

Organic and Biological Chemistry

Trimethylene and the Addition of Methylene to Ethylene

Roald Hoffmann

Contribution from the Department of Chemistry, Cornell University, Ithaca, New York 14850. Received May 31, 1967

Abstract: Extended Hückel calculations on a distorted cyclopropane indicate the presence of a singlet trimethylene intermediate with a CCC angle of 125° , trigonal terminal methylene groups coplanar with the carbon skeleton. This molecule has a high barrier to internal rotation and a low barrier to conrotatory reclosure to cyclopropane. The first excited configuration of trimethylene and cyclopropane is a floppy molecule with no rotational barriers. The electronic structure of trimethylene is unusual with a symmetric π -type level above an antisymmetric combination. Similar level orderings, implying conrotatory closing and concerted 1,2 addition, are found in other "1,3 dipoles." The potential surface for the addition of methylene to ethylene is explored in detail. The most symmetrical approach is symmetry forbidden, and the reaction path is unsymmetrical. It begins as a π approach and terminates as σ . Because of the electronic structure of trimethylene it is possible for this unsymmetrical approach to be stereospecific. The specificity of singlet and triplet methylene additions is attributed not to the difference in spin, but to the difference in the spatial part of the wave function. The ring-opened form of cyclopropanone has an electronic structure different from that of trimethylene and other 1,3 dipoles. It is consistent with the valence-bond formulation of an oxy anion of allyl cation. A consequence of this electronic structure is a disrotatory closure back to the cyclopropanone and propensity to concerted 1,4 addition. The extended Hückel calculations make cyclopropanone and allene oxide unstable with respect to oxyallyl (the ring-opened form). In fact they give no stability for cyclopropanone with respect to conversion to oxyallyl. A π -electron SCF-CI calculation has the ground state of oxyallyl, a triplet, with a singlet only 0.1 eV above.

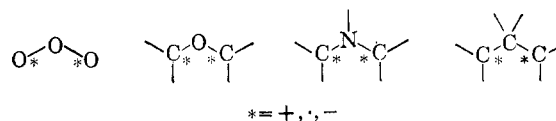
In this paper two aspects of cyclopropane chemistry are discussed: the question of the existence and electronic structure of a trimethylene intermediate $\text{CH}_2\text{-CH}_2\text{CH}_2$, and the detailed transition-state geometry and specificities observed in the addition of methylenes to ethylenes. An important and connected problem, the *cis-trans* thermal isomerization of substituted cyclopropanes and the competing rearrangement to propylenes, has not yet been considered in detail.

Trimethylene

The stimulus for a series of calculations on trimethylene arose from the following: (1) the observation of stereospecific 1,2 addition of tetracyanoethylene oxide to olefins (I),¹ (2) the discovery by several groups of similar cycloadditions of aziridines (II),² (3) the observation of some novel specificities in the pyrolysis of labeled pyrazolines (III),³ (4) the 1,4 cycloaddition of cyclopropanones to cyclic dienes (IV),⁴ and (5) a general desire to learn something about 1,3-dipolar additions, of, for example, O_3 .⁵

- (1) W. J. Linn and R. E. Benson, *J. Amer. Chem. Soc.*, **87**, 3657 (1965).
- (2) A. Padwa and L. Hamilton, *Tetrahedron Letters*, 4363 (1965); J. E. Dolfini, *J. Org. Chem.*, **30**, 1298 (1965); H. W. Heine and R. Peavy, *Tetrahedron Letters*, 3123 (1965); H. W. Heine, R. Peavy, and A. J. Durbetaki, *J. Org. Chem.*, **31**, 3924 (1966); R. Huisgen, W. Scheer, G. Szeimes, and H. Huber, *Tetrahedron Letters*, 397 (1966).
- (3) R. J. Crawford and A. Mishra, *J. Amer. Chem. Soc.*, **87**, 3768 (1965); **88**, 3963 (1966); D. E. McGreer, N. W. K. Chiu, M. G. Vinje, and K. C. K. Wong, *Can. J. Chem.*, **43**, 1407 (1965).
- (4) N. J. Turro, P. A. Leermakers, H. R. Wilson, D. C. Neckers, G. W. Byers, and F. F. Wesley, *J. Amer. Chem. Soc.*, **87**, 2613 (1965); A. W. Fort, *ibid.*, **84**, 2620, 4979 (1962); R. C. Cookson and M. J. Nye, *Proc. Chem. Soc.*, 129 (1963).
- (5) R. Huisgen, R. Grashey, and J. Sauer in "The Chemistry of the Alkenes," S. Patai, Ed., John Wiley and Sons, Inc., New York, N. Y., 1965, p 808; R. Huisgen, *Angew. Chem. Intern. Ed. Engl.*, **2**, 633 (1963).

In all of the above cases there existed a possibility of a ring-opened intermediate, usually classified as a 1,3-dipolar molecule. While the electronic structure of



the ozone molecule is qualitatively well known, the structures of the other, much less stable, and never isolated, molecules are not obvious. With a good deal of theoretical license the simplest molecule, trimethylene, $\text{CH}_2\text{CH}_2\text{CH}_2$, was chosen for detailed study. The results will be shown to apply to the other molecules in the series, as well as to a number of other unsymmetrical, 1,3-dipolar molecules.

The calculations undertaken were of the extended Hückel type.^{6a} The number of degrees of freedom in the general $\text{CH}_2\text{CH}_2\text{CH}_2$ potential surface was reduced to three by fixing C-C distances at 1.54 Å, C-H at 1.10, a tetrahedral central HCH angle, and trigonal terminal CH_2 groups. The remaining degrees of freedom are the CCC angle and the rotations of the terminal methylene groups out of the plane defined by the three carbon atoms. Three geometries defined by the last two angles being 0 or 90° will be important in the subsequent discussion and are drawn in Figure 1. Note in particular that the 90,90 geometry for a small CCC angle goes over to a true cyclopropane structure if the terminal groups change from a trigonal to an almost tetrahedral local geometry.

- (6) (a) R. Hoffmann, *J. Chem. Phys.*, **39**, 1397 (1963), and subsequent papers. The parameters used here are the same except for a H Slater exponent of 1.3. (b) R. B. Woodward and R. Hoffmann, *J. Amer. Chem. Soc.*, **87**, 395 (1965); (c) R. Hoffmann and R. B. Woodward, *ibid.*, **87**, 2046 (1965).

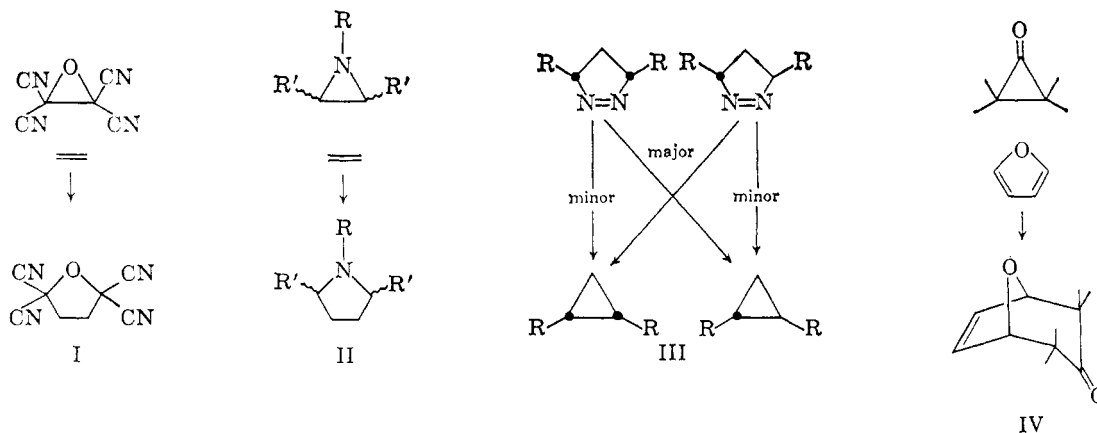


Table I gives several linear sections through the multi-dimensional potential surface of $\text{CH}_2\text{CH}_2\text{CH}_2$ in ground and excited electronic configurations. The column headings are the geometries illustrated in Figure 1 and the rows are CCC angles. The entries are energies in electron volts relative to a cyclopropane.

Table I. Sections through a $\text{CH}_2\text{CH}_2\text{CH}_2$ Potential Surface^a

CCC, deg	Ground configuration			Excited configuration		
	0,0	0,90	90,90	0,0	0,90	90,90
80	4.99	2.76	0.24	5.82	4.31	4.53
100	2.65	2.28	1.08	2.70	2.60	2.62
110	2.10	2.26	1.58	2.40	2.36	2.34
120	1.93	2.36	2.11	2.42	2.37	2.33
130	2.00	2.53	2.31	2.64	2.56	2.51
150	2.65	3.29	2.44	3.56	3.34	3.29

^a The entries are energies relative to a cyclopropane with C-C 1.54 Å, tetrahedral HCH angles. The geometries refer to Figure 1.

There is here as in the case of methylenes an unavoidable confusion in terminology (in specifying "ground" and "excited" electronic configurations and ground and excited states) which must be kept in mind. Whenever one obtains in some calculation two one-electron

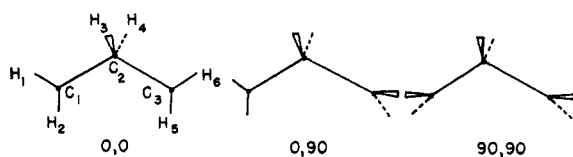
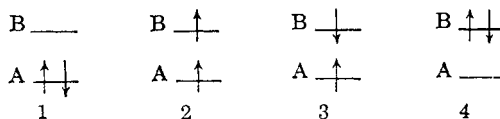


Figure 1. Definition of geometries for trimethylene.

energy levels close in energy (separated by say less than 2 eV), then there are four possible states arising from the placement of two electrons in these two levels. If A is lower in energy than B, then we call the configuration 1 the ground electronic configuration, the singlet and



triplet states 3 and 2 first excited or simply excited configurations, and the state 4 a doubly excited configuration. Now in fact configuration interaction may strongly mix states 1 and 4 and electron interaction will

greatly stabilize the triplet state 2 over the average one-electron energy of its configuration. If the A-B splitting is small, then very likely the triplet state 2 arising from an "excited" electronic configuration will be the true ground state of the molecule while the singlet "ground" electronic configuration 1 will be above it in energy. This is what occurs in methylene and CH_2 and most likely happens in trimethylene as well. The extended Hückel calculations, as other Hückel calculations, unfortunately do not take account of electron interaction, and so when a singlet and triplet arise from a given electronic configuration the calculations presumably yield some average energy of the configuration. Thus in this paper whenever the terms ground and excited appear without the explicit designation "state" they should be taken to mean the ground and excited electronic configurations actually computed, *i.e.*, one-electron energies for the occupation schemes 1 and 2, 3 (the latter two indistinguishable with our deficient method), respectively. The assumption is further made that the potential surfaces of a singlet and triplet of the same orbital symmetry (*e.g.*, 2 and 3) will not differ greatly. This seems to be true for diatomic molecules⁷ and the few well-studied polyatomic cases such as formaldehyde.⁸

With the above caution kept in mind, Table I shows sections through the potential surface for ground and excited configurations.

One immediately notes that the most stable point on the ground configuration potential surface is for a 90,90 geometry at a small CCC angle. This, of course, will become a cyclopropane when the geometrical restraints are further relaxed. The most interesting aspect of the ground energy surface is, however, not the anticipated cyclopropane minimum, but the indication of another subsidiary minimum for a 0,0 structure (*i.e.*, terminal methylenes coplanar with the three-carbon chain) with a large CCC angle of approximately 125°. This minimum will be referred to in the subsequent discussion as the trimethylene intermediate. That it is indeed a potential minimum is not proved by the energy sections shown in the table, but is a consequence of a more extended examination of asymmetric distortions of the molecule from this geometry. The easiest passage from the valley of the trimethylene intermediate to the much deeper valley of the cyclopropane is *via* a conrotatory

(7) See the tables in G. Herzberg, "Molecular Spectra and Molecular Structure. I. Spectra of Diatomic Molecules," D. Van Nostrand Co., Inc., Princeton, N. J., 1950.

(8) G. W. Robinson and V. E. DiGiorgio, *Can. J. Phys.*, **36**, 31 (1958), and references therein.

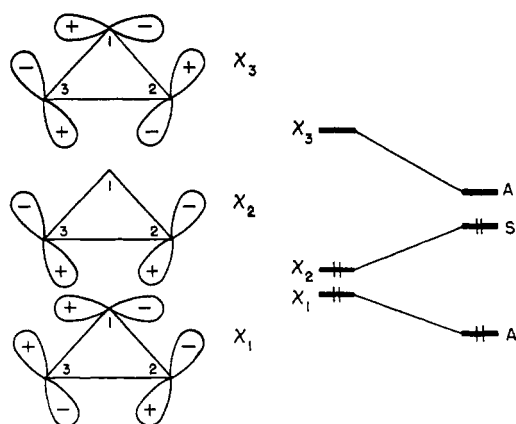


Figure 2. The Walsh orbitals for cyclopropane drawn schematically to indicate their nodal structure. χ_1 and χ_2 are degenerate. The motion of the levels as the 2-3 bond is stretched is shown at right.

motion^{6b} of both methylene groups. The activation energy for this motion is calculated to be quite small, about 1 kcal. While the extended Hückel calculations are not to be trusted for such small energy magnitudes, the shape of the potential surface is believed to be qualitatively reliably reproduced. We will return shortly to a consideration of the trimethylene intermediate. Another matter of interest in the ground configuration potential surface is that for a simply opened cyclopropane, *i.e.*, a 90,90 geometry with a large CCC angle, there is retained a sizable barrier to rotation of a methylene group. This barrier is the difference in energy between a 90,90 and a 0,90 geometry and is 2.52 eV at CCC 80°, 1.20 eV at 100°, 0.25 eV at 120°, and increases again at larger CCC angles. The shape of the potential surface is such that a trimethylene which should by chance find itself in a 90,90 geometry at any CCC angle would prefer to collapse directly to a cyclopropane without rotating a terminal methylene group.

The excited configuration potential surface is quite different. Instead of two fairly sharp minima there now appears a very broad valley ranging over all possible orientations of the terminal CH₂ groups and over a CCC angle range from 100 to 130°. This excited trimethylene is thus a molecule "floppy" in most of its degrees of freedom, with no barriers to internal rotation at all. It should also be noted that these calculations imply a severe geometry change upon a $\sigma \rightarrow \sigma^*$ excitation of a cyclopropane, opening up a CC bond to give this excited trimethylene.

The general shape of the ground- and excited-state potential surfaces is not difficult to understand. As mentioned previously⁹ the extended Hückel calculations give as the highest occupied and lowest unoccupied orbitals in cyclopropane precisely the linear combinations suggested by Walsh¹⁰ some time ago. In Figure 2 these are illustrated; one specific form of the degenerate pair χ_1 , χ_2 is chosen, namely that adapted to the ensuing stretching of the C₂-C₃ bond. The motion of the energy levels as one bond is slowly broken is apparent—those levels which are bonding in the region of bond cleavage are destabilized, while those antibonding in the same region are stabilized. Since some 2-3 bonding is

(9) R. Hoffmann, *J. Chem. Phys.*, **40**, 2480 (1964); *Tetrahedron Letters*, 3819 (1965).

(10) A. D. Walsh, *Trans. Faraday Soc.*, **45**, 179 (1949).

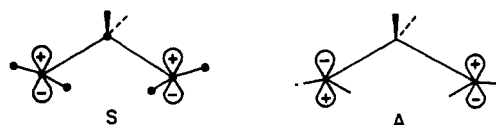


Figure 3. The symmetric (S) and antisymmetric (A) π -type molecular orbitals in trimethylene.

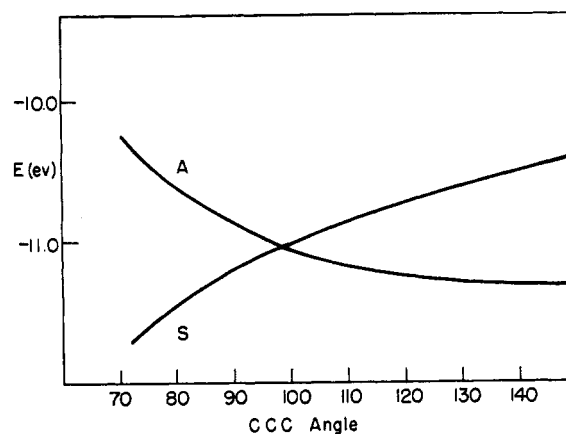


Figure 4. Energies of nonbonding orbitals of trimethylene as a function of CCC angle.

retained even when the CCC angle is quite large there remains a ground configuration barrier to rotating a methylene group. But the excited configuration has an electron promoted from χ_2 to χ_3 . This not only weakens C₂-C₃ bonding but also C₁-C₂ and C₁-C₃ as well, leading to a very flexible excited molecule.

Returning to the ground configuration, the electronic structure of the trimethylene intermediate is extremely interesting. *A priori* one would have expected that if any 1,3 interaction were present, the molecular orbital which is the symmetric combination of terminal 2p_z orbitals (Figure 3, S) would be stabilized over the antisymmetric combination (Figure 3, A). Figure 4 shows the energies of the S and A levels as a function of CCC angle. While the expected order is observed at small angles, at angles above $\sim 100^\circ$ the A level becomes increasingly stabilized over the S, and in particular for the equilibrium calculated geometry of the trimethylene intermediate the A level is below the S level by approximately 0.55 eV. This unexpected behavior can be understood as the result of two competing factors: (1) the direct 1,3 interaction which favors the positive 1,3 overlap S combination disfavors the A molecular orbital; (2) an indirect coupling in which the central methylene group far from being a mere insulator participates in molecular orbital formation (in a manner of mixing which is nothing else but hyperconjugation) and, while leaving the A level unaffected, destabilizes the S level. The clue to the second factor is provided by the form of the S molecular orbital at a CCC angle of 120°. It is

$$0.6860[C_1 2p_z + C_3 2p_z] - 0.1401 C_2 2p_z - 0.2629(H_3 - H_4)$$

Note that the hydrogens on the central carbon contribute significantly to this MO and that there are antibonding interactions as a result of this mixing (C₁ and C₃ with C₂ and (H₃ - H₄)). The mixing pattern can be understood by examining a little interaction diagram (Figure 5) in which are sketched the S and A π levels

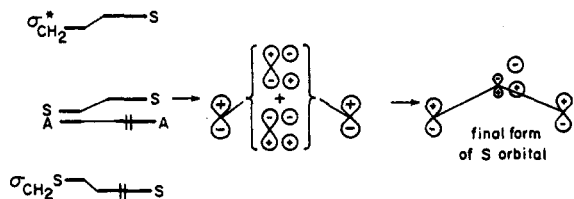


Figure 5. The interaction of the central CH₂ group with the non-bonding S orbital. The center of the figure illustrates the mixing which results in the final composition of the orbital shown at right.

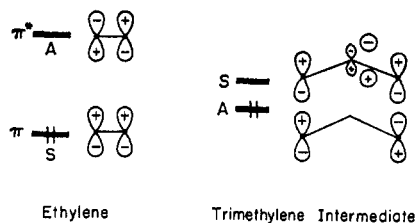


Figure 6. The electronic structure of trimethylene compared to that of ethylene.

and the σ and σ^* combinations of π symmetry arising from the C-H bonds of the central methylene group before and after interaction. The A level by symmetry cannot mix with σ and σ^* . The S level mixes and the decisive factor in its energy movement seems to be that the interaction with σ is stronger than that with σ^* as a result of (1) being closer in energy to σ than to σ^* , (2) more efficient overlap with σ than σ^* . The form of the interacted S level may be obtained from the general rule that if two orbitals of different energy mix, then the lower (energy) one of the two will mix into itself the higher one in a bonding way but the upper orbital will mix into itself the lower one in an antibonding way, so as to create a node between the two. This principle is a general consequence of the correlation of an increasing number of nodes in a wave function with higher energy. This kind of mixing is illustrated in the middle of Figure 5 with the net result, reinforcement at H_{3,4}, cancellation at C₂, shown in the figure at right and indicated by the form of the S orbital specified above.

Thus at large CCC angles the mixing of the central methylene group, destabilizing the S level, dominates, while at small angles the direct interaction stabilizing the S level wins out. The trimethylene intermediate lies in the former region and this has two immediate and important consequences for its reactions. First, using either simple orbital overlap considerations or constructing correlation diagrams it is clear that a species with two electrons in an A level (Figure 6) should close to a cyclopropane in a conrotatory manner. Second, such a species being essentially in electronic structure an "antiethylene," *i.e.*, having its order of levels precisely reversed from that in ethylene (Figure 6), should have selection rules for concerted cycloaddition precisely the opposite of those of an ethylene.^{6c} This is illustrated by the correlation diagrams in Figure 7 for the cycloaddition of trimethylene to ethylene and butadiene. The trimethylene intermediate lowest singlet (two electrons in A) should add stereospecifically to an olefin and not a diene. The conrotatory closing is what is needed to rationalize the observed preferences for inversion of stereochemistry in the pyrazoline to cyclopropane pyrolysis studied by Crawford and by

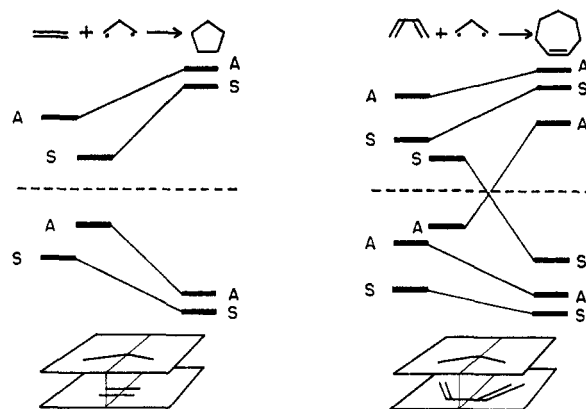


Figure 7. Level correlation diagrams for the addition of trimethylene to ethylene and butadiene.

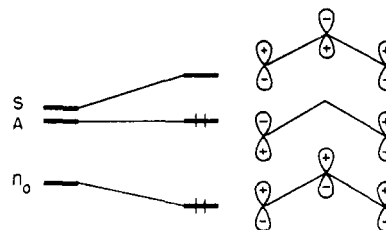


Figure 8. An interaction diagram showing the formation of the level structure of CH₂OCH₂ (ring-opened ethylene oxide) and the resemblance of the levels to those of allyl anion.

McGreer.³ Because of the weak splitting between S and A trimethylene should in fact exhibit the least stereospecificity in this regard when compared to isoelectronic species. The direct cycloaddition of trimethylenes has not been observed despite attempts in that direction,¹¹ but that of some isoelectronic species is very well known and will be discussed below.

Since the one-electron energy difference between the "ground-state" (A)² configuration and the "excited-state" (A)¹(S)¹ configuration is only about 0.55 eV in the trimethylene intermediate geometry, it is anticipated that the triplet (A)¹(S)¹ state, a molecule as mentioned before quite free in geometry, would in fact be at lower energy than the singlet (A)² trimethylene intermediate (but of course at higher energy than the singlet cyclopropane). Some preliminary calculations by Simmons indicate that this is certainly so for the geometry of the trimethylene intermediate.¹²

We can now proceed to justify some of the theoretical license we took in simplifying the problem to trimethylene. Consider a carbonyl ylide—the ring-opened 1,3 dipole derived from ethylene oxide. Figure 8 shows an interaction diagram mixing the central oxygen lone pair with the S combination of terminal CH₂ orbitals. Clearly the resultant 4 π -electron system with a highest occupied antisymmetric level resembles the allyl anion. The same would clearly be true of an azomethine ylide—the ring-opened 1,3-dipolar structure of an ethylenimine or aziridine. The resemblance to allyl anion is even more obvious in the parent compound to this isoelectronic series of 1,3 dipoles "without octet stabilization," *i.e.*, ozone. Figure 9 shows a simplified molecular orbital view of the electronic

(11) M. C. Flowers and H. M. Frey, *J. Chem. Soc.*, 2758 (1960).

(12) H. E. Simmons, private communication.

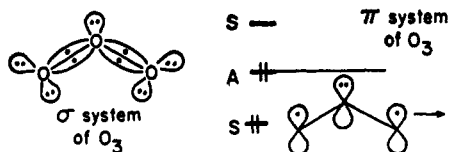


Figure 9. The electronic structure of ozone.

structure of ozone. Superimposed on a σ system of normal single bonds and lone pairs is an allylic π system into which must be placed four electrons.¹³ For all of these molecules a consequence of the resemblance to allyl anion is that they should reclose to their three-membered minima in a conrotatory fashion and that they should add in a concerted manner to π -electron systems with $4q + 2$ electrons. A further discussion of the selection rules for 1,3-dipolar addition will be given elsewhere,¹⁴ and an account of the electronic structure of cyclopropanone may be found at the end of this paper.

The existence of a trimethylene intermediate or an isoelectronic species has been seriously implicated in at least three areas. First this has come up in the broad area of 1,3-dipolar additions which formed the stimulus for this study. It seems to me that the conrotatory reclosure and the concerted addition to ethylenes make the identification of the experimentally inferred intermediate with the calculated geometry fairly clear. In the second instance, a trimethylene diradical has been the keystone of a consistent kinetic scheme for the structural and geometrical isomerization of cyclopropane.¹⁵ The suggestion of a diradical intermediate goes back to the first studies of this reaction, but the primary experimental facts are due to Rabinovitch and coworkers¹⁶ and the kinetic scheme was suggested by Benson.¹⁵ Is the trimethylene intermediate computed here identical with Benson's trimethylene? The geometry of Benson's trimethylene is not specified, but it is implied that the molecule has small barriers to internal rotation and that an activation energy of approximately 10 kcal is needed to effect the reclosure to cyclopropane. Its estimated heat of formation puts it 54 kcal/mol above cyclopropane. The trimethylene intermediate calculated here is 44 kcal/mol less stable than cyclopropane and has a calculated activation energy to reclosure of 1 kcal and a barrier to internal rotation of a single terminal methylene group of about 10 kcal. In view of the poor quality of the calculations it seems to me that the differences are not drastic, and I would like to identify the potential minimum calculated here with Benson's suggested trimethylene intermediate with the reservation that some confidence is felt in the calculated existence of sizable rotation barriers in the molecule.

In the third instance it has been suggested that a trimethylene intervenes in the stereospecific addition of singlet methylene to ethylene.¹⁷ The next section describes our results on this reaction.

(13) See A. D. Walsh, *J. Chem. Soc.*, 2266 (1953), for a discussion of the electronic structure of ozone.

(14) R. Hoffmann and R. B. Woodward, to be published.

(15) S. W. Benson, *J. Chem. Phys.*, **34**, 521 (1961).

(16) B. S. Rabinovitch, E. W. Schlag, and K. B. Wiberg, *ibid.*, **28**, 504 (1958).

(17) W. B. De More and S. W. Benson, *Advan. Photochem.*, **2**, 219 (1964).

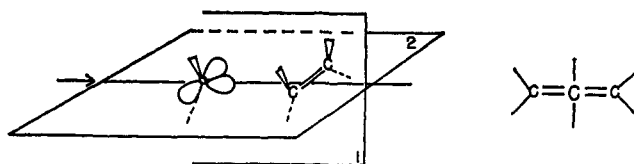


Figure 10. The most symmetrical approach of a methylene to an ethylene.

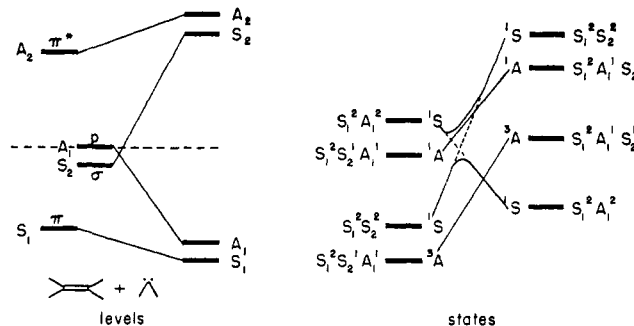


Figure 11. Level and state correlation diagrams for the approach of Figure 10. Since all the levels considered are symmetric with respect to reflection in plane 2, the symmetry designations are noted only for plane 1.

The Addition of Methylene to Ethylene

Figure 10 shows the most symmetrical transition state in the approach of a bent methylene to an ethylene. This transition state possesses C_{2v} symmetry and is closest in geometry to the addition product, cyclopropane. A correlation diagram for levels and states in the C_{2v} approach is drawn in Figure 11. Since all the orbitals involved in the reaction are symmetric with respect to reflection in plane 2, only the symmetry with respect to reflection in plane 1 is used in classifying states. The methylene p orbital has been placed at the nonbonding level and the methylene σ orbital below it, but above the ethylene π level, since we estimate that in ethylene the π level lies perhaps 2.5 eV below nonbonding, while the methylene σ is no more than 1.5 eV in one electron energy below the p. Here and in what follows below I am assuming the reader is familiar with the problems associated with the electronic structure of methylene^{18,19}—a molecule whose ground state is a linear or nearly linear triplet, 3B_1 in C_{2v} or ${}^3\Sigma_g^-$ in $D_{\infty h}$, which arises from what we would call an excited configuration $\sigma^1 p^1$ (see Figure 12). The lowest singlet, thought to lie considerably less than 1 eV above the ground-state triplet, is that of the ground electronic configuration $\sigma^2, {}^1A_1$. The singlet component of the excited configuration, ${}^1B_1, \sigma^1 p^1$, lies about 0.88 eV above the lowest singlet.

Following our previous interpretations of such correlation diagrams as that of Figure 11 we would conclude that the most symmetrical addition is a forbidden process for the σ^2 configuration but an allowed one for $\sigma^1 p^1$. In other words if the singlet addition is an observed process, as it certainly is, it should not occur in this highly symmetrical manner but in some unsymmetrical manner. This prompted a detailed exploration of various geometry approaches of methylene to ethylene.

(18) G. Herzberg, *Proc. Roy. Soc., Ser. A*, **262**, 291 (1961).

(19) P. P. Gaspar and G. S. Hammond in "Carbene Chemistry," W. Kirmse, Ed., Academic Press Inc., New York, N. Y., 1964, p 235.

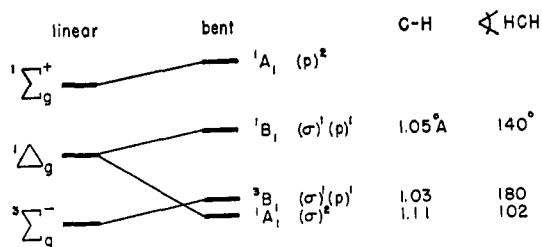


Figure 12. Some experimental molecular parameters for the lower methylene states. The parent configurations are also indicated. For uncertainties in experimental parameters see the original references.

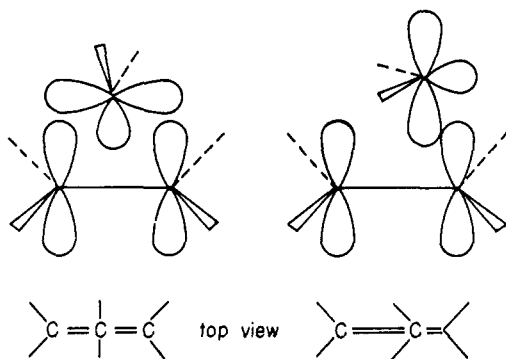


Figure 13. Two geometries of approach of a methylene to an ethylene. At left σ ; at right π .

Two extreme geometries of approach are illustrated in Figure 13. In the σ approach the σ orbital of the methylene impinges on the ethylene π system and the methylene hydrogens are in a position already close to that of the hydrogens in the product cyclopropane. In the π approach the approaching methylene lies in a plane parallel to the ethylene plane, *i.e.*, the p orbital of the methylene impinges on the π system of the ethylene. The correlation diagram of Figure 11 implies that the most symmetrical σ approach is not likely, and that an approach with less symmetry than C_{2v} should be favored. But it says nothing about the relative merits of various less symmetrical reaction paths, *e.g.*, an unsymmetrical σ approach with the axis of the CH_2 initially over a carbon of the ethylene *vs.* a π approach, both of C_s symmetry. The detailed exploration of the potential surface assumed a fixed ethylene and methylene geometry. Some preliminary calculations showed that the methylene carbon moved in the plane perpendicular to the ethylene and containing the ethylene carbons. This left five degrees of freedom in specifying the approach: a distance R and angle θ to locate the methylene carbon with respect to some reference point in the ethylene, and three Euler angles ϕ' , θ' , ψ' to specify the orientation in space of the methylene. These are shown in Figure 14. What we have called a σ approach would be one with $\theta' = 0$, a π approach one with $\theta' = 90^\circ$. We do not have the resources to study the complete potential surface so we will present only the reaction path—the line of minimum energy. Even this is not uniquely defined, for the reaction path varies according to the choice made for the origin from which R is measured. If the location of the ethylene is given by Cartesian coordinates, (0, ± 0.67 , 0) for the carbons, (± 0.952627 , ± 1.22 , 0) for the hydro-

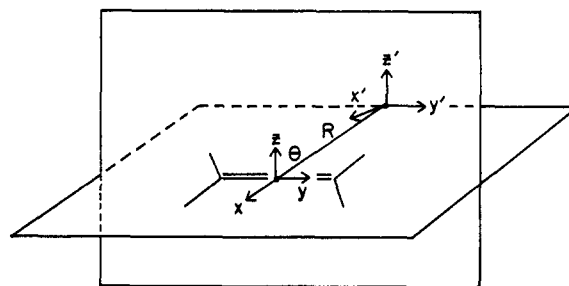


Figure 14. Definition of variables in search of methylene + ethylene potential surface. The origin is taken here at the midpoint of the ethylene (case a) and spherical coordinates R and θ are used to locate the CH_2 carbon (ϕ is not needed since the CH_2 carbon always remains in the perpendicular plane.) Euler angles ϕ' , θ' , ψ' are defined in the x' , y' , z' system using the convention of H. Goldstein, "Classical Mechanics," Addison-Wesley, Inc., Reading, Pa., 1950, p 106.

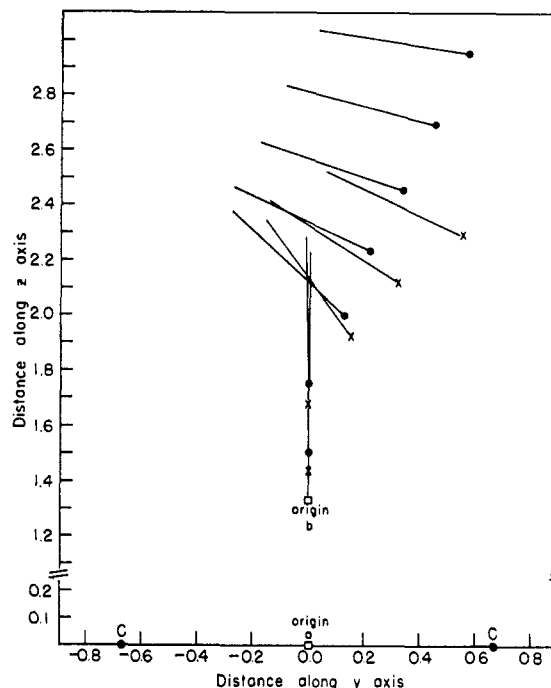


Figure 15. A projection of the favored reaction path on the vertical plane of Figure 14. The C atoms of the ethylene are at (0, ± 0.67 , 0). The filled circles refer to motion with origin at "a," the crosses to an origin at "b." At each R the minimum θ and θ' should be found to within $\pm 1^\circ$. The lines ending in circles or crosses represent the projection of the C-H bonds of CH_2 on the yz plane. Note the interrupted z axis.

gens, then two logical origins for R are (a) the center of the ethylene (0,0,0) and (b) a point near where the methylene group has to end up, *e.g.*, (0,0,1.33368). The calculations show that along each of these reaction paths $\phi' = \psi' = 0$. Thus the path is completely specified by R , θ , θ' . Figure 15 shows the interesting segment of the reaction path, specifically the projection of all atoms on the yz plane for reaction paths a and b. Note the difference between a and b.

In words the reaction pathway computed can be described as follows. At large separation a π approach is favored, slightly off-center presumably as a result of steric interactions of the hydrogens. At short separation the above calculations are worthless since they do not allow the geometry changes necessary in the ethyl-

ene component to convert it into a part of the cyclopropane. But close in the geometry *must* be that of a ground-state cyclopropane, *i.e.*, a σ approach with $\theta = 0$. At intermediate distances the two extremes are connected by a decrease in θ , and a transition from a π to a σ approach, *i.e.*, from $\theta' = 90$ to 0° . What makes a π approach favorable at large separation can be attributed to the virtues of a three-orbital, two-electron transition state over a four-electron one—until the point is reached where there is so much to be gained from having the two new σ bonds formed at the same time that a transition to a σ approach is made. Or to put it in other words, there is a lot of energy to be gained by forming two bonds at the same time; eventually, therefore the optimum θ is never very great. But if θ is close to zero the σ approach is a forbidden one, meaning that there is a prohibitive electronic energy hill to traverse if one forces the reaction that way, and it is better to initiate a π approach. This is strikingly illustrated in Figure 16 where the σ approach is compared to the optimum calculated reaction path.

At this point it is worthwhile to remind the reader of the limitations of the numerical experiment that is being performed here. A potential surface for a chemical reaction of methylene and ethylene is being constructed using a semiempirical method which appears to be trustworthy for qualitative predictions but which is hardly infallible. Not only is there a question of the trustworthiness of the method, but even accepting its simulation of reality the exploration of all the degrees of freedom in this potential surface is out of the question. Each point on the surface consumed about 10 sec on a CDC 1604 computer, so since the focus of interest was the *approach* of the methylene to ethylene, the number of degrees of freedom was reduced to five or six. Even so the potential surface is not being explored, only the reaction path—the minimum of the energy valley for the reaction. Any pair of molecules may choose to effect the reaction in any peculiar way desired—what is being computed here is not a molecular collision but the potential surface on which such collisions may take their course. Perhaps the quantitative features of Figure 15 are not to be trusted, but experience with extended Hückel calculations leads one to accept the qualitative approach geometry obtained.

It should also be pointed out that the energy differences between the reaction path and deviations from it are sometimes small and naturally smaller at larger R . At $R = 3.00 \text{ \AA}$, path a, the minimum energy is -315.947 eV for a point with $\theta = 11.0^\circ$, $\theta' = 79.6^\circ$. For the same R some other computed points have the energies listed in Table II.

Table II

θ	ϕ'	θ'	ψ'	$E, \text{ eV}$
0	0	0	0	-315.593
0	0	0	90	-315.593
0	0	90	0	-315.942
0	90	90	0	-315.929

For the excited configuration of methylene ($^1,^3B_1$) approaching a ground-state ethylene the situation is somewhat more complex. At large separation a symmetrical σ approach is preferred ($\theta = \phi' = \theta' = \psi' = 0$),

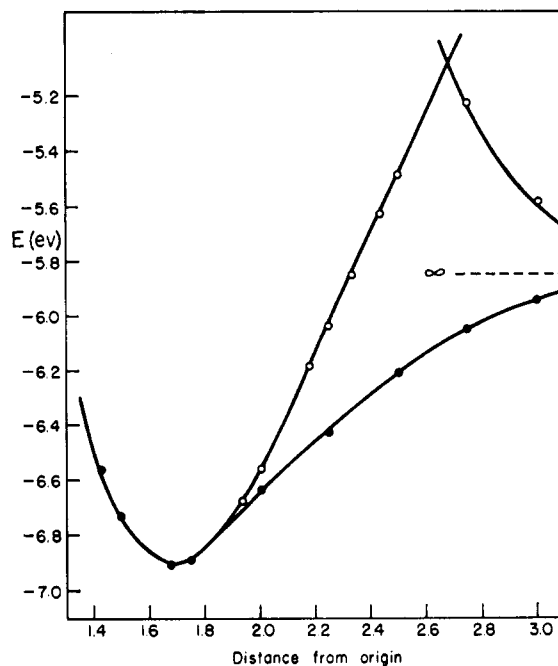


Figure 16. Energy along reaction coordinate measured from origin a (●) and along the symmetrical σ approach (○). The energy scale is with respect to an arbitrary zero.

as would have been anticipated from the correlation diagram. However this complex of an excited configuration of a methylene and a ground-state ethylene *must* correlate with an excited configuration of trimethylene or cyclopropane. As was shown in Table I our calculations give for that configuration a loose, floppy molecule with an open CCC angle, so that while the excited methylene begins its approach at $\theta = 0$ it proceeds by increasing θ until it is in the single loose minimum of the excited trimethylene. These calculations thus lead to the conclusion that insofar as the preservation of stereochemistry at the original ethylene fragment is concerned, the addition of the lowest 1A_1 of methylene should be stereospecific (but unsymmetrical) while the addition of triplet or singlet B_1 methylene should be nonstereospecific. Spin has not entered this argument and we will return to that momentarily.

As for the geometry of the 1A_1 methylene approach, the conclusion reached here is in essence that originally made by Skell and coworkers in their important and original series of papers on carbene reactions.²⁰ They drew an initial π approach guided by the similarity in the selectivity of carbenes and carbonium ions. The same transition state has been discussed by Moore and coworkers.²¹ It remains difficult today to find unambiguous evidence arguing for or against these approach geometries.

As for the degree of specificity in methylene reactions, Skell argued that while it was possible for singlet (1A_1) methylene to form two bonds in a single, concerted, stereospecific, addition process, a triplet (3B_1) methylene attacking a singlet, ground-state ethylene could not produce in a concerted manner a ground-state cyclopropane but must give a triplet intermediate tri-

(20) P. S. Skell and A. Y. Garner, *J. Amer. Chem. Soc.*, **78**, 5430 (1956).

(21) W. R. Moore, W. R. Moser, and J. E. La Prade, *J. Org. Chem.*, **28**, 2200 (1963).

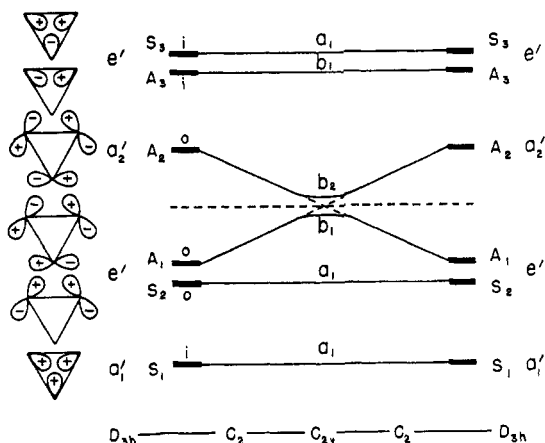


Figure 17. A correlation diagram for a twisting of a methylene group in cyclopropane. See text for notation.

methylene. In this diradical rotation about what would now be formal single bonds should be rapid and certainly competitive with the radiationless decay to a singlet. Thus one would account for the lack of stereospecificity in triplet addition.²⁰ This argument by Skell has proven most fruitful; it has also survived a good deal of criticism.^{19,22,23}

Though the conclusions regarding the stereospecificity of the observed methylene additions are the same here and in Skell's argument, the reasons for these conclusions are quite distinct. In Skell's explanation one focuses on the spin state of the methylene, singlet or triplet. In the argument presented here one emphasizes the spatial part of the wave function. The 1A_1 adds stereospecifically not because it is a singlet but because it can correlate with the lowest singlet configuration of a trimethylene and thus with the ground state of a cyclopropane. The 3B_1 methylene adds nonstereospecifically not because it is a triplet but because the complex of it and a ground-state ethylene must correlate with a triplet state of an excited configuration of the trimethylene, one in which there are no barriers to rotation around terminal bonds. The 1B_1 methylene must also correlate with a singlet state of the same excited configuration, and should also add without retention of stereochemistry, even though it is a singlet. The prediction of nonstereospecific addition of 1B_1 methylene is perhaps the only different conclusion which one would draw from these calculations, though it is not clear that Skell's hypothesis would in fact necessitate stereospecific addition of an excited singlet. At any rate this prediction is hardly a readily verifiable one; even if we had a source of 1B_1 methylene separated from 1A_1 and 3B_1 the resultant trimethylene would be an extremely "hot" species and any nonstereospecificity could probably be equally well attributed to the high excitation.

Clearly these calculations agree with the basic conclusions of Skell that the addition of 1A_1 methylene while initially unsymmetrical is a concerted process which does not proceed through an intermediate, and that the addition of 3B_1 methylene proceeds through an intermediate. While there is an intermediate on the ground trimethylene potential surface, I do not think

(22) H. M. Frey, "Progress in Reaction Kinetics," Vol. 2, G. Porter, Ed., Pergamon Press Inc., New York, N. Y., 1964, p 131.

(23) B. J. Herold and P. P. Gaspar, *Fortschr. Chem. Forsch.*, **5**, 89 (1965).

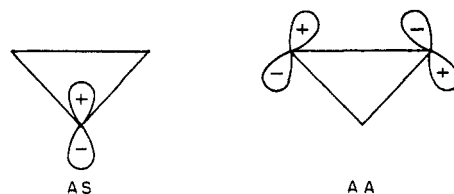


Figure 18. The $b_2(AA)$ and $b_1(AS)$ levels of a C_{2v} twisted transition state.

it is involved in the addition reaction because it is too far removed in structure from either reactants or products and because all stereochemical information would be lost if in fact the addition went through this intermediate. Moreover the reaction path traced in the calculated potential energy surface has no activation energy and yet easily bypasses the trimethylene intermediate potential valley. These conclusions are thus in contrast with the opinion of De More and Benson¹⁷ who feel that in the addition of singlet methylene to ethylene there must be involved the same trimethylene intermediate that intervenes in the geometrical and structural isomerizations. The kinetic parameters they adduce explain the stereospecificity by having the rate of reclosure of the diradical to cyclopropane faster than the rate of rotation around the trimethylene C-C bonds.

A suggestion has also been made that in the additions of 3B_1 methylene to ethylene the lowest triplet of cyclopropane is initially formed.²⁴ This is in accord with our calculations which say that the lowest triplet state of cyclopropane does not retain the cyclopropane geometry but is in fact the lowest triplet (and probable ground state) of trimethylene.

One Mechanism for the Isomerization of Cyclopropanes

At one time a simple mechanism for *cis-trans* isomerization of cyclopropane had been suggested in the literature, in which a single methylene group rotated in place proceeding from D_{3h} through C_2 to a C_{2v} transition state in which the methylene group was symmetrically located in the plane of the three carbons of the ring.²⁵ It was also suggested that an unsymmetrical (C_s) motion from the C_{2v} geometry could lead to the propylene isomerization. This transition-state proposal was criticized¹⁵ and did not gain support; it is nevertheless of interest to reexamine part of it with the methods at disposal here. Figure 17 is a correlation diagram which traces what happens to the six Walsh orbitals in cyclopropane under such a motion. The proper linear combinations for the reduction of symmetry to C_2 are shown; their initial ordering and their disposition in the transition state are taken from an extended Hückel calculation. The sp^2 hybrids pointing into the center of the cyclopropane ring are labeled "i"; the peripheral p-orbital combinations "o." The following considerations make the construction of the correlation diagram understandable: (1) all the i orbitals (S_1 , A_3 , S_3) are not affected by the rotation in the first approximation; (2) S_2 is also not much affected since it initially has no contribution at C_1 ; (3) A_1 is 1-2, 1-3 bonding, so it is destabilized by the rotation; A_2 is 1-2, 1-3 antibonding

(24) J. A. Bell, *J. Amer. Chem. Soc.*, **87**, 4996 (1965); R. F. W. Bader and J. I. Generosa, *Can. J. Chem.*, **43**, 1631 (1965); see also R. J. Cvetanovic, H. E. Avery, and R. S. Irwin, *J. Chem. Phys.*, **46**, 1993 (1967).

(25) F. T. Smith, *ibid.*, **29**, 235 (1958).

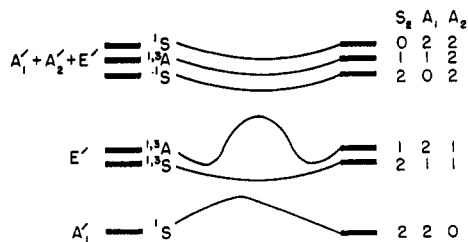


Figure 19. The state correlation diagram for the twisting of a methylene group.

and is stabilized by the motion; (4) formally, a rotation takes A_1 into A_2 and *vice versa*, and the C_{2v} transition-state symmetry allows a crossing there. In fact in the C_{2v} transition state the AS and AA levels have widely different compositions and energies. They are shown in Figure 18. AA should be at higher energy because it is 2-3 antibonding. The actual energies for C-C distances kept as in cyclopropane are AS at -10.906 eV, AA at -8.154 eV. The calculated energy of this transition state is 4.19 eV above cyclopropane. Energy may be gained by pulling the rotating CH_2 group away from the rest of the molecule but it is difficult to see how this would be consistent with a possible transition state leading to propylene isomerization where in fact either the C_1-C_2 or C_1-C_3 bond must become a double bond. Also pulling a CH_2 group away would seem to be heading down the road to a methylene plus ethylene rather than back to cyclopropane. Figure 19 shows the state correlation diagram for this motion. The excited states of cyclopropane nearly all prefer the twisting motion but in fact still better turn out to be a simple bond stretching in one bond. One amusing feature is that one level, $1,^3A$ in C_2 , has a double minimum potential curve with a preferred equilibrium geometry of C_2 rather than D_{3h} or C_{2v} .

According to these calculations this would also then appear to be an energetically unfavorable thermal isomerization mechanism. It is however worthwhile to point out that such a rotation does not do such violence to the electronic structure of the molecule as might have been naively expected. The peculiarity of the electronic structure of cyclopropane, so nicely described by the Walsh model, leads to the equivalent of only one bond being broken in the rotation, not two; notice how only A_1 and not S_1 or S_2 are affected by the motion. We hope to return to a more detailed examination of the isomerization to propylene soon.

Cyclopropanone

The preceding discussion noted that whereas 1,3 dipoles isoelectronic with trimethylene underwent 1,2 cycloadditions, cyclopropanone, in the few cases studied, preferred a 1,4 cycloaddition.^{4,26-28} This implied a fundamental difference between trimethylene and the ring-opened cyclopropanone. Since recent work has led to clearer isolation of this molecule²⁸ it became of interest to examine its electronic structure.

Assuming a C=O distance of 1.20 Å and a C-C distance of 1.50 Å some sections through a potential surface

(26) R. C. Cookson, M. J. Nye, and G. Subrahmanyam, *J. Chem. Soc., Sect. C*, 473 (1967).

(27) A. W. Fort, *J. Amer. Chem. Soc.*, **84**, 2620, 2625, 4979 (1962).

(28) N. J. Turro and W. B. Hammond, *ibid.*, **87**, 3258 (1965); **88**, 3672 (1966); N. B. Hammond and N. J. Turro, *ibid.*, **88**, 2880 (1966).

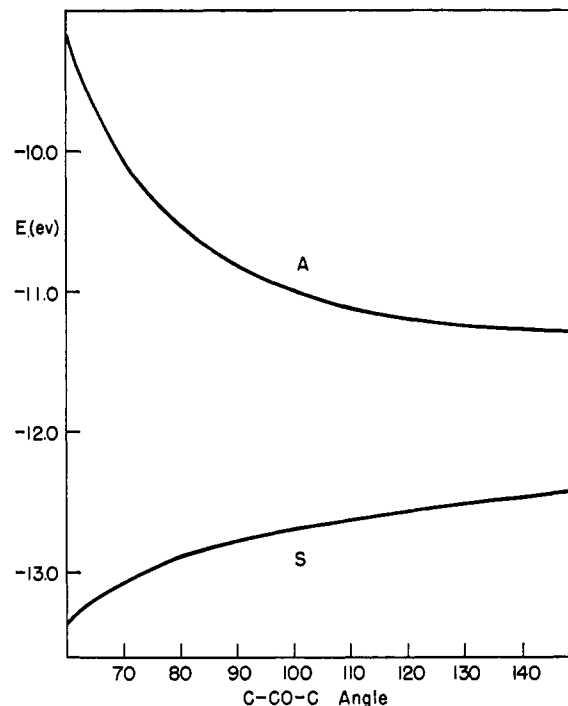


Figure 20. Energy of S and A levels of a 0,0 trigonal cyclopropanone as a function of bending.

face of cyclopropanone very similar to those studied for trimethylene were taken. The results are shown in Table III; the column headings are references to geometrical configurations of the terminal methylenes that were defined in Figure 1.

Table III. Sections through a CH_2COCH_2 Potential Surface^a

Angle CCC, deg	Ground configuration			Excited configuration		
	0,0	0,90	90,90	0,0	0,90	90,90
60	11.840	4.801	1.827	13.193	8.195	4.979
70	9.449	2.918	0.811	9.681	6.625	4.269
80	4.300	1.891	0.586	5.643	4.676	3.777
90	1.763	1.336	0.723	3.461	3.179	3.606
100	0.633	1.005	0.998	2.306	2.330	3.079
110	0.145	0.809	1.317	1.636	1.873	2.560
120	0.001	0.737	1.663	1.365	1.684	2.349
130	0.092	0.796	2.050	1.360	1.710	2.368
140	0.383	0.989	2.498	1.571	1.928	2.575
150	0.872	1.317	2.884	1.987	2.333	2.956

^a The geometries are defined in Figure 1 and the entries are energies in electron volts measured from an arbitrary zero of energy at the most stable point in the system, (0,0) at a CCC angle of 121.1°.

The general features of the surface are similar to those of trimethylene. There is now a much deeper minimum in the ground configuration, for a 0,0 geometry and a CCC angle of around 121°. The excited configuration is conformationally fairly stable in contrast to the floppy trimethylene.

The interesting and anticipated difference here is that in the ring-opened intermediate (which we will call *oxyallyl*) the symmetric S level is lower than A. The splitting is quite pronounced, and Figure 20 shows that the S level is lower at all CCC angles. The immediate consequence of this electronic structure is that oxyallyl

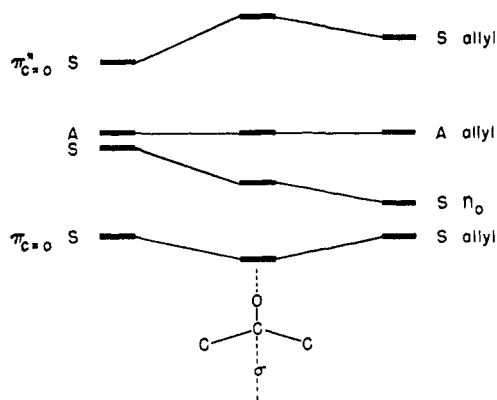
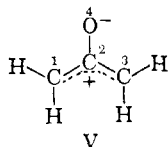


Figure 21. Two ways of rationalizing the ordering of levels in oxyallyl. On the left is the interaction of a carbonyl π and π^* with two nonbonding orbitals. On the right is the mixing of an allyl system with an oxygen p orbital.

should collapse to cyclopropanone in a disrotatory manner and add in a concerted fashion 1,4 (or 1,8, etc.).²⁹ The preference for the disrotatory closing has been checked directly by an extended Hückel calculation.

The simplest way to explain this behavior contrasted to that of trimethylene is just to say that a good valence bond representation of this species is given by the resonance structure V below, and that the characteristic modes of reaction that ensue are just those of an allyl



cation. A more direct way to see this is to draw an interaction diagram (Figure 21) for the mixing of carbonyl π and π^* levels with our S and A combinations. The carbonyl levels are both of S symmetry, but it is important to note that the energy center of gravity of the C=O double bond is below the energy of a 2p electron on carbon, *i.e.*, the C=O π^* is relatively low lying and therefore interacts most strongly with the S combination, pushing it down in energy. Another way to obtain the same level order is to allow the interaction of an allyl system with an oxygen 2p orbital, also shown in Figure 21.

The Pariser–Parr–Pople SCF procedure to be described later on in this paper gives the molecular orbitals of Table IV. The correlation diagrams for the closures

Table IV. SCF Orbitals and One-Electron Energies for Oxyallyl^a

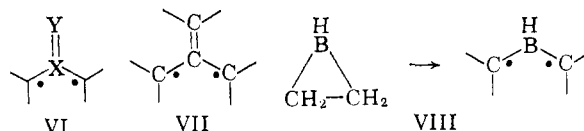
	1	2	3	4
E_i (eV)	-14.913	-9.540	-3.379	+2.604
C_1	0.3194	0.5387	0.7071	0.3283
C_2	0.6185	0.1078	0	0.7784
C_3	0.3194	0.5387	-0.7071	-0.3283
C_4	0.6431	-0.6387	0	-0.4225

^a The AO ordering is given in structure V.

and cycloadditions which lead to the above predictions are then simple to construct. It should of course be

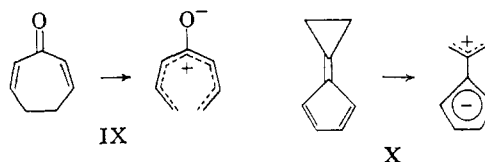
(29) R. B. Woodward and R. Hoffmann, *J. Amer. Chem. Soc.*, **87**, 395 (1965); R. Hoffmann and R. B. Woodward, *ibid.*, **87**, 2046 (1965).

mentioned that there is nothing original about oxyallyl, the “dipolar” or “zwitterion” form of cyclopropanone. It has a long history as a possible intermediate in the Favorskii rearrangement^{30,31} and has been discussed theoretically before.³² It would appear in general that for the molecule VI S would come below A if X=Y had a low-lying π^* level, A below S if X=Y had a high lying π level. The case when X=Y becomes C=CH₂ is the trimethylenemethyl radical VII which for a perfectly symmetrical structure has a degenerate central level pair. A two-electron system like that of allyl cation can also result if the central atom contributes no electrons to the π system; *e.g.*, the hypothetical borane VIII.



Whereas trimethylene is a small valley on the hillside leading to the much deeper cyclopropane minimum, Table III shows that oxyallyl lies in a most deep potential well. Assuming model geometries for classical cyclopropanone and allene epoxide, the extended Hückel calculations result in a cyclopropanone 1.0 eV less stable than oxyallyl, and an allene epoxide structure 0.9 eV less stable than oxyallyl. A careful examination of the potential surface connecting these molecules shows no activation energy for the conversion of cyclopropanone to oxyallyl.

These are of course approximate calculations, sometimes unreliable. Can they be trusted in this instance? The physical evidence for cyclopropanones appears unambiguous.^{28,33} It may be that the result that oxyallyl is more stable than cyclopropanone is reliable, but that the calculations are incorrect in exhibiting no activation energy for the interconversion. We are engaged in some further, more rigorous, calculations on this problem. We also intend to examine the possible stability of ring-opened forms IX and X.



Since the splitting between S and A levels in the optimum geometry of oxyallyl is quite large, it was considered important to inquire if the ground state of oxyallyl could possibly be a singlet and not the anticipated triplet.

To do this a Pariser–Parr–Pople SCF–CI calculation was carried out on the π electrons of this molecule, at a CCC angle of 120°, C–O 1.20, C–C 1.50 Å. The details of the method are described elsewhere.³⁴ We in-

(30) References to the earlier literature may be found in a review by A. S. Kende, *Org. Reactions*, **11**, 261 (1960).

(31) (a) G. Stork and I. Borowitz, *J. Amer. Chem. Soc.*, **82**, 4307 (1960); (b) H. O. House and W. Gilmore, *ibid.*, **83**, 3972, 3980 (1961); H. O. House and W. Thompson, *J. Org. Chem.*, **28**, 164 (1963); (c) E. Smismann, E. Lemke, and O. Kristiansen, *J. Amer. Chem. Soc.*, **88**, 334 (1966).

(32) J. G. Burr, Jr., and M. J. S. Dewar, *J. Chem. Soc.*, 1201 (1954).

(33) J. F. Pazos and F. D. Greene, *J. Amer. Chem. Soc.*, **89**, 1030 (1967).

(34) R. Hoffmann, A. Imamura, and G. D. Zeiss, *ibid.*, **89**, 5215 (1967).

cluded all configurations in the configuration interaction treatment and obtained the ordering of levels in Table V. It should of course be kept in mind that these are

Table V. SCF-CI Results on Oxyallyl^a

¹ A ₁	4.136 ^b	¹ A ₁	0.112 ^b
¹ B ₁	1.967	³ B ₁	[0.0]

^a The states are labeled in C_{2v} symmetry, with the *xz* plane being that of the molecule. ^b In electron volts.

π -electron states only. In particular (*n*, π^*) excited states may arise at low energy in this molecule, but we have no reliable way to estimate their position. The ¹A₁ states are strong mixtures of the (S₁)²(S₂)² and (S₁)²-

(A₁)² configurations of Figure 21 while ¹B₁ and ³B₁ represent predominantly the (S₁)²(S₂)¹(A₁)¹ configuration. ³B₁ is the molecular ground state, but the singlet is not far above it in energy.

Acknowledgment. I am grateful to H. E. Simmons, R. J. Crawford, and R. B. Woodward for discussions concerning this work, and to A. Imamura, P. Clark, W. J. Hehre, and G. D. Zeiss for assistance with the calculations. The minimum searching methods used in exploring the approach of methylene to ethylene are due to K. D. Gibson. Motivation for a good part of this work was found in the interesting studies of R. C. Cookson. Generous support was provided by the Chevron Research Company, the Sloan Foundation, the National Institutes of Health, and the National Science Foundation.

The Electronic Structure of Methylenes

Ronald Hoffmann, Geoffrey D. Zeiss, and George W. Van Dine

Contribution from the Department of Chemistry, Cornell University, Ithaca, New York 14850. Received May 31, 1967

Abstract: LCAO MO calculations of the extended Hückel type are carried out on methylene and methyl-, dimethyl-, phenyl-, diphenyl-, vinyl-, formyl-, nitro-, cyclopropyl-, cyano-, dicyano-, fluoro-, difluoro-, chloro-, dichloro-, bromo-, dibromo-, trifluoromethyl-, and methoxymethylene. We have concentrated on the equilibrium geometries and distortions of the configurations which will give rise to the lowest singlet and triplet states of these molecules. Let us denote by σ the bent methylene in-plane orbital, by *p* the out-of-plane orbital. The configuration σp from which will be derived the lowest triplet (and probable ground state) of these methylenes is bent for all molecules except the cyanomethylenes. The σp minima are deep only for some of the halocarbenes and methoxymethylene. Where a π -electron system is attached to the carbene, the σp configuration prefers to bend in-plane. Diphenylcarbene has a most complicated potential surface with the optimum σp geometry for a bent and twisted C₂ molecule. The lowest singlet potential surfaces have more features still. With respect to in-plane bending there may arise one (formyl), two (alkyl, cyclopropyl), or three (vinyl, phenyl) minima and one of the three in the latter case may be a saddle point unstable with respect to out-of-plane bending. Or the molecule may prefer to bend out-of-plane (nitro). The features of these surfaces are predictable if one knows the relative energy of the two *p* orbitals of the "linear" geometry of the methylene. An analysis of the location of these levels in terms of the molecular orbitals of the substituents is presented.

In this paper we present the results of extended Hückel calculations on methylene and several of its substituted derivatives. Our object in making these calculation is to shed some light on the preferred conformation and electronic structure of the ground and first excited electronic configuration of these molecules.

It must be made clear at the outset that the extended Hückel calculations do not include electron interaction, and as such yield at best an estimate of the average energy of a configuration. They thus do not distinguish between a singlet and triplet state of a given spatial symmetry. In calculations on methylenes this is a particularly significant restriction and so we would like to elaborate on the electronic structure of methylenes, our notation, and precisely what we are and are not calculating.

For methylene itself, CH₂, the ground state has been assigned by Herzberg¹ as ³ Σ_g^- , linear or nearly linear (the corresponding bent symmetry designation is ³B₁ in

C_{2v}). At an undetermined but small energy above this state lies the lowest singlet, a C_{2v}¹A₁ with an HCH angle of 102.4°. Some 2.0 eV above this lies a ¹B₁, also bent, with HCH angle 140 ± 15°. Another 1.5 eV higher lies an unanalyzed ¹A₁ state. Theoretically it is clear that a linear methylene would have two perpendicular 2*p* orbitals (π_u in D_{∞h}) into which two electrons are to be placed. This gives rise to three states, arranged in order of likely increasing energy as ³ Σ_g^- , ¹ Δ_g , ¹ Σ_g^+ . On bending from D_{∞h} to C_{2v} geometry, one of the 2*p* orbitals, the one perpendicular to the plane in which the bending takes place, is to first order unaffected by the bending. This orbital transforms as *b*₁ in C_{2v} and in the subsequent discussion will be referred to as simply "p." The other *p* orbital, *a*₁ in C_{2v} symmetry, mixes with the corresponding symmetry 2*s* orbital on carbon (as well as with a 1*s* H combination and 1*s* on C). As a result of this mixing it is stabilized in energy ("it acquires *s* character"). We will refer to this

(1) G. Herzberg, *Proc. Roy. Soc., Ser. A*, **262**, 291 (1961).

(2) G. Herzberg and J. W. C. Johns, *ibid.*, **295**, 107 (1966).