five-membered ring, are not required to ensure a singlet ground state for dialkyl derivatives of **2**.

Acknowledgment. We thank the National Science Foundation for support of this research and for a grant, which made possible the purchase of the Convex C-2 computer, on which many of these calculations were performed. Some of these calculations were carried out at the San Diego Supercomputer Center, which we thank for a generous grant of time on the Cray XMP-48. This study was initiated while W.T.B. was a Visiting Scientist at IMS and being supported by a fellowship from the Japanese Society for Promotion of Science. W.T.B. expresses his gratitude to JSPS and to the Computer Center at IMS for use of the HITAC M-680H and S-820/80 Computers.

Registry No. 2, 102265-42-9; **3**, 17805-06-0.

Carbenoid Character in Transition Structures for Reactions of Ketenes with Alkenes

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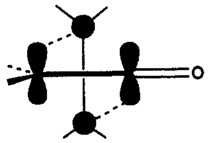
Abstract: The reactions of ketene and methylketene with ethylene and of ketene with propene were studied with ab initio molecular orbital calculations, with the STO-3G, 3-21G, and 6-31G* basis sets and correlation energy corrections at the MP2 level. The cycloadditions proceed via geometries that indicate that the reaction is of the 2 + 2 + 2 type, rather than a [$_\pi 2_s$ + $_\pi 2_a$] cycloaddition. It is a quasi-pericyclic reaction, like carbene cycloadditions and hydroborations, with appreciable interaction of carbon ketene central carbon with both termini of the alkene. Bond formation is very asynchronous, with bond lengths of 1.78 and 2.43 Å. There is appreciable charge separation in the transition structure. The stereochemical preferences of the methylketene and propene reactions are consistent with experimental results on related substituted cases.

Cycloadditions of ketenes to alkenes to form cyclobutanones have been known for most of this century[1] and are probably the most complex and intriguing of the reactions classified by Woodward and Hoffmann as pericyclic.[2] The electronic interactions and geometry of the transition state have been the subject of much speculation.[3] The mechanism of the reaction is considered to be either concerted[4,5] or stepwise,[5] depending upon the electronic character and bulkiness of the ketene and alkene substituents.[4-9] Unsymmetrical ketenes add to cyclic alkenes to give the sterically more hindered product.[4,5] Ketenes add [2 + 2] even when allowed [4 + 2] possibilities appear attractive, as for example with cyclopentadiene.[5a]

Woodward and Hoffmann speculated about a variety of electronic interactions.[10] They considered the possibility that the reaction was a concerted $_\pi 2_s$ + $_\pi 2_a$ cycloaddition, suprafacial on the alkene and antarafacial on the ketene because of the low steric hindrance of the "sideways" approach shown in **A**. They also emphasized that the carbonyl group LUMO is the "spearhead of reactivity".[2] Thus, the additional interaction shown in **B** could occur. Gompper proposed that the interaction of the ketene LUMO occurs unsymmetrically on the alkene HOMO, leading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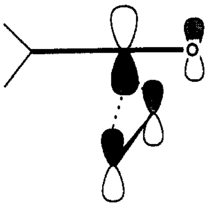
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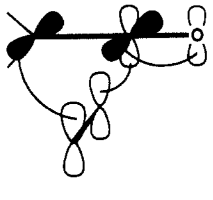
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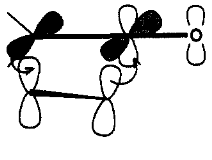
D

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Table I. Bond Lengths (Å), Angles (deg), and Activation Energies (kcal/mol) for the Transition Structures of the Cycloaddition of Ketene with Ethylene

basis set	C_1–C_2	C_4–C_5	C_2–C_4	C_2–C_5	C_1–C_5	C_2–O_3	∠OCC	E_a
RHF/STO-3G	1.388	1.386	1.889	2.214	2.325	1.203	141.3	55.2
RHF/3-21G	1.375	1.402	1.827	2.182	2.372	1.203	139.5	50.2
RHF/6-31G*	1.368	1.369	1.756	2.049	2.441	1.200	137.2	46.6
MP2/6-31G*	1.394	1.400	1.776	2.083	2.433	1.216	137.3	26.7
MP2/6-31G*//RHF/6-31G*								26.9
expt[a]								32.0

[a] From activation energy of pyrolysis of cyclobutanone and heats of formation of reactant and products: Das, M. N.; Kern, F.; Coyle, T. D.; Walters, W. D. *J. Am. Chem. Soc.* **1954**, *76*, 6271. McGee, T. H.; Schleifer, A. *J. Phys. Chem.* **1972**, *76*, 963.

to a zwitterionic species in cases involving electron-rich alkenes. These interactions can be combined to give a [2 + 2 + 2] reaction implied by the arrows in **C**.[10] Others emphasized the ketene π_{CC}-alkene π^*-interaction, leading to the overall "push–pull" interaction suggested by **D**, in which the alkene interacts simultaneously with the nucleophilic π_{CC} of the ketene and the electrophilic π^*_{CO} at the same time.[3b]

Burke carried out a study of this reaction with ab initio minimal basis set calculations, including a small configuration interaction correction for correlation energy contributions.[11a] Burke's extensive study was performed before gradient optimizations were available, so that a saddle point was not located accurately. Burke excluded the existence of a zwitterionic form as a stable intermediate for the parent reaction, and the antarafacial approach ($_\pi2_s$ + $_\pi2_a$) was found to be preferred to the suprafacial ($_\pi2_s$ + $_\pi2_s$) by at least 10 kcal/mol. The reaction mechanism was described as a nonsynchronous concerted antarafacial process with a certain amount of charge separation.[11a,b] Bernardi et al. have described MCSCF calculations on a symmetrical geometry like **A**; this is not a transition structure, since it has two negative force constants.[11c]

We have located the stationary points on the potential energy surface of the parent reaction with the ab initio SCF energy gradient method with STO-3G, 3-21G, and 6-31G* basis sets.[12] The stationary points located at the STO-3G or 3-21G level each had only one imaginary vibrational frequency, corresponding to motion along the reaction coordinate. The transition structure was also located at a correlated level, with the use of the 6-31G* basis set and MP2 correlation energy corrections with full geometry optimizations. The potential surface was explored extensively, but only this saddle point was found. The transition structure for the parent reaction is shown in Figure 1, and some important geometrical parameters and calculated energetics are given in Table I.

The trends in calculated activation energies at various levels are similar to those found for several pericyclic reactions.[13,14] The single bond between the central ketene carbon and one carbon of ethylene is almost fully formed (1.78 Å). The other incipient carbon–carbon bond, between methylene carbon of ketene and the remaining ethylene carbon, is much longer (2.43 Å). This latter carbon is in fact much closer to the central ketene carbon in the transition state (2.08 Å) than to the carbon to which it will be bonded in the product. These features were anticipated by Gompper.[4f] The ketene molecule remains almost planar, which is another indication of the small degree of bonding at CH_2 of the ketene.

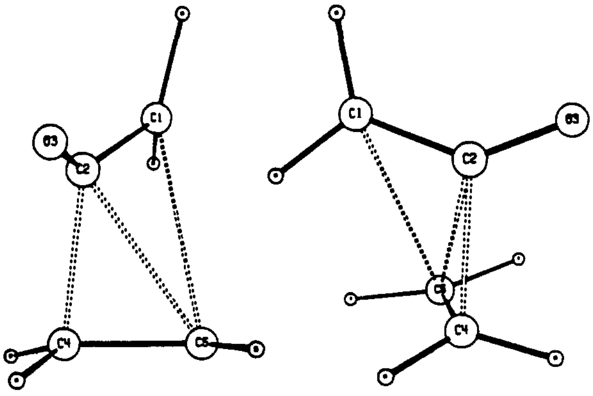

Figure 1. Transition structure for the reaction of ketene with ethylene at the MP2/6-31G* level.

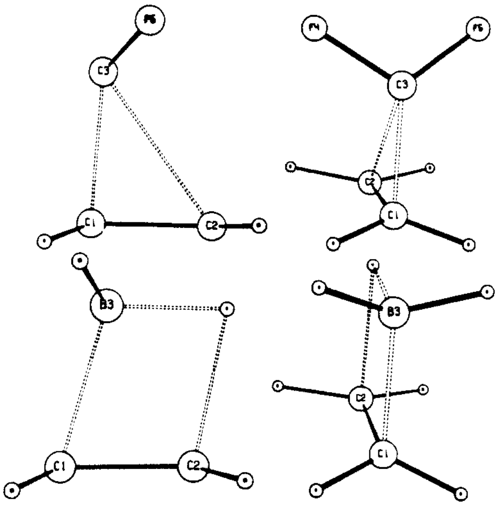

Figure 2. Two views of transition structures for the reactions of CF_2 (top) and BH_3 (bottom) with ethylene (RHF/3-21G).[15,16]

The central carbon atom of the ketene uses the $\pi_{C=O^*}$ orbital for electrophilic interaction and the $\pi_{C=C}$ orbital for nucleophilic interaction with the olefin. The transition structure is similar to those of carbene cycloadditions to alkenes and of hydroborations (Figure 2), where the vacant p orbital of carbon or boron accepts electrons from alkene and the carbene lone pair or borane BH bond donates electrons to the alkenes.[15,16] These comparisons emphasize the importance of the orthogonal donor and acceptor orbitals in influencing transition structures of reactions of this type.[17] In the ketene cycloaddition, the strong interaction of the ketene HOMO at both C_1 and C_2 enforces the nearly perpendicular approach of ketenes to alkenes. The same factors are likely to influence other four-center reactions such as those involving transition-metal carbenoids in olefin metathesis reactions.[18] This bridging interaction also explains why 1,2-addition is always favored over 1,4, since the ketene terminus is in position to close

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Table II. Bond Lengths (Å), Angles (deg), and Activation Energies (kcal/mol) of the Transition Structures for the Reactions of Methylketene with Ethylene and for Ketene with Propene at the RHF/3-21G Level

TS	C_1–C_2	C_4–C_5	C_2–C_4	C_2–C_5	C_1–C_5	C_2–O_3	C–C_6	∠OCC	∠CCC	E_a
1	1.370	1.399	1.810	2.152	2.428	1.212	1.508	137.8	120.0	46.9
2	1.375	1.400	1.816	2.125	2.421	1.212	1.510	136.7	129.1	54.1
3	1.371	1.407	1.792	2.204	2.428	1.209	1.499	138.6	125.2	50.2
4	1.374	1.403	1.815	2.160	2.376	1.208	1.518	138.5	120.7	52.2
5	1.367	1.415	1.747	2.142	2.460	1.222	1.496	136.9	120.0	45.3
6	1.372	1.405	1.804	2.148	2.391	1.210	1.519	138.4	120.1	49.8

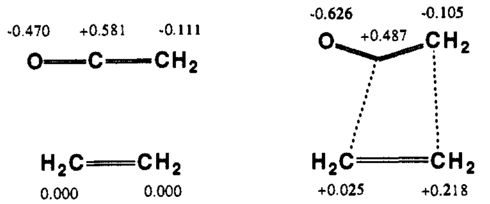

Figure 3. Mulliken charges (MP2/6-31G*) for reactants and transition structure. Atomic charges of hydrogens are added into those of the attached heavy atom.

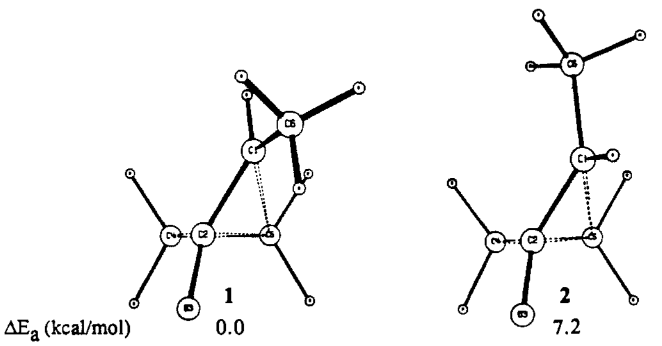

Figure 4. Transition structures for the reactions of methylketene with ethylene at the RHF/3-21G level.

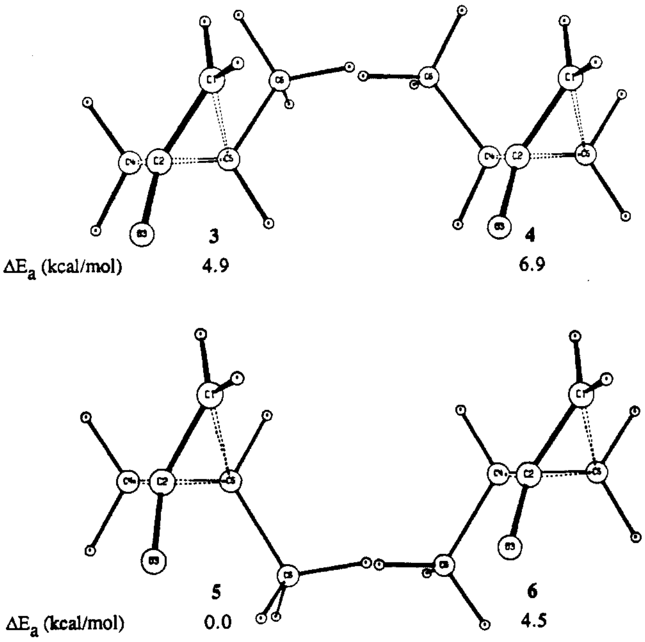

Figure 5. Transition structures for the reactions of ketene with propene at the RHF/3-21G level.

1,2, but cannot close 1,4, even on an *s-cis*-diene, from this geometry.

A Mulliken population analysis[13] at the MP2/6-31G* level (Figure 3) shows that the CH_2 terminal of ethylene becomes more positively charged ($\Delta q = +0.22$) in the transition state relative to the reactants. The oxygen atom shares more electrons ($\Delta q = -0.16$) in the transition state as does the central carbon atom of ketene ($\Delta q = -0.10$). The charges on both the terminal CH_2 of ketene and the central CH_2 on ethylene remain almost constant throughout the reaction pathway. Increased charge separation in the transition state is supported by various experimental observations.[6-9] A measure of this charge separation is provided by the calculated transition-structure dipole moment of 4.9 D.

We have located two transition structures for the reaction of methylketene with ethylene and four transition structures for the reaction of ketene with propene. These transition structures, located at the RHF/3-21G level, are shown in Figures 4 and 5 along with their relative energies. The bond lengths and bond angles around the reaction center and the absolute activation energies are summarized in Table II.

For the reaction of methylketene with ethylene, the difference in activation energy between the two modes of addition is calculated to be 7.2 kcal/mol. Preferred transition state **1** has smaller steric interactions between the methyl group and the terminal ethylene CH_2 group. It may also be stabilized slightly by the electrostatic attraction between the methyl group and the oxygen atom. As a result of both of these factors, the $C_6C_1C_2$ angle in **1** (120°) remains like that in methylketene, while in **2** it is distorted to 129°. The observed preferential formation of the more crowded product[3,4] in reaction with *cis*-alkenes is accounted for by these results.

For the reaction of ketene with propene, four transition structures are possible. Transition structure **5** is the most stable one. It places the methyl on the ethylene carbon that bears substantial positive charge and in the sterically least crowded and electrostatically favored position. The energy differences between these four structures mainly result from the following three effects: (1) preferential placement of the methyl substituent on carbon that bears a partial positive charge (C_5), (2) minimization of unfavorable steric interaction between the ketene CH_2 and the methyl substituent, and (3) electrostatic attraction between the methyl group and the oxygen atom of ketene. It is interesting to note that **3** and **5** are more ionic than **4** and **6** as measured by the shorter C_2–C_4 bonds, longer C_2–C_5 bonds, and shorter C–C_6 bonds in the former than in the latter. If we assume that the energetic effects of methyl substitution pictured in Figure 5 are additive, the activation energy for the reaction of ketene with *trans*-butene can be estimated to be 2.4 kcal/mol greater than the corresponding reaction with *cis*-butene. Therefore, our calculations not only reproduce the experimentally observed regiochemistry but also explain the enhanced reactivity of *cis*-alkenes over *trans*-alkenes.[3,5]

Acknowledgment. We are grateful to the National Science Foundation and the National Institutes of Health for financial support of this research, the UCLA Computing Center and Pittsburgh Supercomputer Center for computer time, and Professors Barry M. Trost, William L. Jorgensen, and Donald H. Aue and Scott Wierschke for stimulating comments.

Registry No. CF_2, 2154-59-8; BH_3, 13283-31-3; *trans*-butene, 624-64-6; *cis*-butene, 590-18-1; ketene, 463-51-4; ethylene, 74-85-1; methylketene, 6004-44-0; propene, 115-07-1.

Supplementary Material Available: Internal coordinates and total energies of optimized transition structures (3 pages). Ordering information is given on any current masthead page.