornenone formation. As expected for the six-membered ring products compared to the strained four-membered ring products, the Diels–

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**Table 1. Reaction Energies (kcal mol<sup>-1</sup>) for the Products of the Diels–Alder Reaction (1) and the Staudinger Reaction (2–5) between Cyclopentadiene and Ketene<sup>a</sup>**

	HF	MP2	MP4SDQ	ZPE
<b>1</b>	-28.36	-37.49	-34.93	5.80
<b>2</b>	-23.10	-28.86	-28.02	4.98
<b>3</b>	-22.92	-28.56	-27.70	4.95
<b>4</b>	-3.42	-8.21	-8.38	4.98
<b>5</b>	-3.04	-7.87	-8.01	5.66

<sup>a</sup> Relative ZPEs are scaled by 0.89.<sup>23</sup>

Alder product **1** is lower in energy than the [2 + 2] products **2** and **3**. At MP4SDQ/6-31G\*//MP2/6-31G\*+ZPE the product of the Staudinger reaction (**2**) is 6 kcal mol<sup>-1</sup> higher in energy than the Diels–Alder adduct **1**. A second [2 + 2] regioisomer (**3**) lies only 0.3 kcal mol<sup>-1</sup> higher than **2**. Thermodynamic control thus favors the Diels–Alder reaction.

**Transition States.** The transition states for the Diels–Alder reaction (**I**) and the [2 + 2] additions between CP and ketene (**II**–**IX**) are drawn in Figure 2. Activation energies at HF through CCSD(T) are summarized in Table 2. Transition state **II**, which leads to **2**, the Staudinger reaction product, is lowest in energy. At MP4SDQ+ZPE, transition state **III**, which also yields **2**, lies 7 kcal mol<sup>-1</sup> higher in energy than **II**. The transition state for the Diels–Alder reaction (**I**) is 11 kcal mol<sup>-1</sup> higher in energy than **II**. Transition state **VI**, which leads to isomer **3**, is 12 kcal mol<sup>-1</sup> higher in energy than **II**. All the remaining transition states are even less favorable. (We were not able to obtain an MP2 structure for isomer **V**. MP2 optimization starting with the HF geometry led to the Diels–Alder product. This might be an artifact of the MP2 potential energy surface since MP2 considerably underestimates activation energies of Diels–Alder reactions.<sup>22</sup> Since **V** is almost 15 kcal mol<sup>-1</sup> higher in energy than **II** at HF, we did not pursue that pathway any further.)

Since the electronic structures of [2 + 2] and [4 + 2] transition states are quite different, energies of the three low-lying transition states **I**, **II**, and **X** were reevaluated at MP4SDQ and CCSD(T). Although the activation energies drop by 5–6 kcal mol<sup>-1</sup> upon improving the theoretical level, the relative activation energies are hardly changed. At the CCSD(T) level, there is a kinetic preference of 12 kcal mol<sup>-1</sup> for the formation of **2**, the exclusive product of the Staudinger reaction, over formation of **1**, the Diels–Alder adduct. Since the reactions are exothermic, back reactions require considerably higher activation energies and are unlikely to occur. Product formation thus underlies kinetic control. In agreement with experiment, **2** is the only product expected to form.

Since the transition states of the [2 + 2] additions have open structures with only one new bond between the CP and the ketene fragments, there are four possible approaches involving initial bond formation between alternatively C1 or C2 of CP and either the alkene or the

carbonyl carbon of ketene. Comparison of the energies of **II** with **VII** and **III** with **VI** indicates that initial bond formation at C1 of CP is more favorable than reaction at C2. This is most likely due to stabilization of the transition structure by formation of an allylic system involving C2, C3, and C4 when CP reacts at C1. Stronger bond alternation in **VI** and **VII** as compared to **II** and **III** confirms that there is less conjugation when CP reacts at C2. **II** is lower in energy than **III** due most likely to a sterically more favorable orientation of the ketene fragment.

Comparison between structures **II** and **IX** shows that the activation energy is much lower when ketene reacts at the carbonyl carbon rather than at the alkene carbon. Again, regioselection is likely to be due to the allylic stabilization within the ketene fragment of **II**. The activation energy for the [2 + 2] reaction of CP with ethene (transition state **XI**) is more than twice as large as for the reaction of CP with ketene.

The activation energy for [4 + 2] addition between CP and ketene (through TS **I**) is 12 kcal mol<sup>-1</sup> higher than that for the Diels–Alder reaction between CP and ethene (through TS **X**). The geometries of **I** and **X** (see Figure 2), however, are virtually identical. The differences in bond lengths in the unsymmetrical transition state **I** are very small. The CP fragment is almost symmetrical with breaking C=C bond lengths of 1.395 and 1.396 Å and C–C bond lengths to the bridging carbon of 1.503 and 1.506 Å. The C–C forming bonds differ by 0.09 Å, the bond to the carbonyl carbon of ketene being shorter than the one to the alkene carbon.

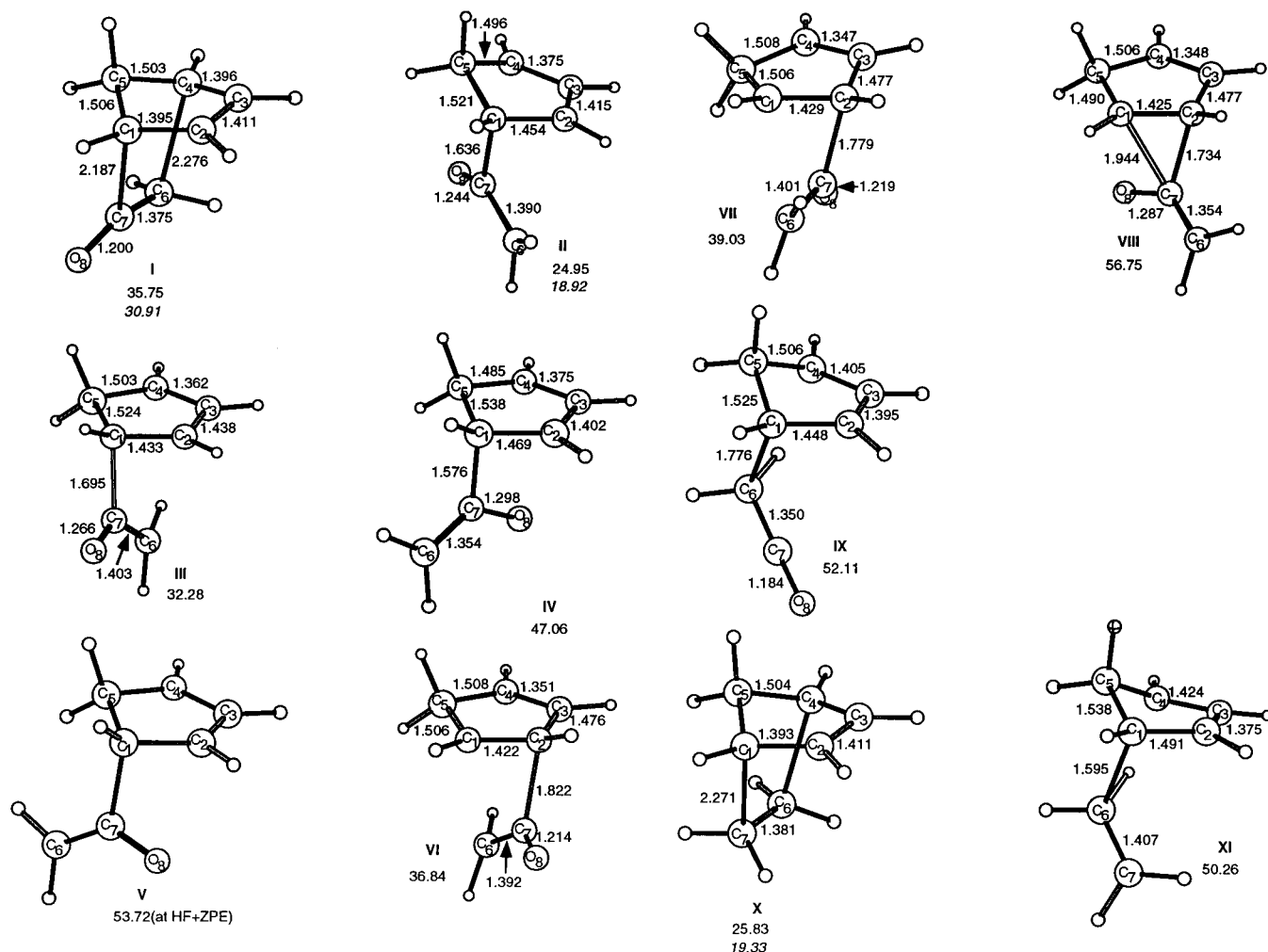
The NPA charges<sup>17–19</sup> and bond orders<sup>21</sup> according to eq 2 for transition states **I**, **II**, and **X** are compared in Figure 3. There is no net charge transfer between the alkene or ketene and the CP fragment in **I** and **X**. The ketene fragment, however, induces slight charge alternation in the CP fragment. The bond orders are very similar in **I** and **X**. Only the double-bond character of the C–C bond is higher in the alkene fragment than in the ketene fragment. One has to keep in mind, however, that the C=C bond in free ketene has a bond order of only 1.64 while the bond order of ethene is 2 by definition. The bond orders of the forming C–C bonds between the CP and ketene fragments in **I** differ only slightly. Both Diels–Alder reactions transition states **I** and **X** appear to be concerted and synchronous.

Transition state **II** for the Staudinger reaction is distinctly different from **I** and **X**. Most important is that in **II**, the ketene fragment approaches CP in a plane perpendicular to that in the Diels–Alder reaction. Only one C–C bond is forming between the ketene carbonyl carbon and C1 of CP. There is no bond between the alkene carbon of ketene and C2 of CP according to NBO and Bader analyses. The forming bond between C1 and ketene is 0.45 Å shorter than the corresponding bond in **I**. The C=O bond is 0.04 Å longer in **II** than in **I**. NBO analysis indicates that in **I** a C=O double bond is present, whereas in **II** only a C–O single bond was found. The C=O thus appears to be involved in forming **II**, while the reaction takes place exclusively at the C=C when forming **I**.

The symmetry of the cyclopentadiene fragment is strongly distorted in **II**. The double bond between C1 and C2 is almost gone (bond length of 1.454 Å and bond order of 1.38); the double bond between C3 and C4 is stretched but still intact (bond length of 1.375 Å and bond order of 1.89). The bond between C2 and C3 is short,

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**Figure 2.** Transition states for Diels–Alder and Staudinger reactions between cyclopentadiene and ethene and between cyclopentadiene and ketene. Activation energies ( $\text{kcal mol}^{-1}$ ) are given at MP4SDQ/6-31G\*\*/MP2/6-31G\*+ZPE and at CCSD(T)/6-31G\*\*/MP2/6-31G\* in italics.

**Table 2.** Activation Energies ( $\text{kcal mol}^{-1}$ ) for the [4 + 2] (I) and [2 + 2] (II–IX) Reactions between CP and Ketene and for the [4 + 2] (X) and [2 + 2] (XI) Reactions between CP and Ethene<sup>a</sup>

	HF	MP2	MP4SDQ	MP4SDTQ	CCSD(T)	ZPE
<b>I</b>	51.10	22.95	34.01	26.63	29.17	1.74
<b>II</b>	36.85	14.85	22.26	14.80	16.23	2.69
<b>III</b>	43.66	23.23	29.89			2.39
<b>IV</b>	48.93	42.04	44.70			2.36
<b>V</b>	51.60					2.12
<b>VI</b>	49.11	27.62	34.44			2.40
<b>VII</b>	50.18	28.32	36.67			2.36
<b>VIII</b>	62.68	51.22	55.29			1.46
<b>IX</b>	69.00	37.11	50.37			1.74
<b>X</b>	39.66	11.80	23.52	17.01	17.60	2.31
<b>XI</b>	76.27	36.84	50.10			0.16

<sup>a</sup> Relative ZPEs are scaled by 0.89.<sup>23</sup>

1.415 Å, and has bond order of 1.45. These data suggest that there is an allylic system present in **II** involving C2, C3, and C4. Analysis of the NPA charges shows that there is a net charge transfer from the CP fragment to the ketene fragment of 0.4 electron. Transition state **II** is thus biradicaloid with partial charge separation.

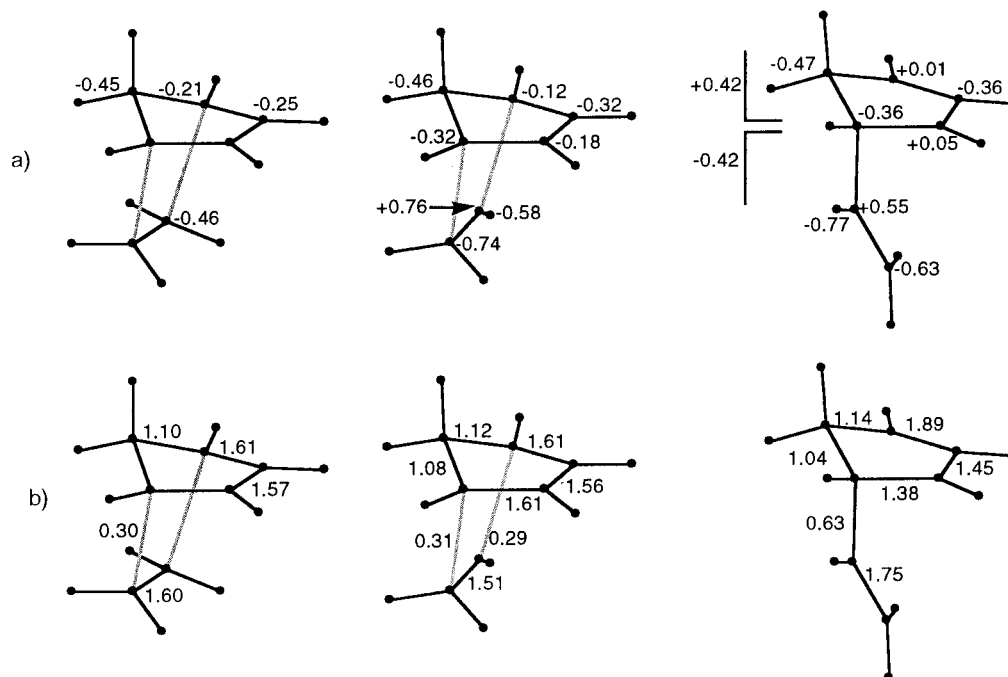
### Discussion

In agreement with experiment,<sup>1–3</sup> our calculations indicate that the exclusive product of the cycloaddition

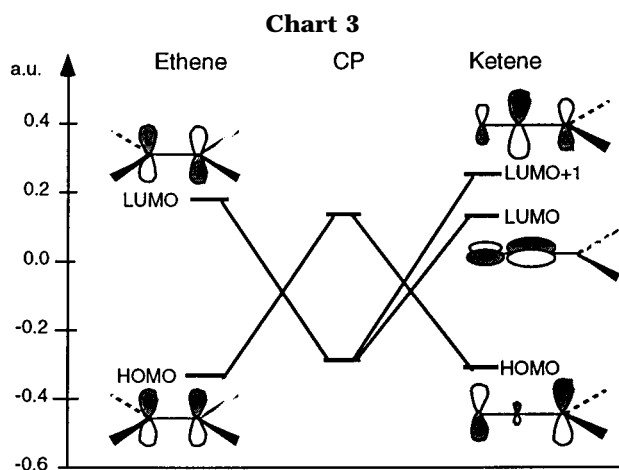
between CP and ketene is **2**, the product of a [2 + 2] rather than a [4 + 2] addition. The product formation is under kinetic control and yields the thermodynamically less favorable cyclobutanone **2**. Although a reaction pathway for a [4 + 2] reaction exists and although the transition state is virtually identical to that of the parent Diels–Alder reaction, the activation energy involving ketene is 12  $\text{kcal mol}^{-1}$  higher. Why is that so?

Using HF/6-31G\* orbital energies, the HOMO(CP)–LUMO(ethene) gap for the parent Diels–Alder reaction is 18  $\text{kcal mol}^{-1}$  smaller than the LUMO(CP)–HOMO(ethene) gap. The former is thus the dominant interaction. The HOMO of ketene is about 10  $\text{kcal mol}^{-1}$  higher than that of ethene, and the LUMO of ketene is 25  $\text{kcal mol}^{-1}$  lower than that of ethene. The dominant interaction, HOMO(CP)–LUMO(ketene), is thus 25  $\text{kcal mol}^{-1}$  smaller involving ketene than that involving ethene. The LUMO of ketene, however, is not  $\pi^*_{\text{C}=\text{C}}$  as in ethene but is  $\pi^*_{\text{C}=\text{O}}$ , which is perpendicular to  $\pi_{\text{C}=\text{C}}$  (see Chart 3). The ketene orbital that corresponds to  $\pi^*_{\text{C}=\text{C}}$  in ethene is LUMO+1. The gap between HOMO(CP) and LUMO+1(ketene) is about 35  $\text{kcal mol}^{-1}$  larger than the corresponding gap involving ethene (Chart 3). The LUMO(CP)–HOMO(ketene) gap is actually smaller than the HOMO(CP)–LUMO+1(ketene) gap.

There are thus two alternatives for ketene to react. Either it employs the LUMO+1 and adopts the same



**Figure 3.** NPA charges (a) and bond orders (b) according to eq 2 for the transition states for the Diels–Alder reaction between cyclopentadiene and ethene and for Diels–Alder and Staudinger reactions between cyclopentadiene and ketene.



approach as in the Diels–Alder reaction of CP + ethene or ketene employs its low-lying LUMO and approaches CP in a perpendicular plane. Transition state **I** corresponds to the former alternative. The higher activation energy for a concerted Diels–Alder reaction involving ketene as compared to ethene can thus be rationalized in terms of frontier orbital control by the larger HOMO(CP)–LUMO+1(ketene) gap as compared to the HOMO(CP)–LUMO(ethene) gap.

A perpendicular approach to a hypothetical Diels–Alder addition employing the LUMO would lead to a transition state in which one of the hydrogens of the ketene fragment points in the direction of the forming C–C bond. In such an approach two C–C bonds can thus not form synchronously. We tried to optimize a transition state for such an approach and found **III**, which rather yields **2** in a [2 + 2] addition. The lowest-energy transition state, however, is **II**, which orients its LUMO, relative to cyclopentadiene, in the same fashion as **III** but is sterically more favorable since the CH<sub>2</sub> group points away from the ring. Involvement of the LUMO of ketene thus automatically yields [2 + 2] products for steric reasons.

Diels–Alder and Staudinger reactions result when ketene employs alternatively the C=C or the C=O bond for bond formation with CP. In the Diels–Alder reaction, the C=C reacts and the carbonyl bond does not participate. In the Staudinger reaction, the carbonyl reacts but NBO analysis indicates that there is a donor–acceptor interaction present between the alkene carbon of ketene and C2 of CP where the ketene C=C donates some electron density to the C2  $\pi$ -orbital. This donor–acceptor interaction is, however, not strong enough to break C=C or to form a bond to C2, as indicated by the lack of a bond critical point between C2 and ketene according to Bader analysis. Analysis of the orbitals of free ketene shows that this mechanism is indeed quite plausible. The ketene oxygen has a lone pair which is parallel to the C=C bond and perpendicular to the C=O bond. This lone pair conjugates with the C=C bond leading to some triple bond character of the C=O bond and thereby weakening the C=C bond as indicated by the C=C bond order of 1.64. In the [2 + 2] addition reaction the C=O bond breaks in the first stage and negative charge is accommodated by the electronegative oxygen atom. In the second stage the C=C bond breaks leaving the  $\pi$ -orbital at the carbonyl carbon which is already parallel and conjugating with the oxygen lone pair. Without any movement or rehybridization, the C=O bond can be reestablished. Note that this C=O bond will be perpendicular to the original C=O bond. We see that there is no need for the carbonyl carbon to react at the perpendicular C=O and C=C  $\pi$ -systems at the same time as required for the [ $\pi^2s + \pi^2a$ ] pathway. The [2 + 2] reaction of CP and ethene has an activation barrier much higher than for the reaction with ketene due to the lack of the donor–acceptor interaction that is stabilized by the electronegative oxygen.

## Conclusions

In agreement with experiment, our theoretical results indicate that the exclusive product of the cycloaddition

between cyclopentadiene and ketene is the cyclobutanone **2**. Product formation occurs under kinetic control. The Diels–Alder adduct **1** is thermodynamically favored.

In terms of frontier orbital control, the [4 + 2] (Diels–Alder) pathway involves interaction between HOMO(CP) and LUMO+1(ketene). The [2 + 2] (Staudinger) pathway involves interaction between HOMO(CP) and LUMO(ketene). Since the LUMO of ketene is 60 kcal mol<sup>-1</sup> lower in energy than the LUMO+1, the [2 + 2] pathway is favored.

The activation energy for the Diels–Alder reaction between CP and ketene not only is 12 kcal mol<sup>-1</sup> less favorable than for the Staudinger reaction but also is disfavored compared to the parent Diels–Alder reaction (CP + ethene). Although transition states involving CP with either ketene or ethene are very similar, the activation energy is 11 kcal mol<sup>-1</sup> higher with ketene than with ethene. This can be rationalized in terms of frontier orbital control since  $\pi^*_{C=C}$ (ketene) is 35 kcal mol<sup>-1</sup> higher in energy than  $\pi^*_{C=C}$ (ethene).

The LUMO of ketene is essentially  $\pi^*_{C=O}$  which is perpendicular to  $\pi^*_{C=C}$ . In the Staudinger reaction, ketene approaches CP in a plane perpendicular to that in the Diels–Alder reaction. Only a weak interaction between  $\pi^*_{C=C}$  and CP is present in the transition state. Since one hydrogen points toward the CP ring in this approach, synchronous bond formation is not possible. The transition state is asynchronous and biradicaloid with partial charge separation and does not correspond to the [ $\pi^2_s + \pi^2_a$ ] mechanism proposed by Woodward and Hoffman.

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