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Theoretical Study of (2 + 2) Cycloadditions. Ketene with Ethylene

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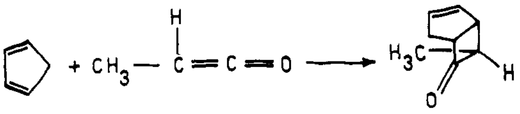
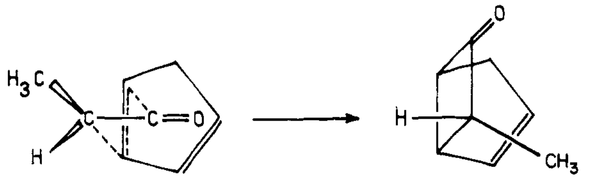
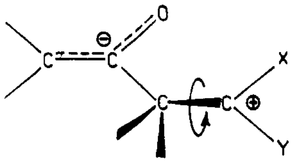
Ab initio, minimal basis set calculations including an interaction of 55 configurations for the cycloaddition of ketene to ethylene indicate a transition state where a single bond is almost formed (1.7Å) between the central C atom of ketene and ethylene. However, there is slight bonding between the terminal CH_2 groups; the rotation of the CH_2 group on ethylene near the transition state requires about 12 kcal/mol. The reaction mechanism can be called a nonsyncronous, concerted one with charge separation as measured by a Mullikin population analysis. The ketene is seen to add in an antarafacial-like way rather than suprafacially. The origin of this preference can be seen from maps of electrostatic potential about ketene. The 2s + 2s approach does not seem to be symmetry forbidden since the SCF ground-state configuration contributes predominantly throughout the pathway, contrary to what one would expect with molecular orbital crossing in symmetry forbidden paths.

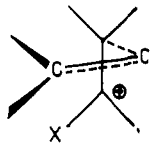
The thermal reaction of ketenes with olefins to form cyclobutanones is a particular case of $(2\pi + 2\pi)$ cycloadditions.[1] It is one of the few cases where the stereochemistry of the adducts is that predicted for the thermally allowed concerted $(2\pi_s + 2\pi_a)$ cycloaddition.[2] The thermal addition of methylketene to cyclopentadiene,[3] for example, gives the more crowded endo position in the adduct in a ratio of 98 to 2 for the exo position.[4-6] This gives support to the supposition that ketenes add as antarafacial partners to suprafacial olefins. In this case the larger of the ketene substituents would point away from the olefin during the addition.





Since a zwitterionic intermediate would probably exist long enough to give a mixture of endo and exo products, its existence is not likely when the ketene substituents are not too bulky to permit an antarafacial approach. This does not mean that there is no charge separation along the reaction pathway. Evidence for such a transition state has been obtained from various experiments which show a linear Hammett plot,[7] a small rate enhancement in more polar solvents,[8] and a small isotope effect.[9] Also, the charge separation can account for the attachment of the central ketene carbon to an outer carbon of a diene rather than to an inner one.



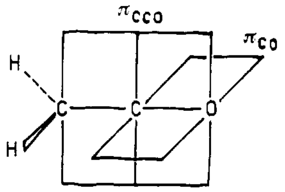


A mechanistic continuum is thus possible for ketene–olefin cycloadditions where the extremes are a one-step (synchronous) concerted $(2\pi_s + 2\pi_a)$ path and a two-step path through a stable zwitterionic intermediate. This continuum is explored here for the ketene–ethylene reaction with an all-electron molecular orbital theory implemented by configuration interaction (CI). In addition, the $(2\pi_s + 2\pi_a)$ approach as well as several initial points on the two-step approach are studied by localized molecular orbitals (LMO) obtained by the Boys method.[10] Maps of electrostatic potential are also made for ketene. One might explain the favorability of one approach over others using this index.

Methods

The RHF-SCF-LCAO-MO method augmented by the interaction of 55 configurations has been used to calculate points on the potential energy hypersurface. The SCF part was performed with the GAUSSIAN-70 series of computer programs[11] and the minimal basis set of three contracted gaussian functions per AO; STO-3G[12] was chosen due to the number of points to be calculated. Three points on the reaction surface were recalculated with the 6-31G basis set and fourth-order Moller-Plesset perturbation found in the GAUSSIAN-82 series.[11b]

For each point, the (55 × 55) CI included all configurations derived from the mono- and diexcitations from those MO's which correlate with the occupied ketene $2\pi_{CC,O}$ and $1\pi_{CO}$ MO's as well as the ethylene $1\pi_{CC}$ MO to the respective $3\pi_{CCO}$, $2\pi_{CO}$, and $2\pi_{CC}$ virtual MO's.



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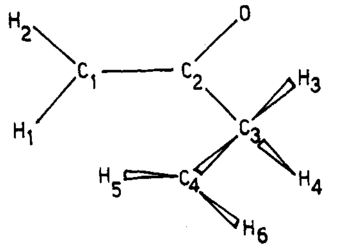

Figure 1. Geometric parameters.

A localization[13] of the SCF ground-state configuration canonical MO's can be reasonably performed when this configuration predominates in the CI expansion. In the Boys localization method a unitary transformation maximizes the sum of the squares of the orbital centroid distances from an arbitrarily defined origin of the molecular coordinate system:

$$D(\phi) = \sum_{i=1}^{n} [\langle \phi_i | \vec{r} | \phi_i \rangle]^2$$

The centroids of charge of these localized orbitals have already been used to measure the progressions of reactions such as the Diels–Alder reaction,[14] 1, 3-dipolar cycloadditions,[15] and the azidotetrazole isomerization.[16]

Finally, maps of electrostatic potential[13] have been made for ketene, and the cartesian grids which form the maps have been calculated according to the formula proposed by Bonaccorsi, Scrocco, and Tomasi.[17]

$$V(\mathrm{M}) = -\sum_{pq}\sum D_{\mathrm{pq}} \langle X_{\mathrm{p}} | \vec{r}(\mathrm{M})^{-1} | X_{\mathrm{q}} \rangle + \sum_{a} Z_{\mathrm{a}} / R_{\mathrm{a,M}} \quad (2)$$

where $R_{\mathrm{a,M}}$ is the distance between the nucleus a and the point charge M, and where D_{pq} is the density matrix.

Calculations

The numbering system for the atoms in the ketene–ethylene supermolecule is given in Figure 1 along with the angles chosen as parameters. The only bond lengths not varied are the CH bonds, which were left throughout at 1.08 Å. The bond lengths between C_2 and C_3 (R_{23}) and between C_1 and C_4 (R_{14}) were taken as a set of independent variables against which all the other variables were optimized.

Various sets of angles can be named, such as ethylene rocking ($\eta, \lambda_{3,4}$), ethylene rotation about ketene ($\theta_{1,2}, \kappa$), ethylene bending ($\beta, \epsilon_{3,4}$). The amount of rotation of the ethylene terminal CH_2 group (ϕ) can be calculated as $^1/_2(\mu_5 + \mu_6)$. The amount of CH_2 pyramidalization (χ) is $^1/_2(z' - z'')$, where $z = \theta$ or μ.

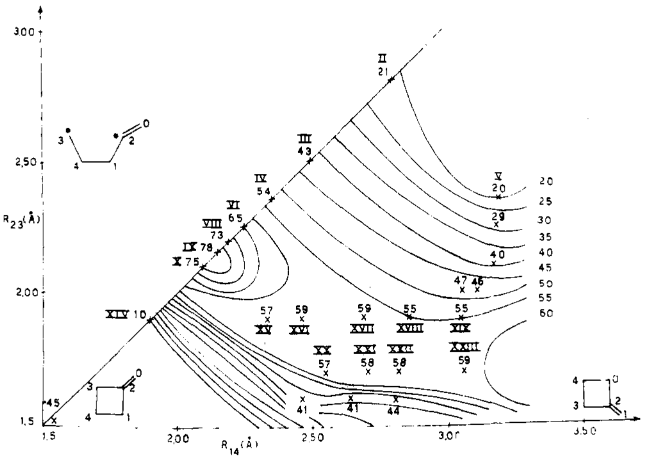

Figure 2. An isoenergetic contour diagram is given for the optimized geometries for the various pairs of R_{23},R_{14}. The zero point of relative energy is for the separated partners.

The order in which the variables were optimized for a given set of R_{23} and R_{14} is the following. First, the remaining bond lengths, γ (ketene bending), and the rotation of ethylene about ketene were varied and form a first group. The next group of variables was varied iteratively and consists of α and ethylene rocking and bending. Lastly δ, ξ, and μ were optimized. The three groups are iteratively optimized. Thus, the 14 angles and 3 dependent bond lengths were gathered into 9 groups of variables corresponding to all expected movements. Nine groups are still too many to optimize each dependently of the others; so these were gathered into three groups where the results of each group could be iteratively optimized with the other two.

For R_{23} less than 2.50 Å all angles and bond lengths were optimized to 5° and 0.03 Å, respectively. The geometry of the product cyclobutanone was chosen as the experimentally found geometry[18] except for the CO bond length which was optimized (1.24 ± 0.2 Å). Ketene was optimized to a precision of ±0.1 Å and 1°, while the geometry of ethylene is that found for the ethylene dimerization reaction.[1]

Results

Geometric Properties. Since this study is essentially a comparison between the concerted and zwitterionic two-step reaction pathways, the choice of the values of R_{14} and R_{23} was made so as to contain these two possible paths on the potential energy hypersurface.

When these two lengths were used as reaction coordinates, an isoenergetic contour diagram can be constructed (Figure 2) which contains both the possible concerted and two-step pathways. The contours in Figure 2 represent the difference in energy between the optimized geometry at a particular combination R_{14},R_{23} and the separated molecules. In this case, the (55 × 55) CI method is used to calculate the energies. The concerted path follows the diagonal line where $R_{14} = R_{23}$, but more about this path will be given later.

The search for the zwitterionic path is thus confined to the bottom right half of Figure 2; yet several modes of approach are still conceivable. Although the choice of the parameters permits any possible nuclear position to be considered for a couple R_{14},R_{23}, an exploration was made at one value of R_{23} (2.25 Å) letting R_{14} vary in such a way that one mode of approach might be seen to be more energetically favorable. In this way a judicious set of R_{14},R_{23} values might be picked for smaller values of R_{23} and the subsequent optimization of the geometric parameters can be limited to certain modes of approach found at R_{23} = 2.25 Å.

Two such modes for the two-step region, which are based on previously proposed, intuitive models, are called the flat and triangular modes. The first is the commonly proposed route for the formation of a zwitterion whereby one

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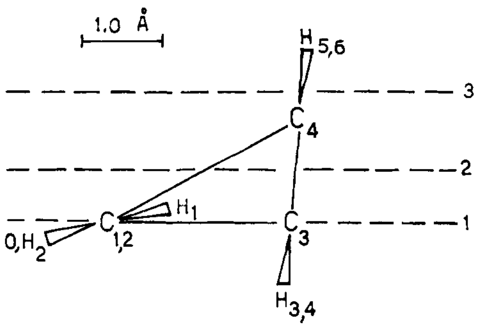
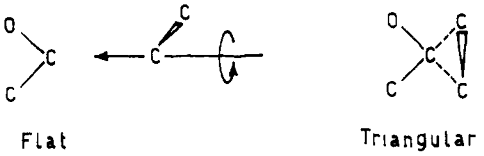


Figure 3. The most stable point for R_{23} = 2.25 Å drawn to scale. The dashed lines 1 and 3 are projections of the planes used for Figure 9 parts a and b, respectively.

ethylene carbon nucleus approaches in the plane formed by the three bent ketene heavy atom nuclei. In the geometry optimizations for this mode the ethylene undergoes bending (β) and rocking (η) and the axis of approach is varied along with the ketene bending angle.



The triangular mode, first proposed by Wagner and Gompper,[19] resembles the flat mode except that C_1 and O are bent down such that the plane of the ketene heavy atoms bisects the ethylene CC bond.

For each of these two modes there are two classes possible wherein H_1 and H_2 are in the plane of the ketene bending or perpendicular to it. As an analogy to the concerted approach these classes are called antarafacial and suprafacial, respectively.

The most stable point for R_{23} = 2.25 turns out to be a compromise between the two modes; this is point VII of Figure 2 and is drawn to scale in Figure 3.

This aspect is kept until R_{23} = 1.90 Å where the lowest total energy is at η = 80°. At this point, C_4 moves toward a union with C_1, but with a rather large range of possible directions.[20] In fact, a reduction of η to 60° at R_{23} = 1.90 Å does not entail an increase of total energy of even 1 kcal/mol. Closing the gaps between C_1 and C_4 with R_{23} held at 1.90 Å entails essentially a reduction first of η to 40° and then α and β. A minimum is found at R_{14} = R_{23} = 1.90 Å where the geometry resembles a stretched cyclobutanone, that is, the concerted (2s + 2s) form It must be noted, though, that a form with η = 20° and R_{23} = R_{14} = 1.90 Å is only 1 kcal/mol higher in energy.

Crossing the barrier at point XVI would demand nearly 5 kcal/mol more than a passage by points XVIII–XIX. Thus, the closing of C_1C_4 was examined at R_{23} = 1.70 and 1.60 Å where a single bond is nearly formed between C_2 and C_3. This formation of a single bond with a distance of 1.6 Å was found by Segal[21] in his study of the diradical two-step dimerization of ethylene. Barriers for the destruction of the tetramethylene diradical were found at the central R_{23} bond length of 1.6 and 1.9 Å.

This is not the case for the two-step path found here. There is a large plateau between R_{23} = 1.9 and 1.7 Å and between R_{14} = 2.5 and 3.0 Å. Although the precision of the optimization procedure is expected to be ±3 kcal/mol for any given point, the stabilization of a zwitterionic intermediate would probably be greater than this due to the allylic group on ketene. In comparison, the tetramethylene intermediate was found to be stable to about 2 kcal/mol for the destruction of the diradical toward formation of the second bond. A priori, this might not be expected, but a barrier to cyclobutanone could be since the turning of the ketene CH_2 group would disrupt the allylic π system.

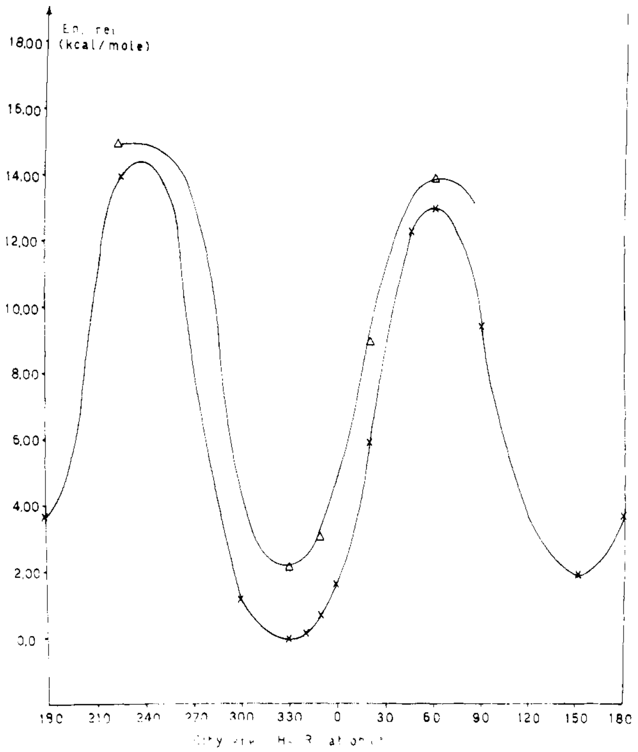


Figure 4. The energy (kcal/mol) relative to point XXIV is given as a function of the rotation of the ethylene external CH_2 group. The zero point of rotation is where a line perpendicular to the plane of the projection of the CH_2 group and passing through C_4 will form a dihedral angle = 0 with the line C_2C_3. The direction of the rotation is toward the oxygen. The crosses are for point XXIV, triangles for XXIV (η = 75°).

The rotation of the terminal ethylenic CH_2 group in the zwitterion would cause a loss of retention of the cis or trans configuration in going from product to reactant. The rotation is not expected to be free in the zwitterion due to the coulombic attraction between the negative allylic system and the positive terminal ethylenic CH_2 groups. A measure of the energy needed for this rotation can be obtained from Figure 4. This figure gives the energy relative to the most stable CH_2 position for points XXV and XXVI. A rotation of 90° for point XXII was found to be unfavorable by 20 kcal/mol. In general, then, the energy needed for the rotation of the positive CH_2 group of the zwitterion is about 12 kcal/mol.

The existence of a zwitterionic form as a stable intermediate is thus questionable from the geometric results. An approach resembling the triangular form is seen until such a point (R_{23} = 1.9 Å) where the bonding of C_4 is transferred gradually from C_2 to C_1. The optimized geometries demonstrate a constant diminishing of the angle η while θ_1 and θ_2, which measure the ketene CH_2 rotation, change in such a way as to favor the bonding between C_4 and C_1. Point XXIII, whose geometry resembles the classically drawn zwitterion intermediate (η = 90°, θ = 0°), is seen to be a point of slightly higher energy lying off this path. It is to be noted, however, that following the path with the gentlelest slope for the reverse reaction from cyclobutanone will pass through point XXIII after continuing along R_{23} + 1.6 Å.

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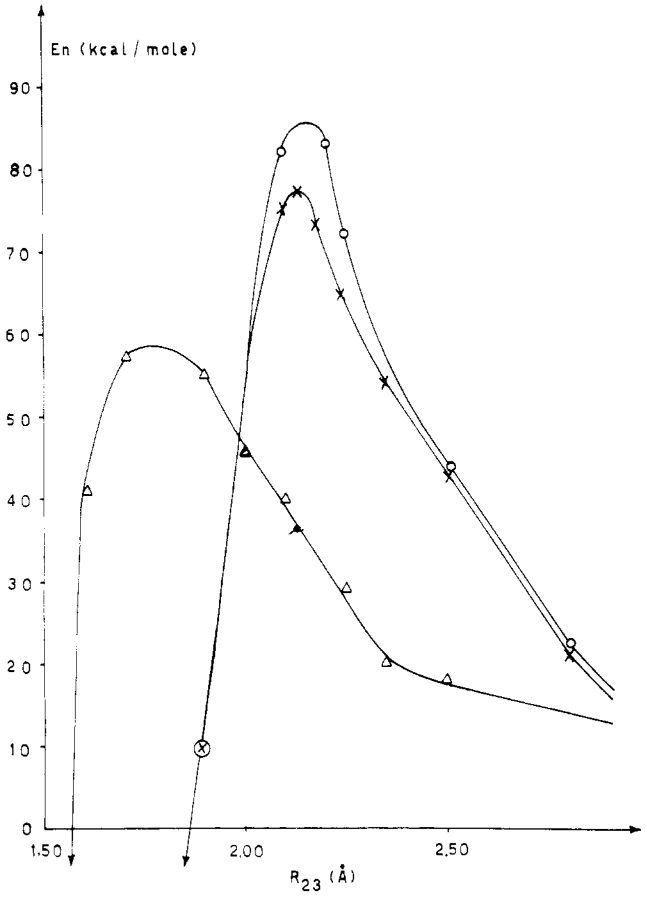

Figure 5. The energy (kcal/mol) relative to the separated partners is given for the optimized points along the coordinate R_{23} (Å) [two-step (△), ($2s_e + 2a_k$) (+), ($2s_e + 2s_k$) (O)].

As for the synchronous concerted path, the ($2s_e + 2a_k$) approach was found to be preferred to the ($2s_e + 2s_k$) from as far out as R_{23} = 2.80 Å until after the concerted transition state, point IX. The ($2s_e + 2s_k$) equivalents to points II, III, VI, and X were higher in energy by 1, 1, 2, 12, and 12 kcal/mol. A comparison of the three approaches along the coordinate R_{23} is made in Figure 5 in terms of the energy relative to the separated partners; the energies were obtained with the (55 × 55) CI method; the two-step mechanism is represented by triangles, the ($2s_e + 2a_k$) by crosses, and the ($2s_e + 2s_k$) by circles. In addition a point resembling the (2s + 2s) transition state for the dimerization of ethylene[22] was calculated at $R_{23} = R_{14}$ = 2.21 Å. The energy relative to the separated partners for the ($2s_e + 2s_k$) reaction at this point is 85 kcal/mol, which is about 15 kcal/mol higher than the corresponding point on the ($2s_e + 2a_k$) curve. In addition, it was found that the suprafacial equivalents to points XV and XIX were both higher in energy by at least 12 kcal/mol. One might suppose from this that the suprafacial approch of ketene is at least 10 kcal/mol less favorable than the antarafacial throughout the whole of the activated region of the energy surface studies. This would explain the stereospecificity obtained when the ketene substituants are not too large.

Energetic Properties. As for the effect of configuration interaction on the ($2s_e + 2a_k$) pathway, we observed an increase in the energy relative to the separated partners when more configurations are added in the region of the activated complex.

This raising of the activation energy with CI including the whole of the π system has also been noted in the studies on the symmetry allowed[3] reactions of ethylene with *cis*-butadiene[24] and with itself.[1] On the other hand, the symmetry forbidden reaction path for the dimerization of ethylene has been seen to be greatly assisted by a CI including the whole of the π system.[1] In the present case, however, this type of limited CI is seen to have little effect on the barrier for the proposed "symmetry forbidden" ($2s_e + 2s_k$) reaction. For the corresponding point at $R_{23} = R_{14}$ = 2.21 Å the activation energy is 85 kcal/mol with CI and 91 kcal/mol without.

The lack of a large effect by CI in this case stems from the fact that the oxygen orbitals can not be considered as mere perturbations on an ethylenic subunit of ketene. In the case of the dimerization of ethylene, the supermolecule has D_{2h} symmetry and thus elements of this symmetry system permit an avoided crossing[25] between molecular orbital configurations. As for the present reaction, cyclobutanone has C_{2v} symmetry and the ($2s_e + 2s_e$) transition state, $R_{23} = R_{14}$ = 2.15 Å, although perturbed from this symmetry, presents the same-symmetry elements as manifested by the atomic orbital coefficients. The situation is illustrated in Figure 6 where the four molecular orbitals habitually cited in ($2\pi_s + 2\pi_s$) reactions are represented by their principal atomic orbital constituents. At the outset ($R_{23} = R_{14}$ = 2.35 Å), the ($2s_e + 2s_k$) reaction can be described in the same terms as the ($2s_e + 2s_e$) reaction slightly perturbed by the oxygen. That is, two perpendicular C_2 axes proper to a system of D_{2h} symmetry can be found. In the product cyclobutanone one C_2 axis can be found colinear with the C=O bond. The four MO's which correlate with those described for the reactants are all antisymmetric to rotation about this axis. At the point $R_{23} = R_{14}$ = 2.21 Å, which is just before the ($2s_e + 2s_k$) transition state, the two perpendicular C_2 axes proper to a system with D_{2h} symmetry remain (in this case the order in the MO configurations is product-like) but the values of the π AO coefficients on ethylene are far from equal. The change in these coefficients from R_{23} = 2.35 to 2.21 Å indicates that the coefficients that diminish in absolute value will pass a point of inflexion whereby the cyclobutanone C_{2v} symmetry elements will be found.

The reduction in the activation energy from the SCF method by inclusion of the CI from these four MO's was more than 50 kcal/mol in the case of the ($2\pi_s + 2\pi_s$) dimerization of ethylene.[1] It is thus significant that not more than 8 kcal/mol was to be gained by a CI for the ($2s_e + 2s_k$) reaction. It is also to be noted that the square of the expansion coefficient for the ground-state, SCF configuration in a (55 × 55) CI equals 0.745 for the transition state of the ($2s_e + 2s_k$) reaction, while the first mono- and diexcitation configurations contribute 0.062 and 0.085, respectively. In the ($2s_e + 2s_e$) reaction the ground-state and first diexcited configurations each contribute 0.42 to the total (55 × 55) CI expansion for the transition-state geometry.

Thus, the reason for the preference of a ($2s_e + 2a_k$) approach to the ($2s_e + 2s_k$) one is not to be found with orbital symmetry rules since there is no real symmetry forbidden path. Before investigating the electronic properties of these concerted paths, the energetics of the two-step path will be discussed.

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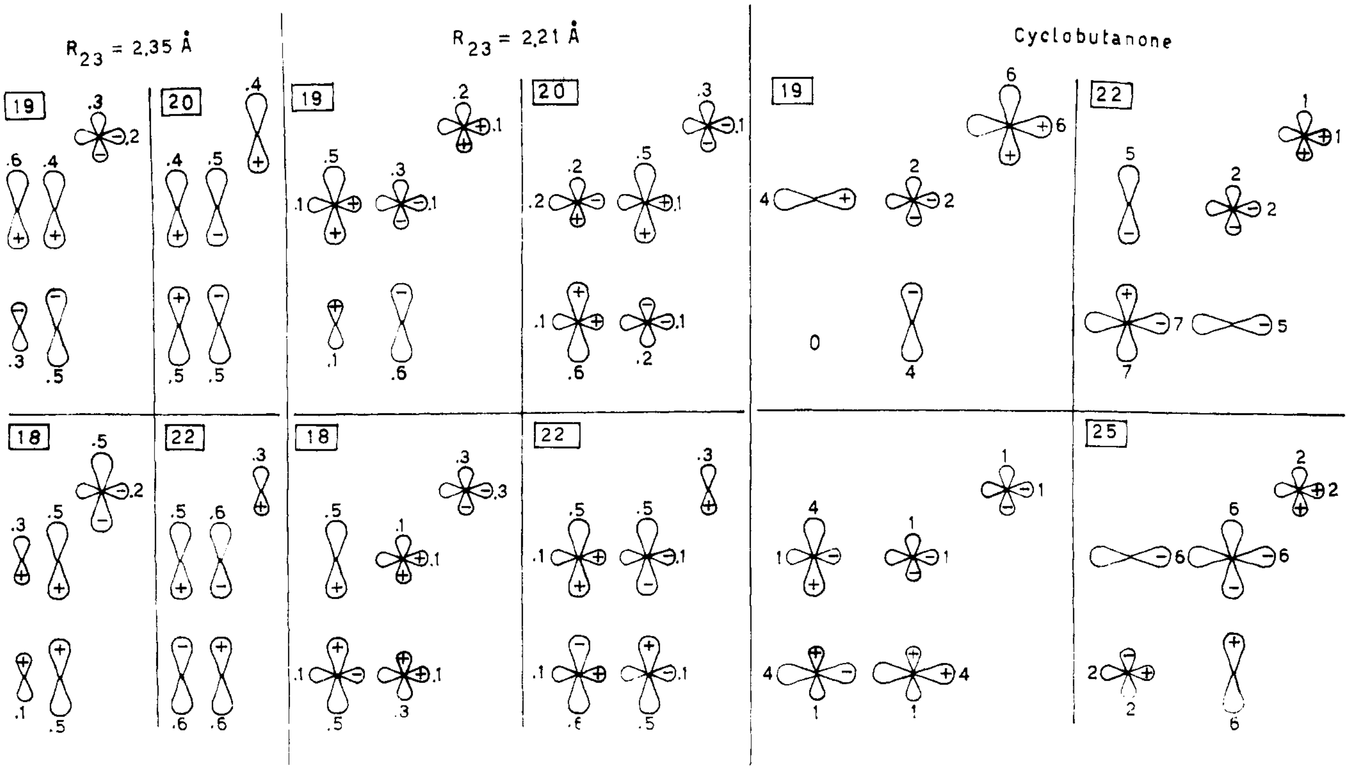


Figure 6. The values and signs of the atomic orbital coefficients are given for two occupied and two virtual MO's for two points along the ($2s_e$ + $2s_k$) pathway and for cyclobutanone. The ketene components are the upper three groups and ethylene the lower two.

First of all, the theoretical energy of activation, 58 kcal/mol, for the two-step addition of ketene and ethylene is too high compared with experiment. Only the activation energy for the gas-phase, thermal, reverse cycloaddition reaction is known for the ketene–ethylene system, that being 52 kcal/mol.[26,27] So the forward activation energy can be calculated with the experimentally known, gas-phase, standard heats of formation of ketene[28] and ethylene[29] (−12 and +12 kcal/mol, respectively) and the estimated heat of formation for cyclobutanone[27] (−20 kcal/mol). This gives a heat of reaction −20 kcal/mol for the formation of cyclobutanone. The forward activation energy can thus be estimated to be 32 kcal/mol, or 26 kcal/mol below the theoretical value. As a comparison, the theoretical barrier to the two-step dimerization of ethylene was found to be 42.4 kcal/mol with the (15 × 15) Cl method,[21] while the experimental value is 43.9 kcal/mol.[30]

The optimization method may be to blame due to an interdependence of variables[20] which would escape detection with the step in angles being as high as 5°. The source of this discrepancy might be in the choice of a minimal basis set. This basis set is seen to treat anions very poorly in terms of total energy.[31] This might be true for zwitterions also, although these species have not been studied for the effect of basis size. As for the discrepancy between the theoretical and experimental heats of reaction (−42.6 and −20 kcal/mol, respectively), it is well known that minimal basis sets treat cyclic molecules better than their linear olefin precursors, thus giving exaggerated heats of reaction for cyclizations. Using the 6-31G basis set, the value is −21 kcal/mol. Furthermore, calculations using this extended basis set and unrestricted, fourth-order Moller-Plesset perturbation using single and double excitations from all noncore orbitals gave an energy of 40.1 kcal/mol higher for point XIX than for point I (the two partners separated by 5 Å). This is compared to 55 kcal/mol with the STO-3G basis. Point XXII gave 56.2 kcal/mol compared to 58 kcal/mol with STO-3G.

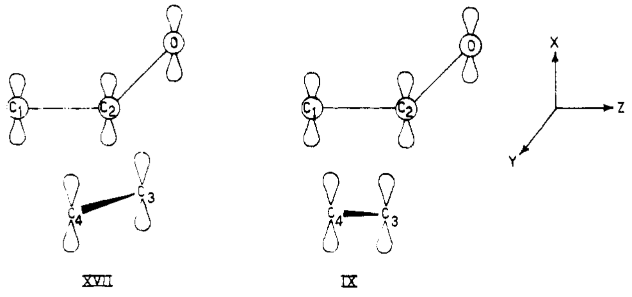
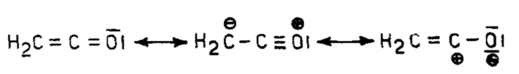


Figure 7. The p orbital and total atomic charges (32) are given for a point on the concerted (IX) and "two-step" (XVII) pathways.

Electronic Properties. (i) The three most common resonance structures drawn for ketene all include four π electrons in three centers. Structures a and c have an oxygen pair participating in this allylic system while a pair is represented on the terminal carbon in structure b. The ionic structure in c stems from the formation of a lone pair on oxygen at the expense of the CO double bond orthogonal to the allylic π system.



$$H_2C=C=\bar{O}| \longleftrightarrow H_2\overset{\ominus}{C}-C\equiv\overset{\oplus}{O}| \longleftrightarrow H_2C=\underset{\oplus}{C}-\underset{\ominus}{\bar{O}}|$$

a b c

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(26) Das, M. N.; Kern, F.; Coyle, T. D.; Walters, W. D. *J. Am. Chem. Soc.* **1954**, *76*, 6271.

(27) McGee, T. H.; Schleifer, A. *J. Phys. Chem.* **1972**, *76*, 963.

(28) Nuttall, R. L.; Laufer, A. H.; Kilday, M. V. *J. Chem. Thermodn.* **1971**, *3*, 167.

(29) Cox, J. D.; Pilcher, G. "Thermochemistry of Organic and Organometallic Compounds"; Academic Press: London, 1970.

(30) As estimated from an activation energy of 62.5 kcal/mol for the cycloreversion reaction of cyclobutane (Kern, K.; Walters, W. D. *J. Am. Chem. Soc.* **1953**, *75*, 6196) and from the experimental heat of reaction of 18.6 kcal/mol reported in ref 21 for the pyrolysis of cyclobutane to two ethylenes.

(31) Radom, L. "The Electronic Structure of Atoms and Molecules"; Schaefer, H. F., Ed.; Academic Press: New York, 1976; Vol. 4, p 346.

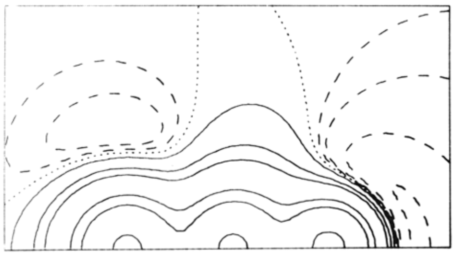


Figure 8. The electrostatic potential about ketene (a) given in the plane of the molecule and (b) in a plane perpendicular to the preceding and including the CCO axis. The dotted line marks a potential of 0 kcal/mol, the broken lines are contours of negative potential with the values −0.005, −0.025, and −0.05 au as one goes out from zero, and the solid lines are positive with the values 0.01, 0.05, 0.1, 0.5, 1.0, and 10.0 au. The nuclei are in centers of high positive potential.

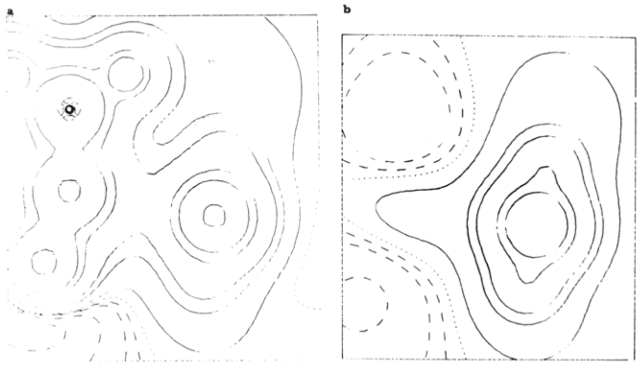
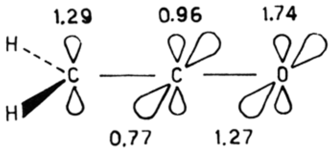


Figure 9. The electrostatic potential for supermolecule VII with the same value of contours as Figure 8: (a) Plane 1 seen in Figure 3. (b) Plane 2. (c) Plane 3.

The π and total atomic charges calculated by Mulliken's population analysis[32] usually follow the major resonance structures. This is seen to be the case for ketene also.



This separation of charge is also seen in the (2s + 2a) and two-step activated complexes. A net separation is seen in the concerted path as well as when one increases R_{14} in relation to R_{23}. The p and total atomic charges calculated for points IX and XVII are shown in Figure 7. Point IX is the concerted $2s_e + 2a_k$ path while the latter is a point for R_{23} = 1.90 Å but where the SCF ground-state configuration still contributes at least 85% to the 55 configuration expansion for the CI ground state.

(ii). Maps of the electrostatic potential[13] can effectively delineate those regions of charge that were estimated by resonance structures and population analyses. Figure 8 gives contours of electrostatic potential about ketene in a plane perpendicular to the molecular plane and along the CCO axis.

A region of negative potential is seen about the oxygen as would be expected from the two π systems and two lone pairs which involve this atom. In Figure 8 the region of negative potential due to the C=C bond is found to be displaced toward C_1 as resonance structure b or the π orbital charge would indicate. The displacement is even greater for the C=O bond, in accord with the weight given to structure c.

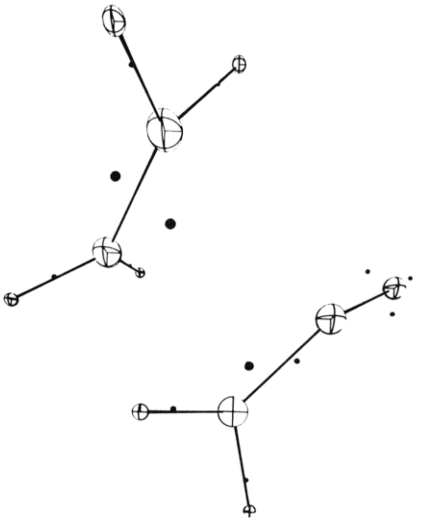


Figure 10. The nuclei and centroids of charge are represented in scale for point VII ($R_{23} = R_{14}$ = 2.25 Å).

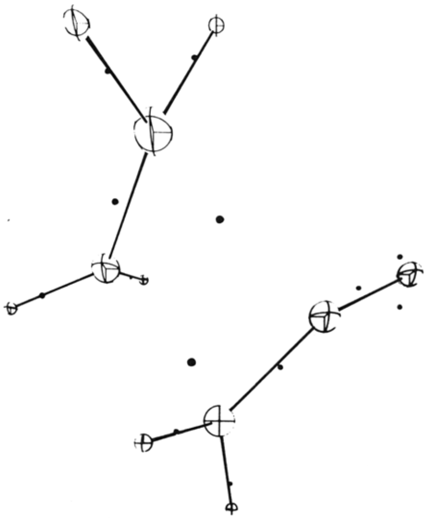


Figure 11. The nuclei and centroids of charge are represented in scale for point X ($R_{23} = R_{14}$ = 2.10 Å).

A ring of positive potential can be pictured around C_2. Within this ring the largest region of positive potential is in the molecular plane. On this basis on might expect the mode of attack by an ethylene (which has two regions of negative potential corresponding to the C=C bond) to be the antarafacial triangular approach, at least at the outset of the attack.

Figure 9 parts a and b are maps for point VII in planes that pass through the ethylene CC bond (cf. Figure 3 for positions). Figure 9 part a shows bonding between the partners, while 9 part b shows the positioning of the ethylene between the two zones of negative potential above ketene.

(iii). Centroids of charge for localized molecular orbitals can be used as measures of the progression of reactions. The synchronous ($2s_e + 2a_k$) path as well as the minimum energy, "two-step" path have been examined in terms of these centroids.

The ($2s_e + 2a_k$) path is precocious in the sense that its transition state arrives earlier on the reaction coordinate $R_{23} = R_{14}$ = 2.15 Å) than the "two-step" path's ($R_{23} \cong$ 1.8 Å, $R_{14} \cong$ 2.75 Å). The change in the centroid positions for the concerted path is seen to be regular in the sense that an ethylene double bond centroid progresses toward C_2 while a ketene CC double bond is displaced toward C_3. The sequence of the progression can be obtained from

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[32] Mulliken, R. S. *J. Chem. Phys.* **1955**, *23*, 1833.

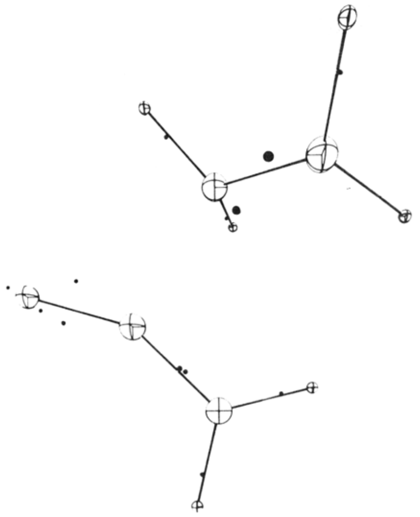

Figure 12. The nuclei and centroids of charge are represented in scale for point XVII (R_{23} = 1.90 Å, R_{14} = 2.69 Å).

Figures 10 and 11 which give the charge centroids for points VII and X, respectively.

The "two-step" path is seen to justify its name when one considers the progression of the LMO centroids. Of the two centroids which shift to form the C_1C_4 and C_2C_3 bonds in cyclobutanone only the ethylene centroid is significantly displaced until R_{23} = 1.9 Å (point XVII, in Figure 12).

Since the SCF ground-state MO configuration contributes overwhelmingly (>90%) to the 55 configuration expansion for the (2s + 2a) activated complex, the LMO's derived from these MO's serve as a valid description. For point XVII, however, this M0 configuration contributes only 70% to the same expansion, while the configurations of the mono- and diexcitations from the HOMO to the LUMO contribute 7 and 15%. Even so, one might expect that the LMO's derived from this SCF configuration would give a qualitatively correct description for this point.

Conclusions

(1) The cause for the stereochemistry of the ketene plus ethylene reaction cannot be attributed to orbital symmetry rules since there is no symmetry forbidden pathway. This can be seen by inspection of the AO coefficients of the two HOMO's and two LUMO's for the activated complexes along the two concerted paths, showing a change in symmetry elements from reactant-like to product-like. A more stringent test of forbiddeness of a pathway is the need for the interaction of the configurations which cross near the transition state, which is not found for the synchronous (2s + 2s) path. This conclusion is independent of the SCF basis set used.

(2) The apparent antarafacial addition of ketene can be explained through electrostatic potential diagrams of ketene and of the supermolecule during the initial stages of approach. The electrophilic and nucleophilic regions are expected to be independent of the basis set, as far as their positions are concerned.

(3) The approach of the molecules is such that a bond is almost formed between the central carbon of ketene and a carbon of ethylene, just before the CH_2 groups rotate toward bonding. This bonding is strong enough to prevent rotation of the ethylene CH_2 group, thus preserving suprafacial stereoproducts. Although there is a certain amount of charge separation in the terminal CH_2 groups, this reaction can be described as a nonsynchronous concerted reaction.[7] This conclusion is dependent on the basis set used since the STO-3G basis tends to favorize the formation of single bonds and cyclic isomers.

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Registry No. $CH_2{=}C{=}O$, 463-51-4; $CH_2{=}CH_2$, 74-85-1.

Intramolecular [2 + 2] Photocycloaddition of 4-Substituted Cyclopent-2-en-1-ones

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The intramolecular [2 + 2] photocycloaddition of 4-(3,4-pentadienyl)cyclopent-2-en-1-ones has been shown to yield the expected straight cycloaddition product, a tricyclo[4.2.1.$0^{4,9}$]nonanone, and a novel product, a tricyclo[4.3.1.$0^{4,10}$]decenone, with a bridgehead double bond. The reaction course can be controlled by side-chain substituents and by the temperature of the reaction.

The synthetic approaches to di- and triquinane compounds have attracted the interest of many workers in the past decade and the synthetic developments in this area of chemistry have been reviewed this year by Paquette.[1] Also, the methods for construction of five-membered rings onto preexisting cyclic compounds have been evaluated by Ramaiah.[2] In these reviews more than 18 methods for cyclopentaneannulation have been discussed, and most recently Trost has presented his development of the formal equivalent of a 1,3-dipolar cycloaddition of a zwitterionic form of trimethylenemethane in the synthesis of carbocycles.[3]

One synthetic route which offers much promise for the synthesis of polyfunctionalized di- and triquinanes is the

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(1) Paquette, L. A. "Topics in Current Chemistry"; Springer-Verlag: New York, 1984; Vol. 119.

(2) Ramaiah, M. *Synthesis* 1984, 529.

(3) Trost, B. M. *Chimia* 1984, *38*, 319 and references therein.