Cyclic Allenes. 2. The Conversion of Cyclopropylidenes to Allenes. A Simplex–INDO Study

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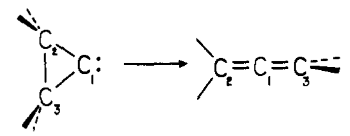
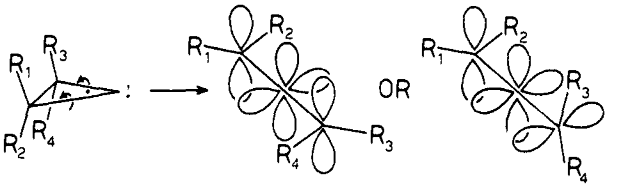
Abstract: The ring opening reaction of both singlet and triplet cyclopropylidene has been studied theoretically. The inadequacy of correlation diagrams as applied to this problem is discussed and the reaction is studied first with severe geometrical restrictions and then with little restriction. The equivalence of the conrotatory, disrotatory, and monorotatory energy surfaces at the nonrotatory axis is pointed out, and from the attachment of the three surfaces it is possible to predict the course of the complex reaction with a substantial degree of accuracy. The theoretically derived reaction pathway accounts for all experimental observations. The Simplex geometry optimization procedure is outlined in the Appendix as an efficient method for optimization of molecular geometries and for following chemical reactions. Some of the difficulties involved in following reaction pathways without prior knowledge of the location of the transition state are illustrated.

The preparation of allenes by the ring opening of cyclopropylidenes (or the corresponding carbenoids) has been used widely in the synthesis of both cyclic[2-6] and acyclic[2,6-8] allenes since the reaction was first reported by Doering[9] in 1958.[10]

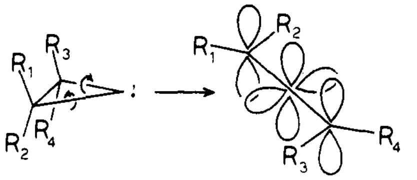


In principle there are four basic modes of ring opening which are accessible to this reaction:

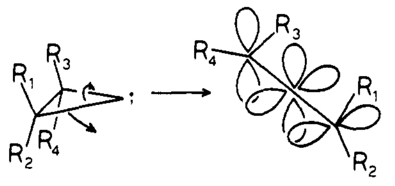
(1) A conrotatory opening leading either to an orthogonal[12] or a planar[13] allene



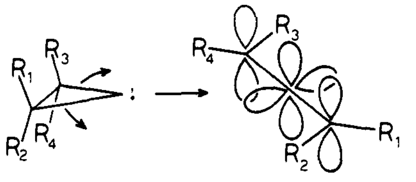
(2) A disrotatory opening to give a planar allene



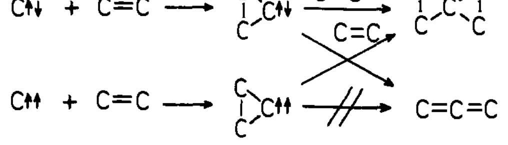
(3) A "monorotatory" opening to give an orthogonal allene



(4) A "nonrotatory" opening to give a planar allene

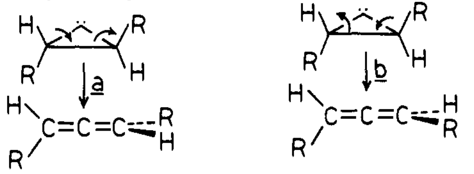


In 1967 Borden,[14] using correlation diagrams, suggested that singlet cyclopropylidene opened by the "monorotatory" mode described above and the triplet did not open at all. This suggestion appeared to be supported by the reports[7,8l,15-17] that while olefins react with singlet carbon atoms to form allenes and spiropentanes, they form only spiropentanes with triplet carbon.[17,18] In both these reactions, cyclopropylidenes were proposed as intermediates:

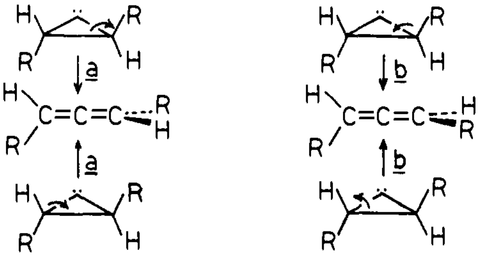


However, later investigations revealed that *no* spiropentanes were formed in the reactions involving triplet carbon[16] and it now appears possible that the triplet carbene was never formed during this reaction.

Dewar[19,20] has studied theoretically the reaction of a singlet carbon atom with ethylene using the MINDO/2 approximate method. These calculations indicate that the initial reaction produces singlet cyclopropylidene, which opens in a nonrotatory manner[19] to give a planar allene and subsequently undergoes internal rotation to yield as a final product normal, orthogonal allene. There is experimental evidence, however, that a planar allene cannot be an intermediate, at least in the formation of certain acyclic allenes. Thus, Jones[21-23] has reported that optically active *trans*-2,3-diphenylcyclopropylidene[24] opens to give optically active 1,3-diphenylallene and similar results have been obtained for active *trans*-2,3-dimethyl-,[22,23] 2,3-dibutyl-,[22] and 2,3-diethylcyclopropylidene.[22] Jones[25] interpreted these results in terms of steric control of a conrotatory ring opening:



with path a being preferred over path b for steric reasons. This interpretation is further supported by the assignment of absolute configurations to each of the enantiomers of 1,3-diphenylallene,[25] 1,3-dimethylallene,[24,26] and of their precursors.[22,24] These results could equally be rationalized in terms of steric control of monorotatory openings:



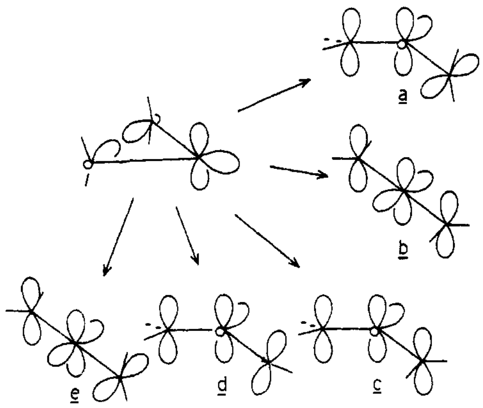
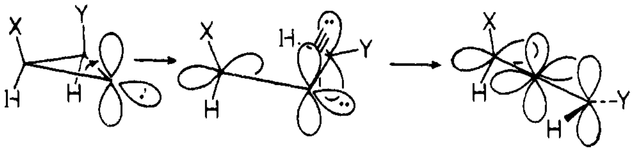


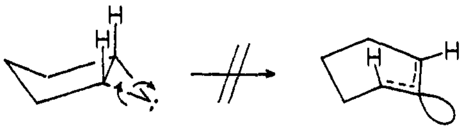
Figure 1. Possible initial product geometries formed during the isomerization of cyclopropylidene to allene: (a) bent orthogonal; (b) linear planar; (c) bent planar; (d) bent nonplanar; and (e) normal orthogonal allene.

with paths a being favored relative to paths b.[28,29]

Optically active cis-2,3-disubstituted cyclopropylidenes (unsymmetrical substitution) have also been shown to yield optically active allenes,[33] and in the cases investigated the resultant asymmetry did not appear to be derived from steric control. It was therefore suggested that a monorotatory opening occurred in which the rotating group supplied a pair of electrons to the vacant p orbital of the carbene,[33] i.e., electronic factors were proposed to determine which group would rotate.



This retention of optical activity precludes the intermediacy of any planar species, thus eliminating the disrotatory and nonrotatory ring opening modes, at least in the systems mentioned here.[34] On the other hand, monorotatory opening of 6-carbenabicyclo[3.1.0]hexane would lead to a geometrically impossible,[1a] orthogonal 1,2-cyclohexadiene. Similarly, conrotatory opening (to a planar allene) would give an impossibly strained transoid allene:



Therefore, in this case at least, it seems that the opening must proceed in a disrotatory or nonrotatory sense.

In view of the several modes of ring opening available to cyclopropylidene, the current interest in the subject, and the differing experimental and theoretical evidence for various modes in substituted cyclopropylidenes, it seemed an appropriate question for closer scrutiny and particularly for examination with the newly developed Simplex[37] technique for optimization of molecular geometries.

Results and Discussions

Correlation Diagrams. First, however, it is appropriate to discuss this question briefly with reference to the appropriate correlation diagrams. These diagrams, based upon the principle of conservation of molecular orbital symmetry,[41] have provided valuable insight into the intimate details of numerous molecular rearrangements, but are of limited utility in the present case. The reason for this is several-fold. First, the monorotatory mode, which at this point must be regarded as a serious contender for the ring opening process, conserves no element of molecular symmetry and is thus not amenable to an orbital symmetry treatment.

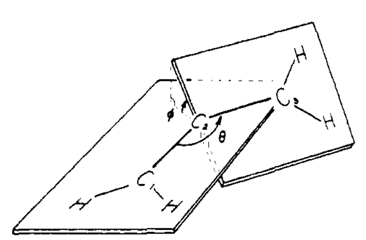


Figure 2. Definition of the angles θ and ϕ used throughout this work.

Second, the ordering of the energy levels in the products and in cyclopropylidene itself is not totally unambiguous and, depending on these orderings, different outcomes may be predicted. In cyclopropylidene, the relative ordering of the two nonbonding orbitals is presumably such that the pure p orbital, antisymmetric with respect to the plane of the molecule, is of higher energy than the symmetric orbital possessing considerable s character. If the initially formed product is a linear, orthogonal allene there is also little difficulty, but four alternative initial geometries must also be considered: (a) orthogonal bent; (b) planar linear; (c) planar bent; and (d) nonplanar bent. These are illustrated in Figure 1. In some of these the intuitive ordering is adequate, but in others recourse must be made to more sophisticated calculations. Even so, in most cases two or more of the crucial orbitals are so similar energetically that the distinction between allowedness and forbiddenness loses its clarity. Most importantly, however, it is under precisely these circumstances that subtleties such as a change in the ring opening mode might be expected to occur during the reaction. These changes cannot be revealed except in the most detailed analysis of the reaction pathway.

Energy Surfaces. A complete analysis of this problem would involve the calculation of a reaction surface with fifteen ($3n - 6$) geometrical variables and while this is certainly within our present capabilities it probably is unnecessary and wasteful of computer time. As shall be seen below, a moderately complete analysis of the reaction surfaces has been made, but we chose initially to carry out a series of exploratory calculations on geometries constrained so that potential surfaces could be prepared for each of the simple reaction modes (dis-, con-, mono-, and nonrotatory).[42]

Singlet Surfaces. Calculations for the conrotatory and disrotatory openings were carried out with the C(1)-C(2)-C(3) bond angle varying from 60 to 180° in steps of 30°. At each value of this angle (θ), calculations were made in which the dihedral angle (ϕ) between the plane of either methylene group and the plane of the three carbon atoms was varied from 0 to 90° in 15° increments. All other bond lengths and angles were kept constant[44] and the two methylene groups were rotated simultaneously so as to maintain the symmetry necessary for a disrotatory or conrotatory mode (see Figure 2).

Using only two variables it is possible to represent the energy surfaces as contour diagrams by projection onto a plane the two edges of which define the angles θ and ϕ. It is then seen that the diagrams for the conrotatory and disrotatory openings have a common edge (the θ axis, $\phi = 90°$) corresponding to nonrotatory opening. Consequently these three processes are represented in the same energy contour diagram in Figure 3.

In this diagram the geometry of cyclopropylidene is defined by the origin, O. Motion along the axes OM and ON are respectively disrotatory and conrotatory isomerization of cyclopropylidene without opening the C(2)-C(1)-C(3) angle. Motion along the OY axis represents a nonrotatory opening to a planar, linear allene Y, and motion along the edge YZ corresponds only to molecular rotation and not to any change in molecular geometry. The point P has a geometry corresponding to normal orthogonal allene.

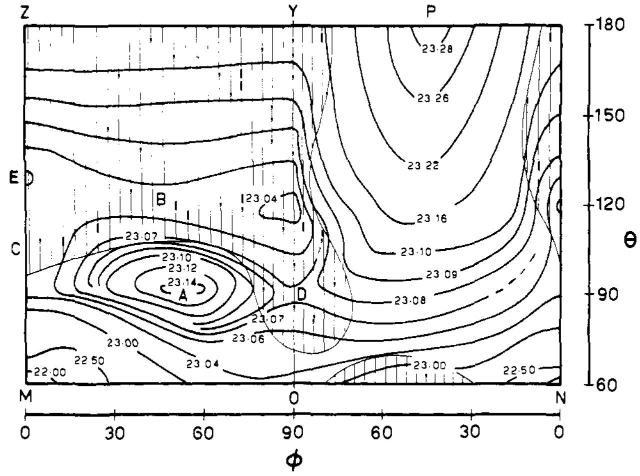


Figure 3, Energy contour diagram for the conrotatory, disrotatory, and nonrotatory openings of singlet cyclopropylidene. The energies are all negative and in atomic units. The left half of the figure represents disrotatory motion, the right side, conrotatory motion. The shaded portion defines the geometries in which the triplet is of lower energy than the singlet. See the text for a discussion of various features of this diagram.

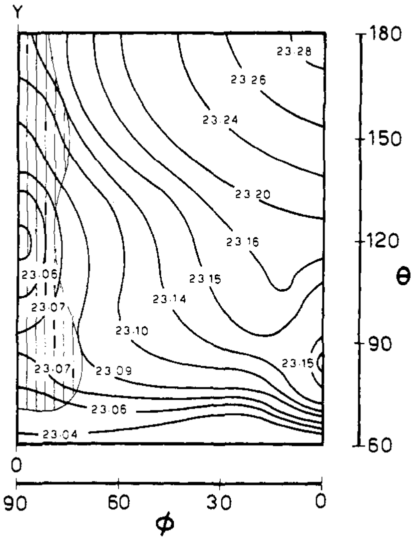


Figure 4, Energy contour diagram for the monorotatory opening of singlet cyclopropylidene. The energies are all negative and in atomic units. This diagram can be regarded as being perpendicular to Figure 3 and attached to it by superimposing the common lines OY, i.e., $\phi = 90°$. See the text for a discussion of the value of this operation.

From this crude energy surface we can make some interesting tentative observations which are substantiated by the more detailed calculations below. First there is no energy minimum at the point which corresponds to cyclopropylidene itself. While this could be taken as evidence for the absence of cyclopropylidene as an intermediate, we should stress that our geometric assumptions (both C–C bonds 1.31 Å and completely planar methylene carbons) substantially increase the energy of this species.[44] The nearest minimum is located at A, which corresponds to a cyclopropylidene partially opened in a disrotatory sense. This suggests that the initial opening of cyclopropylidene would favor the disrotatory mode.

From A, the reactive "intermediate" has three paths by which it might sensibly escape: via the saddle at C resulting in racemization of an optically active cyclopropylidene; via the saddle at B leading to a planar allene formed by a disrotatory opening; and finally by the lowest energy pathway over the saddle D, at which the two methylenes have returned to a nonrotated position, and down the hill to the perpendicular allene product P.

Evidently escape via the saddle at C has not been realized experimentally since, to our knowledge, no products derived unequivocally from a racemized cyclopropylidene have been reported. Some escape by this route and also over the saddle at B is possible, however, since in none of the reactions described earlier was the reaction 100% stereospecific.[48]

The most favored pathway indicated by these calculations, viz., O-A-D-P is interesting and fully compatible with the experimental data presently available,[5,21-23,25,27,33,35,36] though somewhat at variance with the calculations of Dewar et al.[19,20] which predicted that the path would be largely nonrotatory.

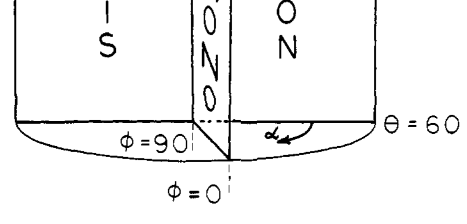
Our calculations outlined above indicate a change of ring opening mode during the reaction, that is, the reaction appears to be opening in a disrotatory sense (O → A), but reverses its motion (A → D) to yield a nonrotated transition state and then continues on to its product (D → P) in a conrotatory motion. The overall reaction thus appears to be conrotatory.

How does this apparent change of ring opening mode manifest itself in the relevant correlation diagrams? Put most simply, the key lies in the relative energies of the two nonbonding orbitals which make up the carbene site. An examination of the eigenvectors during this opening indicates that the symmetrical sp^x orbital, initially having a high degree of s character and therefore lower energy, causes a disrotatory opening to be allowed. However as the unique C–C–C bond angle increases, this orbital becomes less s-like and in fact at the saddle D ($\theta = 90°$) it is of ***higher*** energy than the antisymmetric "p" orbital—hence favoring a conrotatory opening for the remainder of the process.

Any conclusion as to the exact reaction path taken by the opening cyclopropylidene even with the severe geometrical constraints we have arbitrarily imposed[44] must take into account that the reacting species need not necessarily be symmetrical, i.e., not strictly conrotatory or disrotatory, but may include an unsymmetrical monorotatory mode or a spectrum of combinations in between. The monorotatory opening can be described adequately by the same variables θ and ϕ where the latter has the same definition as before except, of course, that it refers to the angle of rotation of only one of the methylenes; let us call it C_aH_2; the other methylene, C_bH_2, does not rotate throughout the entire process. The monorotatory energy contour diagram is shown in Figure 4. This figure also has an edge common to both the conrotatory and disrotatory diagrams, viz., the nonrotatory edge. It appears to be a trivial exercise, but in fact it is most constructive, to visualize this figure attached, and perpendicular to Figure 3, the line of intersection being the nonrotatory opening axis. Furthermore we can imagine this now as being the beginning of a solid of revolution about OY, the solid being made up of a series of planes each passing through OY and making an angle α with the conrotatory plane. In such an event, each point can be defined by three variables θ, ϕ, and α. θ has its previous significance, ϕ is the angle of rotation of C_aH_2, and α defines the degree of rotation of C_bH_2 such that

$$\phi(C_bH_2) = \phi(C_aH_2) \cos \alpha$$

both angles being measured in the conrotatory sense (i.e., $\phi(C_bH_2) = -\phi(C_aH_2)$ for a symmetrical disrotatory arrangement). Schematically, these operations are summarized as:



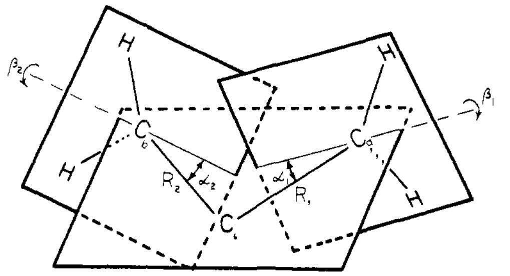


Figure 5. Definition of the independent variables permitted in all Simplex optimizations.

This cylinder of revolution now has a very distinct value: we can visualize, and if we wished could represent, all possible opening processes on one diagram. Actually without performing the calculations for any more planes in this solid, we can answer a most important question: Subject to the given approximations, does the opening proceed as described above, or does the species lose its symmetry and thus move out of the plane of Figure 3? The answer to this question is that the reaction does, most probably, leave the plane of Figure 3, and in the process loses all elements of symmetry.

The reasoning behind this conclusion is as follows: We can identify certain contour lines as defining equienergetic surfaces. Thus the contours of energy −23.07 au, all of which meet at the nonrotatory axis OY, must define the same curved surface of −23.07 au. Furthermore, it is either an unfortunate coincidence, or the lines of energy −23.08, −23.09, and −23.10 au also define, respectively, curved equienergetic surfaces cutting both planes. Thus, a reacting carbene, climbing out of the energy well at A, when it reaches the −23.10 au contour can explore this surface in the disrotatory, conrotatory, and monorotatory regions without having to go to the higher energy needed to pass through the nonrotatory state D. Furthermore from these diagrams, if progress from the disrotatory configuration through the monorotatory plane were to take place even approximately in the region of −23.1 au this conversion is indicated as taking place at the same time as the methylene C_aH_2 continues its forward motion, but without a substantial increase in the angle θ beyond 90–100°.

Following from this admitted speculation we examine the reaction more closely by placing more reasonable, less demanding constraints on the system and allowing substantially more degrees of freedom than the three discussed above. In the next set of calculations only two geometrical parameters were maintained constant: the H–C–H angles were 115° and the C–H bond lengths were 1.08 Å. The angle θ was increased in steps and at each value of θ the optimum combination of the following six variables was determined: (1) the angle between the bisector of the H–C_a–H angle and the C(1)–C_a bond, α_1; (2) the dihedral angle between the C_aH_2 group and the ring plane, β_1; (3) the angle between the bisector of the H–C_b–H angle and the C(1)–C_b bond, α_2; (4) the dihedral angle between the plane of the C_bH_2 group and the ring plane, β_2; (5) the C(1)–C bond distance, R_1; and (6) the C(1)–C_b bond distance, R_2. These variables are shown in Figure 5.

An iterative method, a modification of the Simplex algorithm,[49] was used to determine the optimum combination of these six variables. The object of this exercise was to optimize the geometry of cyclopropylidene by maintaining $\theta = 60°$ and finding that combination of geometric variables which yielded the minimum in energy, then, to increase the angle θ and reoptimize the geometry, and to keep repeating this process until θ was 180°, at which point one might hope to have followed completely the reaction path.

But there is a difficulty, and this is illustrated by reference to the simple hypothetical reaction defined precisely by the two variables R and S in the energy contour diagram of Figure 6.

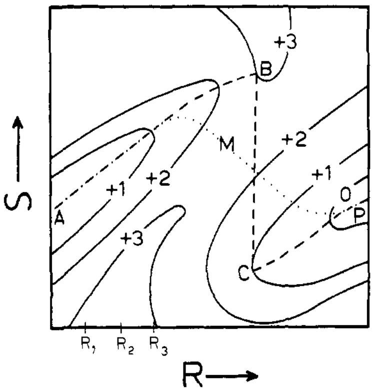


Figure 6. A hypothetical energy contour diagram for a reaction described precisely by two variables, R and S, but in which an increase in R does not adequately describe progress along the reaction coordinate. See text for a discussion of the significant points of this diagram.

This overall reaction shows little change in S and a gross change in R. The correct reaction pathway is given by A-M-P and the reaction coordinate then is the progress along this path. However, in order to calculate the reaction pathway without constructing a complete contour diagram one might be forgiven for optimizing the geometry at A, increasing R to R_1, reoptimizing the geometry, and repeating the process for R_2, R_3, . . . , R_p. But in doing this, we in fact do not follow the true reaction pathway. Instead we follow the path A-B-C-P and the only way in which we could have done this correctly would have been to know the location of the transition state first, and then to have worked away from it toward both the starting material and the product. This, of course, defeats the purpose of the exercise, since the location of the transition state would require the construction of something approaching a complete contour diagram. One may be fortunate, and if nature cooperates in such a way that increases in an obvious simple variable such as the C_a–C(1)–C_b bond angle of cyclopropylidene closely approximates progress along the reaction coordinate, it may be possible to obtain a reasonably accurate picture of how the reaction proceeds. Such would be the case in Figure 7.

There are two ways in which one can estimate the closeness with which the true reaction pathway has been followed. First, as is shown in Figure 6, a sudden change in energy, and/or a geometric variable, corresponding to a small increase in the parameter in question is a bad sign. This has been termed a "catastrophic collapse".[50,51] And second, if the reverse path is calculated in the same manner a good choice of reaction coordinate is indicated by identical forward and reverse pathways. Differing pathways, or chemical hysteresis,[50,55] demand that the choice has been imperfect, and the magnitude of the hysteresis is a measure of the inadequacy with which the reaction coordinate has been defined. It is emphasized, however, that catastrophic collapses and chemical hysteresis are merely the consequences of an unfortunate choice of the reaction coordinate and are not the hallmarks of a new type of nonclassical reaction surface or pathway as some may infer from the literature.[50]

In spite of these potential difficulties[56] and because the angle θ appeared adequately to describe the progress of the cyclopropylidene ring opening, we ventured to proceed, but with one precaution: the angle θ was increased from 60 to 180° then decreased again to 60°, thus executing a complete cycle: cyclopropylidene → allene → cyclopropylidene (see Table I).

The geometry of the species calculated at $\theta = 60°$ with these less stringent constraints was in good agreement with that expected for cyclopropylidene, having the planes of both methylenes almost perpendicular to the ring (total twist was 2.63° in a disrotatory sense[57]) and almost bisecting their respective C–C–C angles.[58] The C–C bond lengths were similar

Table I. The Variation, with the Angle θ, of the Six Independent Variables Defined in the Text and in Figure 5 for the Opening of Singlet Cyclopropylidene[a]

θ, deg	α_1, deg	β_1, deg	α_2, deg	β_2, deg	R_1, Å	R_2, Å	Energy[b]
60	35.88	91.93	36.10	89.30	1.469	1.457	25
72	15.72	118.15	15.31	63.10	1.388	1.387	36
84	8.83	126.33	6.00	50.10	1.346	1.345	65
90	4.00	131.43	7.27	46.01	1.329	1.342	83
96	8.83	123.83	0.97	35.10	1.346	1.345	97
108	9.92	93.59	−3.31	−2.59	1.323	1.326	74
120	8.73	89.55	−1.95	−5.02	1.312	1.323	55
126	11.80	96.09	−2.68	−3.84	1.323	1.326	45
144	9.00	96.88	−3.95	−6.10	1.314	1.316	20
150	5.30	93.55	−4.89	−3.64	1.309	1.306	15
162	7.12	99.38	−3.32	−7.35	1.314	1.316	5
173	5.25	101.88	−2.70	−8.60	1.314	1.316	1
180	3.73	98.55	−2.70	−5.52	1.309	1.306	0
176	3.37	104.38	−2.07	−9.85	1.314	1.316	0
165	3.37	103.38	−4.07	−12.85	1.311	1.299	4
150	4.52	97.96	−4.21	−7.90	1.310	1.313	14
140	4.56	107.25	−2.51	−13.55	1.314	1.315	26
120	6.39	100.46	−3.58	−9.14	1.310	1.313	56
115	7.99	107.25	0.93	−12.93	1.314	1.315	67
100	6.92	103.11	4.87	−10.87	1.319	1.331	84
90	8.17	94.36	6.44	1.00	1.319	1.331	79
80	8.64	88.48	2.97	−0.42	1.335	1.361	54
70	12.46	87.49	4.42	−1.04	1.360	1.407	50
60	21.23	92.36	14.12	2.36	1.425	1.454	72

[a] The lower entries (with decreasing θ) refer to the "reverse" reaction. [b] The energies are in kcal/mol above the 180° geometry which was −14 598 kcal/mol.

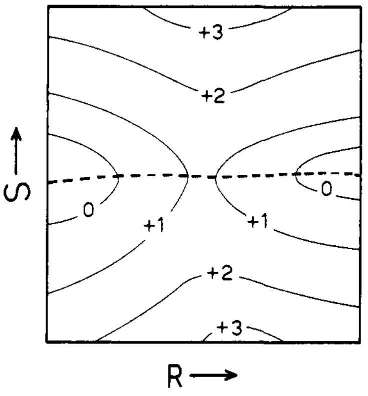


Figure 7. A hypothetical energy contour diagram for a reaction described precisely by two variables R and S, in which an increase in R is an adequate description of progress along the reaction coordinate.

(C(1)-C(2), 1.457; C(1)-C(3), 1.469; C(2)-C(3), 1.463 Å[59]) and the total energy of the system was 19 kcal/mol lower than that obtained using "expected" bond lengths and angles.[60]

As the angle θ was increased from 60 to 90° the methylene groups twisted in a disrotatory manner,[61] each methylene assuming a greater degree of planarity, the C–C bond lengths decreased appropriately, and the molecule maintained quite closely a σ plane of symmetry.

Increasing θ to 96° caused that methylene which had rotated least to reverse its direction of motion, while the other continued to twist in the same direction. Although a conrotatory *motion* had begun the static *geometry* was still of a disrotatory nature, but was far less symmetrical.[62] This molecule represented a maximum in energy and if assumed to be the transition state yielded $E_{\text{act}} = 72$ kcal/mol.[63]

As θ was increased further, the conrotatory motion continued rapidly, the molecule eventually attaining the orthogonal form with reasonable bond lengths and bond angles.[65] The variation of the total energy of the system with θ is shown in Figure 8.

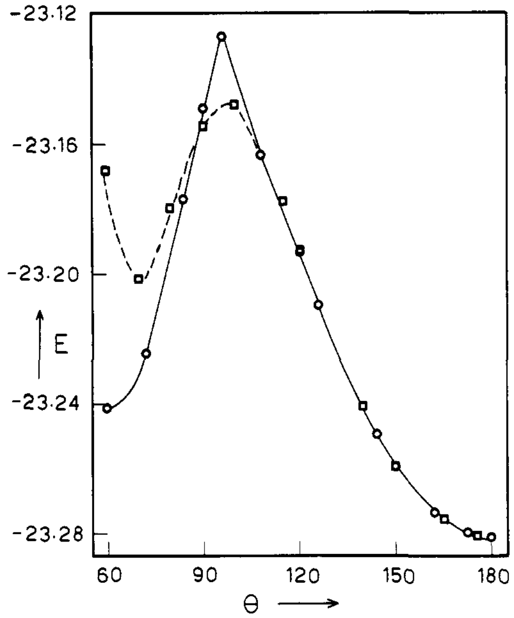


Figure 8. A plot of the variation of the total energy of the reacting singlet cyclopropylidene as a function of the angle θ. Circles denote points calculated for the forward reaction, squares denote the "reverse" reaction.

This calculated mode of opening accommodates all the experimental evidence[5,21-23,25,27,33] as well as do the previously postulated monorotatory[5,14,33] and conrotatory[5,25] modes. In the case of optically active monocyclic trans-2,3-disubstituted cyclopropylidenes[21-23,25] the initial disrotation would occur until steric hindrance between one of the substituents and hydrogen became substantial, at which point that CHR group with the inner R would reverse its rotation (Figure 9). In the case of optically active, monocyclic cis-2,3-disubstituted cyclopropylidenes,[33] the initial disrotation should occur so that both hydrogens are brought inward (to minimize steric repulsions). The CHR group which (for electronic reasons) ac-

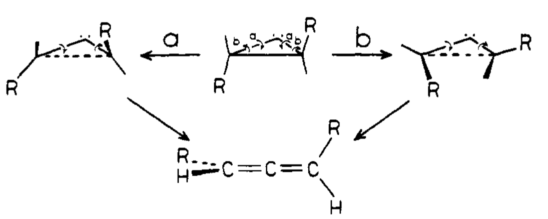


Figure 9. Asymmetric induction in the opening of optically active trans-2,3-disubstituted cyclopropylidenes. The paths on the left are sterically favored.

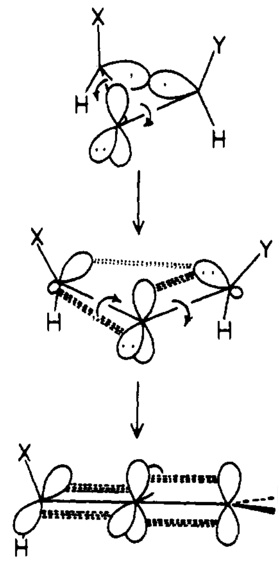
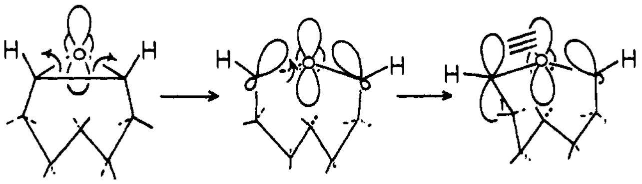


Figure 10. Asymmetric induction in the opening of optically active cis-2,3-disubstituted cyclopropylidenes. X facilitates electron donation *from* the carbene center to the carbon bonded to it and/or Y facilitates donation *to* the vacant carbene orbital.

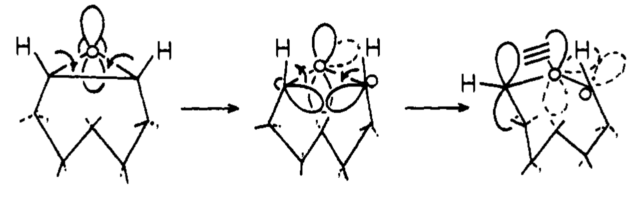
cepts an electron pair from the filled sp^x orbital then reverses its direction of rotation (Figure 10). In either case, this pathway accounts for the formation of the appropriate enantiomers (as might be expected since the pathway is, overall, monorotatory).

The application of this "mixed-mode" mechanism to the opening of n-carbenabicyclo[$(n-3)$.1.0]alkanes (giving cyclic allenes) is somewhat more complex. In the case of the small, cyclic allenes,[66] for which conrotatory or monorotatory opening is geometrically impossible, the initial disrotatory opening probably continues to planarity (note that the maximum C-C-C angle (ca. 120° in 1,2-cyclohexadiene) for these species is not much greater than that where the change in sense of rotation occurs). Disrotatory opening to planar, bent allenes ($\theta < 127°$) is symmetry allowed.

For the generation of medium[67] (C_7 and C_8) ring allenes, which are probably bent and neither orthogonal nor planar,[1] the initial disrotatory opening would occur until the dihedral angle was approximately that of the product. At this point one group would stop its motion (if the dihedral angle of the product is "overshot" this group reverses) and the other would continue rotating until a normal π bond to it is achieved;[68]



The initial disrotatory opening is pictured as bringing both hydrogens outward, as the opposite sense, if continued to planarity, would give a doubly *transoid*, bent, planar allene. If, however, the initial disrotatory opening is of this sense, then that group ultimately achieving a normal π bond would reverse, while the other stops at (or continues rotating to yield) the proper dihedral angle:[68]



To our knowledge, there are no experimental data which would enable one to choose between these possibilities.[68]

For the generation of large, cyclic allenes,[66] the mixed-mode mechanism would probably be followed just as in the generation of acyclic allenes if the starting carbene had cis-fused rings. For bicyclic carbenes with trans fusion, this would also be true if the ring size is large enough. However, optically active 9-carbena-*trans*-bicyclo[6.1.0]nonane opens **in** the sense opposite to that expected from the optically active monocyclic trans-disubstituted cyclopropylidenes,[35,36] presumably because of ring strain.[34,69,70]

It is of interest that although the small cyclic allenes were expected to be generated by a completely different mode of opening than acyclic allenes, and although these calculations were done for unsubstituted allene, a "mixed-mode" of opening, enabling a spectrum of mechanism dependent on ring size, is predicted. It is also worthy of note that Salem has predicted reversals of the sense of rotation in another cyclopropane system.[53]

Following this reaction on the reverse path leads to a difficulty. In the range $\theta = 180$ to 110°, as can be seen from Figure 8, the energies of the forward and reverse paths run closely in parallel. The geometrical changes for the reverse process are also largely the converse of the forward reaction: binding at C(2), with rotation in a conrotatory sense, except that the degree of rotation is always slightly more than for the corresponding forward reaction. Then in the region of $\theta = 110°$ the paths diverge. First, the energies are substantially different, but more importantly, the geometries differ drastically. This is the region where, during the forward reaction, there was a most rapid change in the rotation of the two methylenes and the change from disrotatory to conrotatory motion. It does not appear that there has been a catastrophic collapse during the forward reaction, however, since the E vs. θ curve is smoother, as also are plots of the angles of rotation of the methylenes vs. θ.

More distressing is the fact that as the reverse reaction is continued the pathway does not lead back to cyclopropylidene, but rather to a severely bent orthogonal allene. Evidently what has happened is that the reverse reaction has not been able to negotiate the tortuous path of the forward reaction, but has instead followed through a lower energy "pass" to a more accessible but less stable product.

This points out another problem involved in attempts to follow reaction pathways without recourse to complete $(3n-6)$ dimensional energy diagrams. Consider again a hypothetical two-dimensional energy contour diagram, Figure 11. Starting from either A or B and considering R as the reaction coordinate, it would be possible to follow the true reaction pathway relatively closely to C, but in the reverse reaction either A or B might be selected depending upon the minute details in the region of X. It is interesting and perhaps relevant that, to our knowledge, there is no report of the reverse reaction of allene → cyclopropylidene.[73-76]

Certainly we would not claim that the reverse path calculated here remotely approximates the real forward path. On the other hand the calculated forward path does have consid-

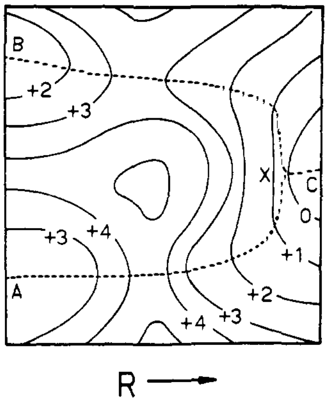


Figure 11. A hypothetical energy contour diagram in which the "reverse" reaction may not lead to the starting material of the forward reaction.

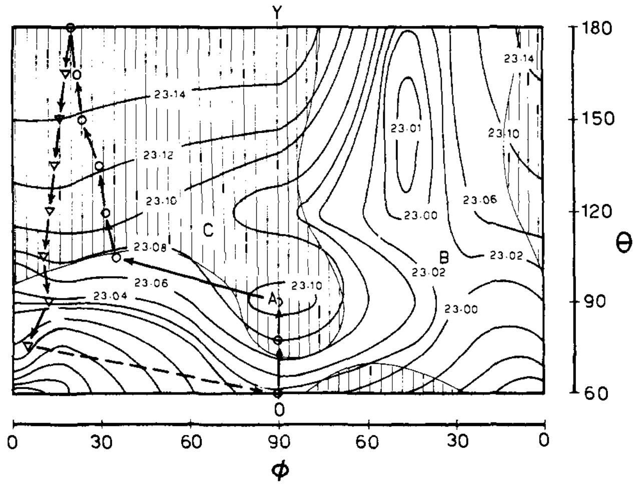


Figure 12. Energy contour diagram for the conrotatory (right half of figure) and disrotatory (left half) openings of triplet cyclopropylidene. The energies are all negative and in atomic units. The shaded portion defines the geometries in which the triplet is of lower energy than the singlet. See the text for a discussion of the various features of this diagram.

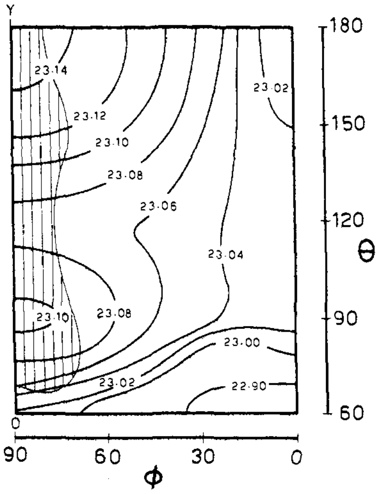


Figure 13. Energy contour diagram for the monorotatory opening of triplet cyclopropylidene. The energies are all negative and in atomic units. The diagram can be regarded as being perpendicular to Figure 12 and attached to it along OY. See the text for a discussion of the value of this operation.

erable merit in its ability to account for the experimental data, in its continuity, and its similarity to the path predicted from Figures 3 and 4, but closer scrutiny is necessary, particularly in the region of the transition state, before it can be claimed to accurately describe the "real" reaction pathway.

The Triplet Reaction. The energy contour diagrams for the conrotatory and disrotatory openings of the triplet cyclopropylidene are combined in Figure 12. The first significant feature seen in this figure is that the local minimum most nearly corresponding to the geometry of cyclopropylidene itself is, at A, partially opened (by a nonrotatory process) more probably as the result of the geometric approximations rather than as a reflection of reality. Considering first the conrotatory portion of the diagram the only reasonable course for the reaction would be over the "saddle" at B. However, inclusion of the disrotatory segment in the same diagram shows that this pathway would be discarded by the reacting molecule in favor of the completely disrotatory opening through the "pass" at C and downhill to a linear planar form which is the most stable geometry of the triplet allene.[1]

Examination of the monorotatory diagram, Figure 13, and considering its attachment to the above diagram at the common nonrotatory axis, indicates that while there might be some local exploration of the monorotatory mode as far as the −23.09-au contour, the reacting species would have no need to venture further in this direction, since an exoergic outlet is afforded it at C. Thus, tentatively, we would expect the course of reaction for the opening of the triplet cyclopropylidene to be an almost purely disrotatory process.

The shaded portions of these two figures represent those areas in which the triplet state is calculated to be more stable than the singlet of the same geometry and it is seen that as the molecule is ascending to the "transition state pass" at C it may reasonably undergo intersystem crossing to the singlet of the same geometry and therefore follow, for the remainder of the reaction, the path described for the singlet. The overall stereochemistry would then be the same as for the singlet reaction.

We have also examined this reaction by the Simplex procedure. The starting point ($\theta = 60°$) again gives a thoroughly reasonable geometry for the cyclopropylidene (see Table II) and the energy of this species is 22 kcal/mol higher than for the most stable singlet of approximately the same geometry. As θ increases from 60 to 90° the cyclopropylidene opens in essentially a nonrotatory manner with both methylene carbons becoming almost planar.[77] As θ is increased further to 105° a disrotatory motion is evident and the σ plane is conserved to a substantial degree. The geometry with $\theta = 105°$ represents an energy maximum and if taken as the transition state yields[63] $E_{\text{act}} = 74$ kcal/mol. Further increase of the angle θ up to 180° results in a smooth energy vs. θ curve and the strict retention of the σ plane to yield a linear planar allene with C–C bond lengths of 1.331 and 1.339 Å. The overall reaction as calculated by this procedure is endoergic by 35 kcal/mol and would not be expected to be of importance experimentally. There are no reports in the literature, to our knowledge, of a triplet cyclopropylidene opening to an allene.[78]

The attempt to follow the reverse reaction is even less successful for the triplet than for the singlet: The geometry throughout twists reluctantly in a disrotatory sense and is relatively symmetrical down to about 90°, but it is substantially more planar than for the forward reaction. In the region of 90°, however, the forward and reverse reactions differ widely in both energy and geometry. This process continues to 75°, beyond which point a "catastrophic collapse" apparently occurs when the geometry and energy change drastically to values relatively similar to those of cyclopropylidene itself.

The problem can be better understood by virtue of the simplicity of the reaction. Throughout both the forward and reverse reactions the geometry of the reacting species is well described as being close to the disrotatory segment of Figure 12. The points calculated for the forward and reverse paths are

Table II. The Variation, with the Angle θ, of the Six Independent Variables Defined in the Text and in Figure 5 for the Opening of Triplet Cyclopropylidene[a]

θ, deg	α_1, deg	β_1, deg	α_2, deg	β_2, deg	R_1, Å	R_2, Å	Energy[b]
60	30.00	91.00	28.00	89.00	1.467	1.450	0
75	23.37	89.80	15.00	91.30	1.375	1.369	9
90	5.98	89.97	1.79	86.32	1.338	1.347	60
105	0.76	146.00	−3.81	34.44	1.357	1.354	74
120	−0.80	151.00	−1.63	32.56	1.357	1.354	68
135	0.44	155.15	−0.76	31.10	1.349	1.345	47
150	−0.81	154.53	−3.26	23.60	1.349	1.345	40
165	0.44	158.53	−1.51	23.10	1.331	1.339	36
180	−1.43	161.03	−0.89	21.85	1.331	1.339	35
165	0.44	163.53	−0.26	20.60	1.331	1.339	36
150	−2.68	164.78	−0.89	16.85	1.331	1.339	39
135	−0.49	166.28	−1.95	14.47	1.348	1.339	40
120	−2.37	168.78	−1.33	13.22	1.348	1.339	45
105	−0.20	169.46	−1.80	12.07	1.363	1.358	57
90	6.05	164.46	4.45	14.57	1.363	1.358	74
75	23.31	181.15	26.48	5.28	1.382	1.365	110
60	30.55	265.74	41.40	87.33	1.453	1.456	3

[a] The lower entries (with decreasing θ) refer to the "reverse" reaction. [b] The energies are in kcal/mol above the starting material (−14 551 kcal/mol).

represented approximately on that figure. Of course the optimization of some of the minor variables would result in small differences in the absolute energies and general characteristics primarily in the region of cyclopropylidene, but adequate detail remains particularly around the geometry of the product to enable us to see what is happening. The forward path follows closely the expected "real" path particularly if geometric optimization in the region of the saddle C were to relocate it slightly. On the reverse route, however, the molecule cannot "look ahead" to the pass which it should take, and blindly follows the valley of least resistance, which gradually leads it further and further away from the transition state geometry. As this misled species presses further toward $\theta = 60°$ its valley finally disappears, whence it is left to tumble right across the diagram to the region of the geometry of cyclopropylidene.

Because of the fortunate simplification of this reaction to basically two variables, it appears that the forward reaction path as calculated by the Simplex procedure is quite a good representation of the actual reaction pathway at least as viewed through the eyes of the INDO approximation.

Acknowledgment. We gratefully acknowledge helpful communications with Professors M. J. S. Dewar and W. Schmidt regarding this work. Financial support from the donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

Appendix: The Simplex Optimization Technique

Simplex optimization, an iterative method for the rapid, simultaneous optimization of a large number of variables, was first developed by Spendley, Hext, and Himsworth.[79,80] The basic Simplex algorithm consists of the following steps:

(1) For each variable assign initial low and high values.

(2) For N variables set up an $N \times (N+1)$ matrix as follows:

$$\begin{array}{cc|cccccccc}
 & & \multicolumn{8}{c}{\text{Point Number}} \\
 & & 1 & 2 & 3 & 4 & & N-1 & N & N+1 \\
\hline
\text{Variable Number} & 1 & L & H & A & A & \dots & A & A & A \\
 & 2 & L & L & H & A & \dots & A & A & A \\
 & 3 & L & L & L & H & \dots & A & A & A \\
 & \vdots & \vdots & \vdots & \vdots & \vdots & & \vdots & \vdots & \vdots \\
 & N-1 & L & L & L & L & \dots & L & H & A \\
 & N & L & L & L & L & \dots & L & L & H
\end{array}$$

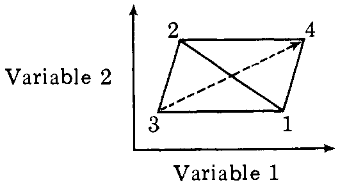
where L represents the low value of the variable in question, H, the high value, and A, the average. Each column gives the respective values of each of the N variables. Thus calculation 4 has the first two variables set at their average values, variable three at its high value, and the remaining $(N-3)$ variables at their low values. Each of the $(N+1)$ points to be calculated represent the $(N+1)$ vertices of an N-dimensional simplex in the N-dimensional space[81] of the independent variables. A two-dimensional simplex would thus be a triangle on a surface, a three-dimensional simplex, a tetrahedron, etc.

(3) Evaluate the response[82] for each of the $(N+1)$ points.[83]

(4) Replace the worst point[84] by a new point obtained by a projection from the point to be discarded through the center of the opposite hypersurface using the following rule:

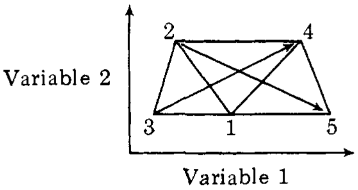
$$\text{New value} = \frac{2\sum_{i=1}^{N} W_i(\text{Old value})_i}{\sum_{i=1}^{N} W_i} - \text{Old value}$$

where (Old value)$_i$ is the value of a variable for the point in molecule i, W_i is the weight[85] assigned to this point, and the summations are over the N points being retained. Old value is the value of the variable in question for the point being discarded. This rule is succinctly summarized as "twice the average of the best minus the worst" and is depicted for two variables where point 3 gives the worst response as:



(5) Evaluate the response (i.e., energy) at the new point and return to step 4.

(6) If the new point happens to give the worst response in the new simplex then the projection procedure would return to the point previously discarded, resulting in an interminable oscillation. In this event the second worst point is discarded in order to allow the simplex to "escape". Graphically, assuming the energy $E_3 > E_2 > E_1$ and $E_4 > E_2$:



(7) Evaluate the response for the new point and return to step 4.

(8) Continue until a suitable response is obtained.

Because of the nature of the original matrix it may be partitioned into four submatrices after variable M and point ($M + 1$). The upper left submatrix may then be used in the original manner to operate on the first M variables, the remaining ($N - M$) variables being set at their low values. At any point the simplex may be expanded to include the remaining variables by adding the two right submatrices. In this event, the value for each variable in the upper right matrix is the average of the respective variables at the ($M + 1$) points already evaluated.

	1	2	3	...	M	$M+1$	$M+2$	...	$N+1$
1	L	H	A	...	A	A	A	...	A
2	L	L	H	...	A	A	A	...	A
3	L	L	L	...	A	A	A	...	A
⋮	⋮	⋮	⋮		⋮	⋮	⋮		⋮
$M-1$	L	L	L	...	H	A	A	...	A
M	L	L	L	...	L	H	A	...	A
$M+1$	L	L	L	...	L	L	H	...	A
⋮	⋮	⋮	⋮		⋮	⋮	⋮		⋮
$N-1$	L	L	L	...	L	L	L	...	A
N	L	L	L	...	L	L	L	...	H

This expansion procedure may be repeated as frequently as is desired. We have found it useful to "guess" reasonable values for variables (such as bond lengths) which may be expected to have a strong influence on the response, temporarily to fix these values and optimize those remaining (such as bond angles and dihedral angles which have a lesser effect), and then to expand the simplex to include the "strong" variables. This procedure has given us better responses with fewer iterations than has the use of the full matrix throughout.[1b,86,87]

There are two major deficiencies with the basic Simplex algorithm as so far described: (1) there is no method of decreasing the size of the simplex to allow for convergence at a point; and (2) there is no objective method for deciding when the optimum has been reached.

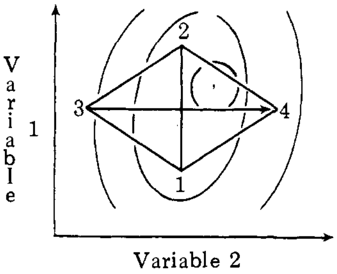
Spendley, Hext, and Himsworth[79] have attempted to solve this second problem by reasoning that any point near the optimum will remain in the simplex for a large number of successive iterations. They determined empirically the minimum "lifetime" of a point if it were to be reasonably close to the optimum, but the lifetimes are unfortunately rather long for our purposes and increase rapidly with the number of variables, as can be seen from Table III.

Table III. The Dependence on the Number of Independent Variables of the Minimum Lifetime of a Point for It to Be Considered As Being Close to the Optimum Value[a]

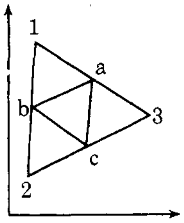
No. of variables	Minimum lifetime
2	3
5	9
10	21
20	52
30	92

[a] The lifetime is expressed in terms of the number of successive simplices in which the point appears.

We reasoned that an indication of the approach to an optimum would be when the most recently calculated point was the worst in the newly generated simplex, i.e., resulting from a "step" across the optimum. Illustrated in two dimensions this would be:



Furthermore in such an event the newly generated points frequently step back and forth across the optimum without getting any closer to it.[86] We chose therefore to reduce the size of the simplex whenever the newly generated point was the worst in the new simplex. The method we chose for doing this was to generate a new simplex by using the centers of each of the hyperfaces of the old simplex, a process we refer to as "rotation". It is illustrated in two dimensions as the generation of the simplex a, b, c from 1, 2, 3. Hence the steps 6 and 7 above were omitted and "rotation" was used in their stead.[88]



The second problem, that of deciding when to terminate the process, was solved by the simple expedient of assuming that when the difference between the best and worst responses in the current simplex was less than a predetermined value[89] the simplex had converged.[89,90,91] Upon convergence, the center of the last simplex was calculated, since if the simplex were straddling the optimum the center might represent a lower energy than any of the points.

Finally, in any work such as the above where the geometry is optimized, one parameter varied and the geometry reoptimized, it is economical to use the final values of the parameters from optimization k in setting up the initial simplex for optimization ($k + 1$). This was done by setting

$$L_{\mathrm{NEW}} = V_{\mathrm{OLD}} - (H_{\mathrm{OLD}} - L_{\mathrm{OLD}})/2$$

and

$$H_{\mathrm{NEW}} = V_{\mathrm{OLD}} + (H_{\mathrm{OLD}} - L_{\mathrm{OLD}})/2$$

where L_{NEW} and H_{NEW} are respectively the low and high values of the variable in question to be used in the new simplex, V_{OLD} is the optimized value from the previous simplex, and H_{OLD} and L_{OLD} are respectively the high and low values of the parameter used in the first simplex.

This Simplex procedure is quite efficient. For each of the optimizations used in this paper an average of 40 iterations was necessary. Using the conventional filled hypercube, with three values of each variable, 729 calculations would have been necessary, with five values, 15 625 calculations, and with ten values, no less than 10^6 calculations.

A Fortran V[92] program has been written to perform the Simplex optimizations with either CNDO/2[93] or INDO[39] total energy as the response. The program will accommodate a maximum of 20 atoms, 54 independent variables, and 50 atomic orbitals.[94]

A completely different set of modifications of the basic

Simplex algorithm has been used by Nelder and Mead,[95,96] while Dewar,[19,50,56m,p,q,98] Schmidt,[99] and van Dijk et al.[100] have each reported results obtained by using these modifications in conjunction with M1NDO/2 or CNDO/2.

Finally, it should be noted that the various Simplex algorithms are quite general, and can be of use in a wide variety of chemical or nonchemical problems.[101]

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(13) The term "orthogonal" allene refers to the usual ground state geometry of allene in which the two terminal methylenes are mutually perpendicular. The "planar" allene in which all seven atoms are coplanar is a real possibility as an intermediate in reactions involving cyclic allenes where the orthogonal geometry is sterically infeasible. In acyclic systems, if a planar allene is the primary product of a reaction, it may easily revert to the ground state orthogonal geometry. The planar allene need not necessarily be linear, and bending at the central carbon around an axis perpendicular to the plane of the nuclei appears to be a particularly facile deformation.[1a,b]

(14) W. T. Borden, *Tetrahedron Lett.*, 447 (1967).

(15) (a) C. MacKay, P. Polack, H. E. Rosenberg, and R. Wolfgang, *J. Am. Chem. Soc.*, **84**, 308 (1962); (b) J. Dubrin, C. MacKay, and R. Wolfgang, *ibid.*, **86**, 959 (1964); (c) M. Marshall, C. MacKay, and R. Wolfgang, *ibid.*, **86**, 4741 (1964); (d) J. Dubrin, C. MacKay, and R. Wolfgang, *ibid.*, **86**, 4747 (1964); (e) P. S. Skell and R. R. Engel, *ibid.*, **87**, 1135 (1965); (f) P. B. Shevlin, *ibid.*, **94**, 1379 (1972).

(16) P. S. Skell, J. E. Villaume, J. H. Plonka, and F. A. Fagone, *J. Am. Chem. Soc.*, **93**, 2699 (1971).

(17) P. S. Skell, J. J. Havel, and J. J. McGlinchey, *Acc. Chem. Res.*, **6**, 97 (1973).

(18) (a) P. S. Skell and P. C. Woodworth, *J. Am. Chem. Soc.*, **78**, 4496 (1956); (b) P. S. Skell and A. Y. Garner, *ibid.*, **78**, 5430 (1956); (c) P. C. Woodworth and P. S. Skell, *ibid.*, **81**, 3383 (1959); (d) P. S. Skell and R. R. Engel, *ibid.*, **87**, 1135, 2493 (1965); (e) *ibid.*, **88**, 3749 (1966).

(19) M. J. S. Dewar, E. Haselbach, and M. Shanshal, *J. Am. Chem. Soc.*, **92**, 3505 (1970). These calculations suggest an energy of activation for the ring opening of 50 kcal/mol. More recent calculations[20] have lowered this to 14 kcal/mol. There is no suggestion in this latter paper that different geometric changes are indicated.

(20) M. Bodor, M. J. S. Dewar, and Z. B. Maksic, *J. Am. Chem. Soc.*, **95**, 5245 (1973).

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(22) W. M. Jones and J. W. Wilson Jr., *Tetrahedron Lett.*, 1587 (1965).

(23) J. M. Walbrick, J. W. Wilson Jr., and W. M. Jones, *J. Am. Chem. Soc.*, 90, 2895 (1968).

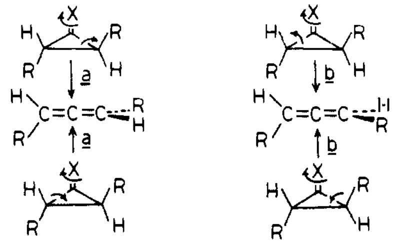
(24) Prepared from optically active *trans*-2,3-diphenylcyclopropanecarboxylic acid via the *N*-nitrosocarbamate.

(25) W. M. Jones and J. M. Walbrick, *Tetrahedron Lett.*, 5229 (1968).

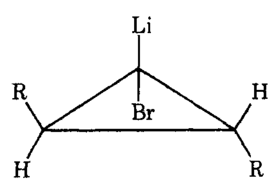
(26) S. F. Mason and G. W. Vane, *Tetrahedron Lett.*, 1593 (1965).

(27) (a) W. L. Waters and M. C. Caserio, *Tetrahedron Lett.*, 5233 (1968); (b) W. L. Waters, W. S. Linn, and M. C. Caserio, *J. Am. Chem. Soc.*, **90**, 6741 (1968).

(28) Although paths a would be expected to be preferred over paths b in the opening of free cyclopropylidenes, if the opening occurs from a carbenoid or diazoakane precursor then paths b may have less steric interaction between the substituents and the leaving group(s):



Jones' work[23] has therefore shown that if diazo-*trans*-2,3-diphenylcyclopropane opens *with* loss of N_2 rather than by the initial formation of the carbene, then the repulsive interactions between the phenyl substituents and the leaving group are less than between the phenyl groups and the rest of the molecule. Furthermore, if the "leaving group" does not have the ring plane as a mirror plane as in i then *one* of the two paths a or *one* of the two paths b may be favored.



i

(29) The proposal of steric control of conrotatory or monorotatory openings is consistent with the fact that trisubstituted cyclopropylidenes open to

allenes, whereas tetrasubstituted cyclopropylidenes (where either rotation would involve steric repulsion) do not.[30,31]

(30) W. R. Moore and J. B. Hill, *Tetrahedron Lett.*, 4343, 4553 (1970).

(31) Tetrasubstituted cyclopropylidenes in general undergo intramolecular C–H insertion to give bicyclobutanes.[30,32]

(32) (a) L. Skattebøl, *Tetrahedron Lett.*, 2361 (1970); (b) W. R. Moore, K. G. Taylor, P. Müller, S. S. Hall, and Z. L. F. Gaibel, *ibid.*, 2365 (1970); (c) R. Vaidyanathaswamy and D. Devaprabhakara, *Chem. Ind.* (*London*), 515 (1968).

(33) W. M. Jones and D. L. Krause, *J. Am. Chem. Soc.*, **93,** 551 (1971).

(34) The opening of the carbene (or carbenoid) derived from optically active 9,9-dibromo-*trans*-bicyclo[6.1.0]nonane gives optically active 1,2-cyclononadiene of opposite configuration[35] from that anticipated[36] from a simple steric repulsion model. However 9-carbena-*trans*-bicyclo[6.1.0]nonane is strained torsionally in the same manner as *trans*-cyclooctene so that inward rotation of the hydrogens would increase the energy of the system. Evidently this torsional strain is sufficient to overcome the reluctance of the methylenes to rotate inwardly and the abnormal monorotatory or conrotatory opening is observed in this cyclic system.

(35) (a) A. C. Cope, W. R. Moore, R. D. Bach, and H. J. S. Winkler, *J. Am. Chem. Soc.*, **92,** 1243 (1970); (b) W. R. Moore and R. D. Bach, *ibid.*, **94,** 3148 (1972).

(36) W. R. Moore, H. W. Anderson, S. D. Clark, and T. M. Ozretich, *J. Am. Chem. Soc.*, **93,** 4932 (1971).

(37) The Simplex algorithm, and the modifications of it used in this work[1b] are discussed in the Appendix. In this work, total energies were calculated using unrestricted[38] LCAO–SCF–MO calculations, in the INDO approximations.[39,40]

(38) J. A. Pople and R. K. Nesbit, *J. Chem. Phys.*, **22,** 57 (1954).

(39) J. A. Pople, D. L. Beveridge, and P. A. Dobosh, *J. Chem. Phys.*, **47,** 2026 (1967).

(40) See also: J. A. Pople and D. L. Beveridge, "Approximate Molecular Orbital Theory", McGraw-Hill, New York, N.Y., 1970.

(41) R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **8,** 781 (1969).

(42) A priori, it is conceivable that carbenoids, rather than free carbenes, are the intermediates in this reaction. However, the reactions of atomic carbon with olefins, described above, imply that free carbenes do undergo opening to the allenes. In addition, Jones' data[8n] indicates (at least partial) intervention of free carbenes in the generation of allenes. Finally, Reinarz and Fonken[43] have shown appropriately substituted 6-carbenabicyclo-[3.1.0]hexanes yield the analogous allenes *and* intramolecular C–H insertion products of the bicyclic carbene.

(43) (a) R. B. Reinarz, Dissertation, The University of Texas at Austin, Austin, Texas, 1973; *Diss. Abstr. Int. B*, **34,** 1948-B (1973); (b) R. B. Reinarz and G. J. Fonken, *Tetrahedron Lett.*, 4013 (1973).

(44) In all these preliminary calculations the C–C bond lengths were maintained at 1.31 Å, the C–H bond lengths at 1.08 Å, the H–C–H bond angles at 115°, and the central carbon was kept on the line of intersection of the two methylene planes.[45] While the value of 1.31 Å was expected to lead to some difficulties in the region of the cyclopropylidene geometry, it was chosen for consistency with the calculations in the first paper in this series.[1a,46] It will be seen subsequently in this paper that the fuller optimization does most emphatically substantiate these fears. Increments of 7.5° were used in the calculations for the conrotatory process.

(45) This approximation has been used by others[47] for similar systems. Its main effect is to cause the unique C–C–C angle to be larger than normal.[47] In our case the use of a C–C bond length of 1.31 Å further aggravates the situation.

(46) "Tables of Interatomic Distances and Configuration in Molecules and Ions",' *Chem. Soc., Spec. Publ.*, **No.** 11, M146 (1958), and references cited therein.

(47) R. Hoffmann, G. D. Zeiss, and G. W. VanDine, *J. Am. Chem. Soc.*, **90,** 1485 (1968).

(48) The saddle at C may, in fact, be an artifact of the INDO method since, as discussed earlier,[1a] the "hill" at E appears to be a consequence of the lack of inclusion of configuration interaction.

(49) See the Appendix for an outline of the Simplex procedure.

(50) (a) M. J. S. Dewar and S. Kirschner, *J. Am. Chem. Soc.*, **93,** 4291, 4292 (1971); (b) M. J. S. Dewar, *Angew. Chem.*, **83,** 859 (1971); *Angew. Chem., Int. Ed. Engl.*, **10,** 761 (1971).

(51) Calculations implying similar "catastrophic collapses" have been reported by others.[50,52,53,54]

(52) L. Salem, J. Durup, G. Bergeron, D. Cazes, K. Chapuisat, and H. Kagan, *J. Am. Chem. Soc.*, **92,** 4472 (1970).

(53) (a) L. Salem, *Bull. Soc. Chim. Fr.*, 3161 (1970); (b) L. Salem, 23rd International Congress of Pure and Applied Chemistry, Vol. 1, Butterworths, London, 1971, p 97; (c) Y. Jean, L. Salem, J. S. Wright, J. A. Horsley, C. Moser, and R. M. Stevens, *Pure Appl. Chem., Suppl.*, 1, 197 (1971); (d) *J. Am. Chem. Soc.*, **94,** 279 (1972).

(54) K. Hsu, R. J. Buenker, and S. D. Peyerimhoff, *J. Am. Chem. Soc.*, **93,** 2117 (1971); **94,** 5839 (1972).

(55) See also ref 53 and L. Salem, *Acc. Chem. Res.*, **4,** 322 (1971).

(56) For further discussion of the problems of, and approaches to, determining, and following, reaction coordinates see ref 1b, 50, and: (a) K. Fukui, *J. Phys. Chem.*, **74,** 4161 (1970); (b) J. W. McIver Jr. and A. Komornicki, *J. Am. Chem. Soc.*, **94,** 2625 (1972); (c) J. W. McIver Jr. and R. E. Stanton, *ibid.*, **94,** 8618 (1972); (d) A. Komornicki and J. W. McIver Jr., *ibid.*, **95,** 4512 (1973); (e) H. B. Bürgi, J. D. Dunitz, and E. Shefter, *ibid.*, **95,** 5065 (1973); (f) H. B. Bürgi, *Inorg. Chem.*, **12,** 2321 (1973); (g) H. B. Bürgi, J. D. Dunitz, and E. Shefter, *Acta Crystallogr., Sect. B*, **30,** 1517 (1973); (h) H. B. Bürgi, J. D. Dunitz, J. M. Lehn, and G. Wipff, *Tetrahedron*, **30** 1563 (1974); (i) J. W. McIver, Jr., *Acc. Chem. Res.*, **7,** 1972 (1974); (j) A. Komornicki, Ph.D. Thesis, State University of New York at Buffalo, Buffalo, N.Y., 1974; *Diss. Abstr. Int. B*, **35,** 1220-B (1974); (k) S. Ehrenson, *J. Am. Chem. Soc.*, **96,** 3778, 3784 (1974); (l) G. A. Shchembelov and Y. A. Ustynyuk, *ibid.*, **96,** 4189 (1974); (m) M. J. S. Dewar and S. Kirschner, *ibid.*, **96,** 5244, 5246, 6809, 7578 (1974); (n) A. Komornicki and J. W. McIver, Jr., *ibid.*, **96,** 5798 (1974); (o) Y. Jean and X. Chapuisat, *ibid.*, **96,** 6911 (1974); (p) M. J. S. Dewar, S. Kirschner, and H. W. Kollmar, *ibid.*, **96,** 7579 (1974); (q) R. S. Case, M. J. S. Dewar, S. Kirschner, R. Pettit, and W. Slegeir, *ibid.*, **96,** 7581 (1974); (r) K. Fukui, S. Kato, and H. Fujimoto, *ibid.*, **97,** 1 (1975); (s) P. Murray-Rust, H. B. Bürgi, and J. D. Dunitz, *ibid.*, **97,** 921 (1975); (t) T. A. Halgren, I. M. Pepperberg, and W. N. Lipscomb, *ibid.*, **97,** 1248 (1975); (u) S. Wolfe, H. B. Schlegel, I. G. Csizmadia, and F. Bernardi, *ibid.*, **97,** 2020 (1975); (v) H. F. Schaeffer III, *Chem. Br.*, 11, 227 (1975); (w) R. E. Stanton and J. W. McIver Jr., *J. Am. Chem. Soc.*, **97**, 3632 (1975); (x) H. E. Schoemaker, N. M. M. Nibbering, and R. G. Cooks, *ibid.*, **97,** 4415 (1975); (y) C. W. Bauschlicher, Jr., H. F. Schaefer III, and C. F. Bender, *ibid.*, **98,** 1653 (1976).

(57) The total twist is defined as the sum of the angles of twist of each methylene plane, from the planes perpendicular to the ring measured in either the con- or the disrotatory sense.

(58) The deviation from bisection is such that the methylenes move slightly apart toward the divalent carbon.

(59) These bonds are shorter than might have been expected. Inspection of the eigenvectors reveals extensive hyperconjugation between the vacant "p" orbital and the C–H bonds.

(60) In order to estimate the ability of the Simplex method to deduce reasonable geometries this energy was calculated for a cyclopropylidene having the three carbons located at the corners of an equilateral triangle: C–C bond lengths, 1.54 Å; C–H, 1.08 Å; H–C–H, 115°; the plane of the ring bisecting the H–C–H angles; and the plane of each methylene bisecting the appropriate C–C–C angle. The singlet has an energy of −23.2114 au (44.1 kcal/mol above allene) and the nonbonding sp^x orbital was of lower energy than the nonbonding "p" orbital. The triplet had an energy of −23.1721 au (24.6 kcal/mol above the singlet). These "expected" geometries for singlet and triplet cyclopropylidene *do not* correspond in geometry or energy with any points represented in Figures 3, 4, 12, or 13.

(61) The total twist[57] being 85.42°.

(62) The angles of twist of the methylenes differed by 21.07° and the nonplanarity of the two methylenes differed by 7.86°.

(63) Strictly speaking this is the barrier height. While recognizing the differences between activation energy and barrier height,[64] we will continue using the more common term activation energy.

(64) M. Menzinger and R. Wolfgang, *Angew. Chem., Int. Ed. Engl.*, **8,** 438 (1969).

(65) C–C lengths, 1.306 and 1.309 Å; angle between the two methylene planes, 93.03°; and nonplanarity of the methylenes, 2.70 and 3.73°. The energy of this species was 0.5 kcal/mol above that calculated for a "standard" allene:[1a] C–C, 1.31 Å.

(66) We define cyclic allenes as having large rings if the ring size is nine or greater (these have normal geometries for both singlet and triplet). Similarly, medium rings are those with seven or eight members (deformed singlets, normal triplets) and small rings those with six or fewer members (both singlets and triplets deformed).[1]

(67) We recognize that 7-carbenabicyclo[4.1.0]heptane is diverted completely into other paths.[12a–i]

(68) If the ring causes a more symmetrical twisting of the π system these proposed mechanisms would be "short-stopped" (assuming disrotatory twisting to be favored).

(69) Molecular models suggest that the initial disrotation would be strongly resisted by the polymethylene chain.

(70) Optically active 1,2-cyclononadiene[71] also disobeys the Lowe–Brewster rules.[72] It would be of interest to determine the sense of asymmetric induction for the progressively larger cyclic allenes to ascertain whether variance from acyclic sense of induction and from the Lowe–Brewster rules go hand in hand.

(71) P. Crabbé, E. Velande, H. W. Anderson, S. D. Clark, W. R. Moore, A. F. Drake, and S. F. Mason, *Chem. Commun.*, 1261 (1971).

(72) (a) J. H. Brewster, *J. Am. Chem. Soc.*, **81,** 5475 (1959); (b) G. Lowe, *Chem. Commun.*, 411 (1965); (c) J. H. Brewster, *Top. Stereochem.*, **2,** 33 (1967).

(73) The overall thermodynamics of the reverse reaction (endoergic by 25 kcal/mol) is undoubtedly a factor also.

(74) The photocyclization of 1,2-cyclononadiene is the only exception[76] known to us. However, as discussed in the first paper in this series,[1a] other factors may be involved here.

(75) It should be noted that this "reverse path" corresponds to a valley on the singlet energy contour diagram for deformed allenes given in ref 1a. Similarly, the "product" corresponds to a minimum on that diagram at $\theta = 80°$, $\phi = 90°$.

(76) H. R. Ward and E. Karafiath, *J. Am. Chem. Soc.*, **90,** 2193 (1968); 91, 522, 7475 (1969).

(77) Nonplanarities, at $\theta = 90°$, were 1.79 and 5.98°.

(78) However, note that because all triplet allenes, cyclic or acyclic, are planar and geometrically amenable to disrotatory opening this path is in principle feasible in all cases.

(79) W. Spendley, G. R. Hext, and F. R. Himsworth, *Technometrics*, **4,** 444 (1962).

(80) See also a discussion of the Simplex method by C. Lowe, *Trans. Inst. Chem. Eng.*, **42,** T334 (1964).

(81) The geometrical properties of simplices in Euclidean *N*-dimensional spaces may be found in D. M. Y. Somerville, "An Introduction to the Geometry of *N*-Dimensions", Dover Publications, New York, N.Y., 1958.

(82) In all our calculations, the response is evaluated by an INDO calculation of the energy.

(83) That is, for each of the ($N + 1$) molecules.

(84) That is, with highest energy.

(85) All averages in this paper were weighted according to the total ener-

(86) P. W. Dillon, unpublished results.
(87) In this particular study bond lengths were fixed temporarily.
(88) Since "rotation" could eliminate the best point, this is retained and if the best point in the new simplex is not as good we immediately proceed to step 4 and move toward the minimum.
(89) We have found a value of 0.3 kcal/mol yields adequate geometries in a reasonable number of iterations.[86]
(90) This is based upon the fact that near the optimum each partial derivative is close to zero and $R_j - R_1 \approx (\partial R/\partial V_i)(V_{ij} - V_{i1}) \approx 0$ where R is the response function, R_j the response at point j, and V_{ij} is the value of the ith variable at the jth point. In principle there could arise a problem if the $(V_{ij} - V_{i1})$ terms were too small as the result of a large number of rotations in which case the simplex might appear to converge without actually reaching the optimum. We have not had any such difficulty to date however.[86]
(91) A similar expedient was chosen to determine when to expand the simplex and free the temporarily fixed variables. Thus, simplex expansion was performed when the total spread in energies was <1 kcal/mol.
(92) The Univac 1108 version of Fortran IV.
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Gaseous Ions. 2.[1] MINDO/3 Study of the Rearrangements of Toluene and Cycloheptatriene Molecular Ions and the Formation of Tropylium

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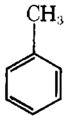
Abstract: Several reaction paths for rearrangement of toluene molecular ion (TMI) to cycloheptatriene molecular ion (CHMI) have been studied, using MINDO/3. The results are in qualitative agreement with experiment and lead to the following conclusions: (a) the activation energy for interchange of ring hydrogen in TMI is less than for methyl-ring exchange; (b) there are several paths from TMI to CHMI with similar overall activation energies; (c) scrambling of hydrogen in CHMI is easier than in TMI: (d) loss of hydrogen from CHMI is easier than from TMI.

The mass spectra of various compounds C_7H_7X, including toluene (**1**) and cycloheptatriene (**2**), show a strong peak at *m/e* 91 ($C_7H_7^+$) which has been attributed to tropylium[2] (**3**). If the starting material is isotopically labeled, the fragmentation patterns observed indicate that extensive scrambling of carbon and hydrogen occurs during formation of **3**.[2-7] In the preceding paper[1] we reported a detailed MINDO/3 study of the conversions of benzyl cation (**4**), and of other tolyl cations, into **3**. Here we report a similar study of the parts of the $C_7H_8^{+\cdot}$ potential surface relevant to the interconversion of toluene molecular ion (TMI, **5**) and cycloheptatriene molecular ion (CHMI, **6**) and their conversions to $C_7H_7^+$ species. As will be seen presently the results are not only consistent with the very extensive experimental data now available but in conjunction with them seem to lead to definite mechanisms for the various processes involved.



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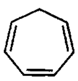

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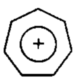

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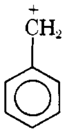

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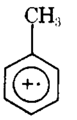

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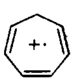

6

Procedure

The calculations were carried out using a spin-unrestricted version[8] of MINDO/3[9] together with the associated DFP geometry program.[9] The procedure was otherwise the same as in part 1.[1] All geometries were optimized with respect to all geometrical variables, no assumptions whatsoever being made.

Notation

Reactions are indicated in the text in parentheses, e.g., (**5** → **6**). Transition states are represented likewise, but using square brackets, e.g., [**5** → **6**] would be the transition state for (**5** → **6**).

Results and Discussion

(1) **Properties of 5 and 6.** Figure 1 shows the geometries, heats of formation, and distributions of formal charge calculated for TMI (**5**) and CHMI (**6**),

The heat of formation calculated for **5** (212.2 kcal/mol) agrees very well with experiment (215 kcal/mol[10]). The geometry is interesting, corresponding to a distortion of the ring in the direction of the classical structure **7**. This can be understood very easily in terms of PMO theory[11] by arguments