

APPLICATION OF THE PRINCIPLE OF LEAST MOTION TO
THE STEREOCHEMISTRY OF ORGANIC REACTIONS

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ABSTRACT

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APPLICATION OF THE PRINCIPLE OF LEAST MOTION TO THE STEREOCHEMISTRY OF ORGANIC REACTIONS

The Principle of Least Motion technique, as developed by Hine³³ and Tee³⁸, has been applied to 1,2- and 1,3-eliminations, homoenolisations, enolisations and various types of molecular rearrangements. Calculations were performed, utilising the computer programs LESMOT and LESMOT/2 written³⁸ in Fortran IV, for all the conceivable stereochemical alternatives of each process. In reactions involving acyclic molecules, consideration of numerous reactant-product conformations permits a reasonable estimation of the transition state geometry. The results were found to be in satisfactory agreement with the predictions of the Conservation of Orbital Symmetry approach where applicable, and experimental observations where available. The advantages and limitations of the method are discussed.

ACKNOWLEDGEMENTS

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Thanks are also due to the Chemistry Department for providing financial assistance, and the Computer Science Department for the use of their facilities.

WILLIAM OF OCKAM (c 1295-1349) "Pluralities non est
ponenda sine necessitate" - that is - "Multiplicity
ought not to be posited without necessity"

- Ockam's Razor (Principle of Economy)

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GENERAL INTRODUCTION

A large variety of chemical reactions have, in principle, more than one stereochemical pathway. The stereo-path followed may be one step of an overall conversion or, in the case of a concerted process, may constitute the entire mechanism. Attempts to explain the stereoselectivity* of concerted organic reactions have resulted in a variety of speculations, theories and principles.

The most elegant qualitative explanation of the problem of stereoselection in "molecular"** reactions was proposed by Woodward and Hoffmann¹. The basic postulate, which is applicable to both thermal and photochemical processes, states that those reaction paths are favoured in which orbital symmetry is conserved. Using the above theory the authors¹ successfully rationalised a large volume of previously unexplained experimental data, and furthermore, were able to predict the stereochemical routes of as yet unknown reactions, thus stimulating further research in that field.

* Stereoselectivity is defined as the propensity to produce one stereoisomeric product in predominance over all the other possible products of a reaction^{2,3}.

** "Molecular" reactions are defined as a group of concerted reactions which are neither ionic nor radical, and which have "no mechanism"⁴.

Alternative theoretical approaches have been set forth by several authors.

Longuet-Higgins and Abrahamson⁵ developed an approach based on the premise that in a concerted process the orbitals or electronic states pass adiabatically from reactant to product. Their application of orbital and state correlation diagrams to electrocyclic reactions provided the opportunity to follow the process along its entire course.

An intensive exploration of various methods of calculation pertinent to problems of chemical reactivity has been carried out by Fukui⁶. He initiated the Frontier Orbital method, which assumes that for any reaction the product will be determined solely by the interaction of the Highest Occupied Molecular Orbital (HOMO) of one component with the Lowest Unoccupied Molecular Orbital (LUMO) of the other and all the remaining orbitals can be neglected. This method has been applied most successfully to simple hydrocarbons⁷ where the general form of HOMOs and LUMOs is determined by symmetry.

The development of the Perturbational Molecular Orbital (PMO) theory of Aromaticity (based on Huckel theory) for the interpretation of thermal and photochemical electrocyclic reactions is attributed to Dewar⁸. Applications of the PMO to various systems of interest resulted in the conclusion: "Thermally induced pericyclic reactions proceed preferentially via "aromatic" transition states whereas their

photochemical counterparts lead to products that are formed via "antiaromatic" transition states"⁹.

Another way in which stereochemical conclusions may be reached was suggested by Zimmermann¹⁰. The treatment categorises the array of orbitals in the transition state of an electrocyclic reaction as being either Huckel or Mobius*. The former case represents a thermally allowed process; the latter a photochemically allowed process. An alternative simple method involving a circle mnemonic for the allocation of the degenerate energy levels along the reaction coordinate was also presented¹¹. In this latter case correlation diagrams are constructed from which the allowedness of the reaction may be decided.

The concept of utilizing orbital interactions as a measure of the allowedness of an electrocyclic reaction was initiated by Salem¹³, who developed a theory which provides explicit expressions for the interaction energy of two conjugated molecules as a function of the various atomic overlaps. Application of the above to cycloadditions and unimolecular decomposition reactions¹⁴ resulted in the estab-

* Cyclic systems with $4n+2$ electrons are termed Huckel since they fit the Huckel rule and have molecular orbital solutions of the normal Huckel type. Systems which need $4n$ electrons for stability may be referred to as Mobius because it was recognised¹¹ that their molecular orbitals are similar to those of Heilbronner's¹² Mobius cyclic polyenes.

lishment of the following principle¹³: Thermal addition of two molecules will be preferred whenever the HOMO of one molecule interacts strongly with the LUMO of the other molecule. Furthermore, in cases where the interaction energy between the orbital of an excited electron of a molecule and the neighbouring (or slightly higher energy) orbital of the other is large, or if the interaction energy between the hole (top occupied orbital) of a molecule and the neighbouring (or slightly lower energy) orbital of the other is large, the preferred reaction will be the photochemical addition.

A somewhat similar approach was presented by Pearson¹⁵, who proposed the use of symmetry rules as the criteria for the allowedness of chemical reactions such as bimolecular additions, unimolecular rearrangements and nucleophilic substitutions. His method was shown to be equally applicable to elucidation of molecular structure and the correlation between the frequencies of electronic transition and stability.

Finally, Oosterhoff and van der Lugt¹⁶ performed valence bond type calculations for both the thermal and photochemical cyclisation of butadiene in order to gain insight into the mechanism of photoinduced concerted reactions. It was found that the driving force for the photoinduced disrotatory ring closure derives from a favourable symmetric excited state in contrast to the antisymmetric state considered by Woodward and Hoffman¹.

All of the aforementioned approaches, although based on different premises, give the same predictions as the Woodward-Hoffmann rules.

An interesting and entirely different type of quasi-theoretical approach which has been known for a number of years but has not been applied to organic reactions until recently is the Principle of Least Motion (PLM)^{22,38}. According to this principle, "those elementary reactions will be favoured that involve the least change in atomic position and electronic configuration"²².

The advantage of the PLM method (discussed in the next section) lies in its simplicity and ease of application. Correlation of energy levels is dependent upon the presence of suitable symmetry elements and thus restricts the use of the orbital symmetry method. However, PLM calculations^{38,39} do not require the presence of symmetry. Also, in those cases where orbital symmetry arguments are incapable of distinguishing between two allowed processes leading to stereochemically different products, the PLM technique may possibly assist in removing the ambiguity³⁹.

The purpose of the project described in this thesis was the application of PLM to various types of organic reactions in order to gain insight into their stereochemistry and to further our knowledge of the transition states involved. Simultaneously, these applications provided an opportunity for the critical evaluation of the PLM technique; its reliability and limitations.

INTRODUCTION TO THE PRINCIPLE OF LEAST MOTION

The possibility that molecules prefer to react along those paths in which they undergo the least modification has always been intuitively attractive. Occasionally, certain reactions were accounted for by the use of various hypotheses of minimum structural change. For instance, Franck and Rabinowitsch¹⁷ rationalised the results of bimolecular gas reactions by relating the heat of activation to the collision radii and the nuclear distances of reactant and product. Similarly, Eyring and Sherman¹⁸, while studying bimolecular surface reactions, found that the activation energy for adsorption is a function of the distance between the surface C-atoms. Furthermore, Eyring's treatment of potential surfaces, which serves as a basis for his Transition State Theory, utilises the dependence of activation energy on internuclear distance.

The Principle of Least Molecular Deformation was first formulated by Muller¹⁹. Later Peytral²⁰ applied the above principle to pyrolytic reactions carried out above 1000°C. However, owing to the complexity of reactions in that temperature range, the application was not justified, and the postulate did not gain recognition until 1938, when Rice and Teller²¹, in discussing the role of free radicals in elementary organic reactions, enunciated the Principle of Least Motion.

The Principle of Least Motion (PLM) is a statement of two basic conditions that favour a lower activation energy for an elementary reaction.

The first of these is the least motion of the atoms. Consider a hydrogen transfer reaction



As the reaction proceeds the R-H bond stretches and the energy of the system increases according to a quadratic law (cf. Hooke's law). This increase continues until bonding between H and R' is able to compensate. The energy of the system then decreases as H-R' bond formation advances, until the H-R' bond relaxes to its equilibrium position. A shortening of the distance over which H must be transferred allows the transition state to be reached with less R-H bond stretching (and/or more H-R' bond making) and hence should result in a lower activation energy. Thus, for two very similar atom transfer reactions with almost identical potential energy surfaces, the one requiring the lesser motion of the atom transferred should have the faster rate.

These arguments are illustrated in Figure 1 (overleaf). Curves I and II represent potential energy wells containing the reactants (R-H + R') and the products (R + H-R') respectively. The energy barrier for the interconversion of these species is maximal at point a. Curve II' represents another potential well of the products which is

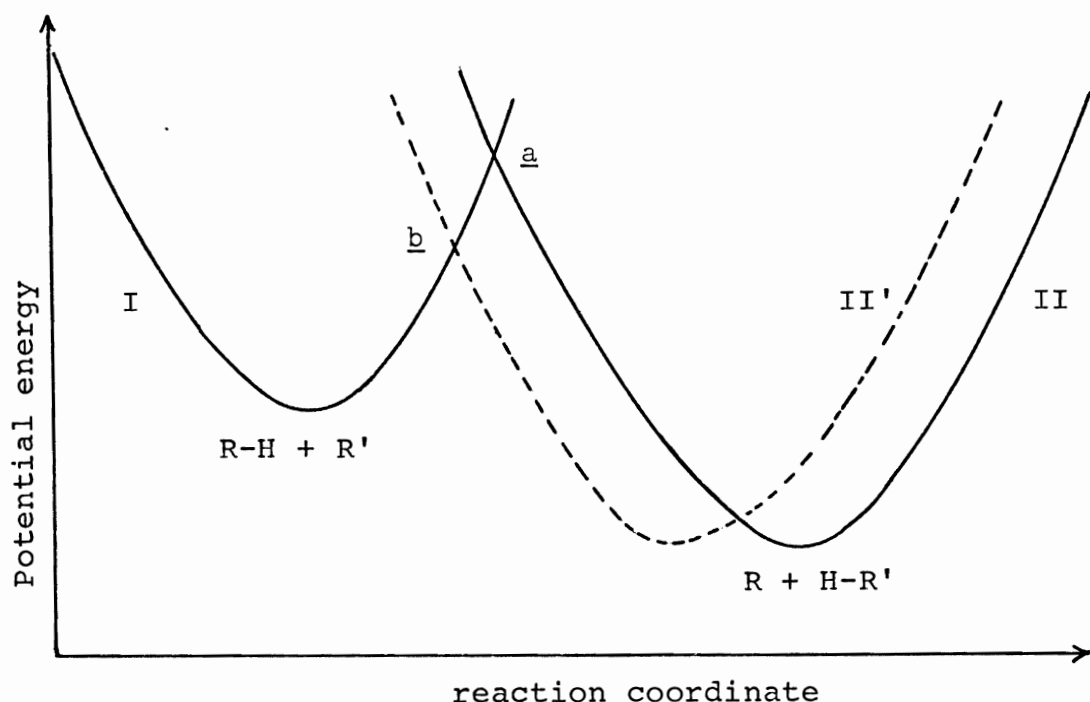


Fig. 1. Effect of the motion of the nuclei on the potential energy barrier for interconversion.

closer (in a geometric sense) to that of the reactants. The interconversion leading to products in this well requires less R-H bond stretching, allows earlier H-R' bond making, and thus its energy barrier (point b) is lower.

The other condition is the least change in electronic configuration. Consider now the crossover point of the two potential energy curves I and II in Figure 2 (overleaf). In the region of this point the two systems have nearly identical energies and nearly identical geometries, and there will be considerable mixing of the electronic states of $R-H + R'$ and $R + H-R'$. This mixing results in a separation represented by the dashed portion of the diagram. The greater the similarity of the electronic states, the

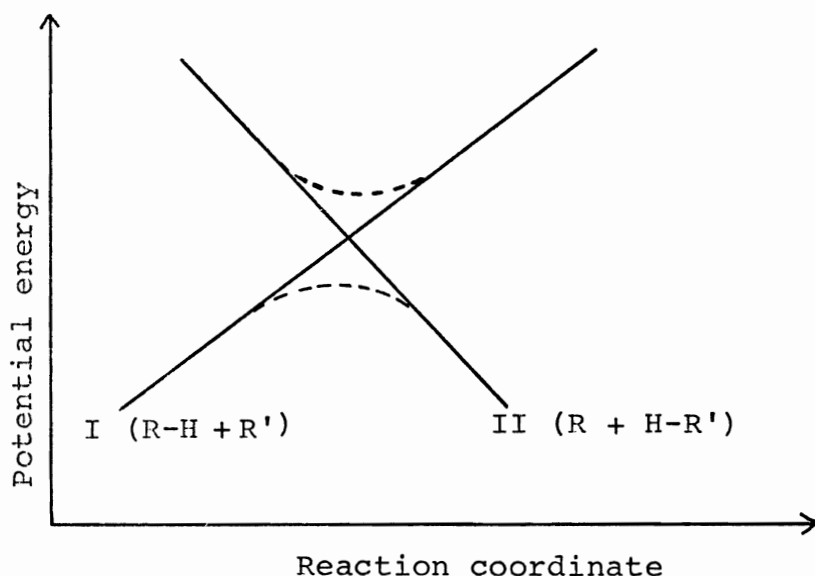


Fig 2. Cross-over point of curves I and II magnified.

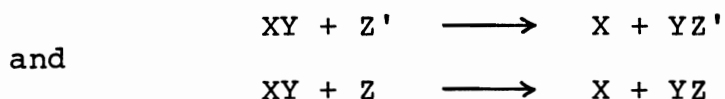
greater will be the mixing and the separation, and hence the lower will be the barrier to the interconversion in equation 1.

Applications of the Principle of Least Motion.

Following Rice and Teller²¹, Hine²² applied the PLM to reactions of resonance stabilised species. His discussion was based on an earlier method by London²³, involving the estimation of the potential energy of a system as a function of a "geometric coordinate". This coordinate is a measure of atomic displacements in the system. It should also be mentioned that Polanyi and coworkers²⁴ previously applied the same technique to proton-transfer reactions. These applications proved to be of great help in the

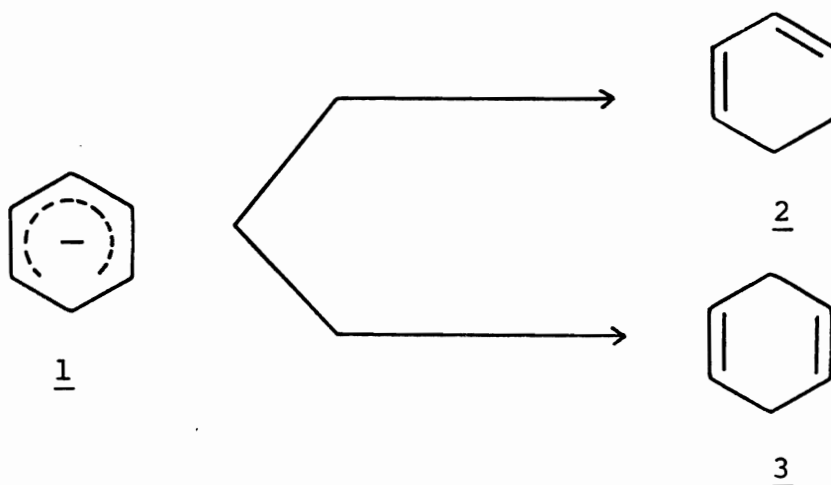
rationalisation of both the Bronsted catalysis equation, and the change in magnitudes of Bronsted α and β values with concomitant changes in reactant structures²⁵⁻²⁹.

Hine²² reasoned, by means of potential energy considerations, that for two closely related reactions of the form



the corresponding rates should vary according to the extent of the change in the internal geometry of Z and Z' during the reaction in such a way that the process involving the lesser change should be faster. Similarly, for reactants having two potential products, the kinetically controlled product derives from the pathway requiring the least structural change.

For a semiquantitative treatment, Hine²² chose the protonation of the cyclohexadienyl anion (1) by an alcohol molecule. He constructed potential energy curves for both 1,3- and 1,4-cyclohexadiene (2 and 3).



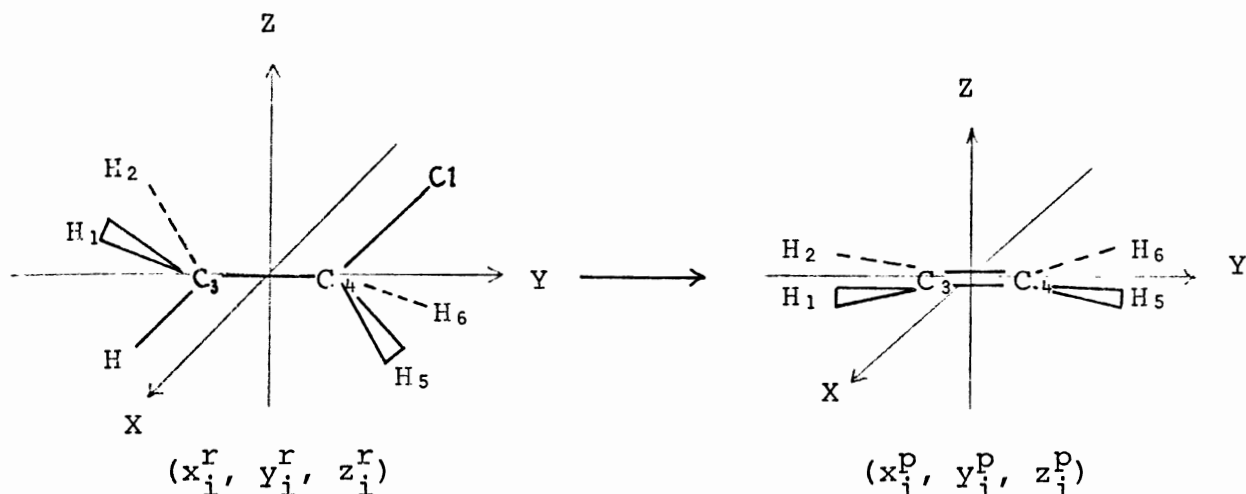
By making appropriate corrections for changes in internal geometry due to changes in hybridisation, he estimated the activation energy for the formation of the 1,4-cyclohexadiene (3) to be lower by approximately 0.53 kcal/mole. Comparing the above value with two independent experimental results of 1.5 kcal/mole³⁰ and 4.3 kcal/mole³¹, Hine concluded that his semi-empirical approach, although not sufficiently refined to represent the exact differences in activation energy, is nevertheless applicable for the rationalisation of certain experimental results, since it functions in the correct direction with an appropriate order of magnitude.

An even simpler approach, involving the calculation of the sums of the squares of the changes in bond numbers in going to each product in question, and the selection of the preferred product based on the magnitude of the above sums (i.e. the molecule having the lowest sum is preferred), was also presented²². Despite the naivete of the treatment, it correctly predicted the order of positional reactivity, and supplied proper answers to the anomalies arising from several types of reactions of resonance stabilised species. However, a more recent application using bond orders obtained from Huckel type molecular orbital calculations gave incorrect predictions³².

For the application of PLM to β -eliminations a somewhat modified technique has been employed³³. It was

postulated that the reaction will occur in such a way as to involve the minimum expenditure of energy in changing the relative positions of the atoms in the reactant molecule to their corresponding positions in the product molecule. If the stretching and bending of bonds essentially obey Hooke's law, then the energy required to stretch or bend a bond is proportional to the square of the distance stretched or bent. Since earlier calculations of potential energies proved to be inaccurate²², the treatment was simplified by considering only the magnitude of changes in atomic positions. This approach would demand that all the force constants for the displacements of various atoms be identical if it were completely applicable. In the present case, however, where considerations are given only to the displacements of the atoms in various directions, it amounts largely to the approximation that the various atoms move in isotropic force fields. Thus, provided that the energy change associated with the making and breaking of bonds is essentially the same for all the possible stereochemical routes of a given reaction, then the minimum sum of the squares of the atomic displacements should identify the preferred path.

The above method was demonstrated on the E_2 transformation of ethyl chloride to ethylene³³.



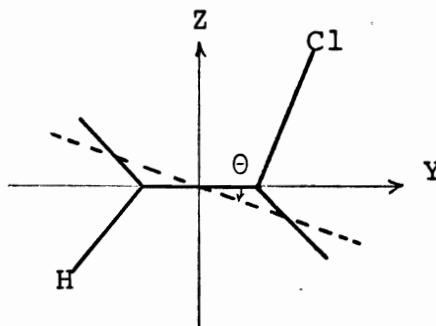
Four distinct cases were considered corresponding to dihedral angles between the leaving groups of 0° , 60° , 120° and 180° . In all four cases both the reactant and the product were placed in a three-dimensional Cartesian coordinate system, the coordinates of each atom* being calculated from published structural data^{34,35}. Following this, the product was superimposed on the reactant in such a fashion as to obtain the best fit (by visual inspection), and its coordinates were expressed as a function of a parameter related to the assumed position of the superimposed product.

For the case of pure trans-elimination the product

* The calculation ignored those atoms not common to the reactant and product, since it was assumed that the difference is due to the relaxation of the non-planar incipient ethylene fragments to the planar arrangement.

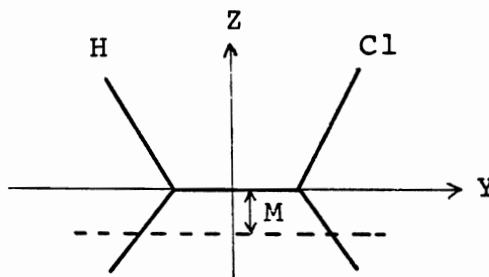
was rotated about the X-axis by an angle of θ ; thus its coordinates were expressed as

$$\begin{aligned}x_i &= x_i^p \\y_i &= y_i^p \cos \theta \\z_i &= y_i^p \sin \theta\end{aligned}$$



In pure cis-elimination the product was shown to require a displacement in the Z-direction by a quantity M, therefore its coordinates were set as

$$\begin{aligned}x_i &= x_i^p \\y_i &= y_i^p \\z_i &= -M\end{aligned}$$



For the two intermediate cases a combination of rotation and translation was necessary, thereby requiring their coordinates to be expressed as a function of both θ and M.

Using the coordinates for both the reactant and product, the sum of the squares of the atomic displacements were computed according to the equation

$$E = \sum_i^n D_i^2 = \sum_i^n (x_i^r - x_i)^2 + (y_i^r - y_i)^2 + (z_i^r - z_i)^2 \dots (1)$$

where x_i^r , y_i^r and z_i^r are the coordinates of the reactant and x_i , y_i and z_i are those of the superimposed product.

The above equation was then minimised with respect to the parameter θ or M (or both) by setting $\partial E/\partial \theta$ or $\partial E/\partial M$ (or both) equal to zero. Table I shows the results.

Table I. Variation of E_{\min} with the Dihedral Angle for 1,2-Elimination from Ethyl Chloride.

Dihedral angle, deg	$E_{\min}, \text{\AA}^2$	θ, deg	$M, \text{\AA}$
0	0.421		0.347
60	1.326	7.33	0.300
120	1.130	18.50	0.173
180	0.185	21.15	

In his previous paper, Hine has shown²² that a difference of 0.02\AA^2 could account for activation energy differences in the order of 1 kcal/mole. Thus the above numbers lead to the conclusion that the pure trans-elimination will be preferred. This result is in agreement with experimental results^{36,37}. Furthermore, the order of preference found for the various dihedral angles concurs with published data³⁶.

As the size of the molecule increases and/or the number of symmetry elements decreases, hand calculations of the type carried out by Hine³³ become increasingly complex. Therefore, Tee³⁸ proposed a generalised method which is

based on the following:

Given x_i^r, y_i^r, z_i^r , and x_i^p, y_i^p, z_i^p as a set of coordinates for the reactant and product, respectively, it is required that the latter set be transformed to a new set x_i, y_i, z_i such that E (eqn. 1) has a minimum. The most general transformation is carried out by a translation of the origin of the axes to (x,y,z) , followed by rotation about the axes by $\theta_x, \theta_y, \theta_z$. Thus in general the minimisation must be carried out with respect to six variables $x, y, z, \theta_x, \theta_y, \theta_z$. A computer program using an iterative technique was written³⁸ to perform this minimisation. A detailed account of the above method will be given in a later section.

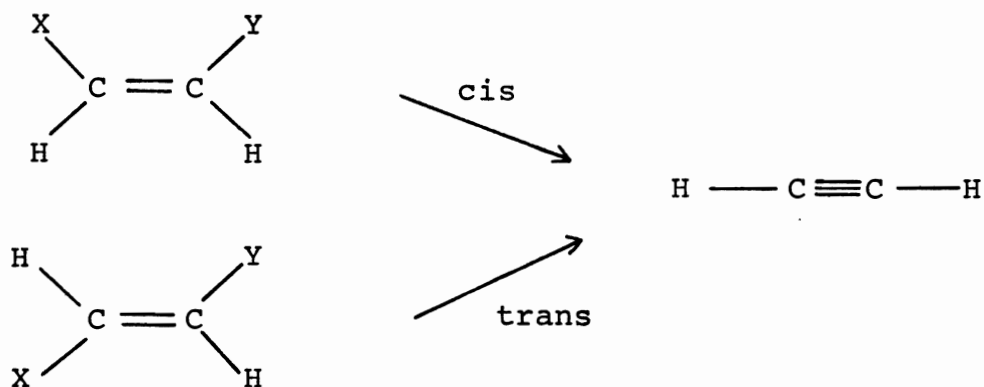
Applications of the PLM Using the Generalised Method.

In this section the systems considered by Tee^{38,39} will be outlined briefly, since the subject of this thesis is an extension of this earlier work.

1. β -Eliminations.

Ethylene formation from ethyl chloride was repeated using the same molecular parameters as were used earlier³³. Calculations were performed for dihedral angles ranging from 0° to 180° in 30° increments. Results paralleled those of Hine³³. Preferred trans-elimination was also shown for

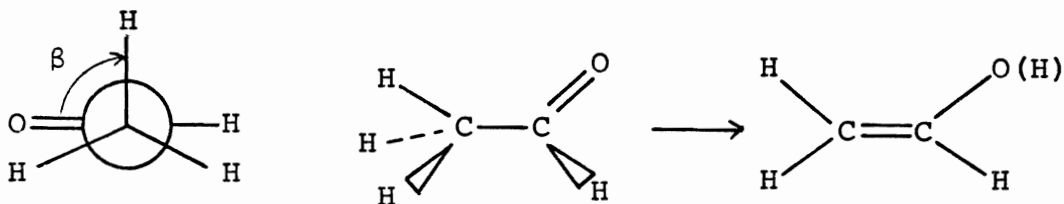
acetylene formation from simple olefins.



For both ethylene and acetylene formation it was predicted that substitution will enhance preference for anti-elimination.

2. Enolisation.

Proton abstraction from the carbon atom α to a carbonyl group was studied using acetaldehyde as a model compound.



Calculations were carried out for various dihedral angles, β .

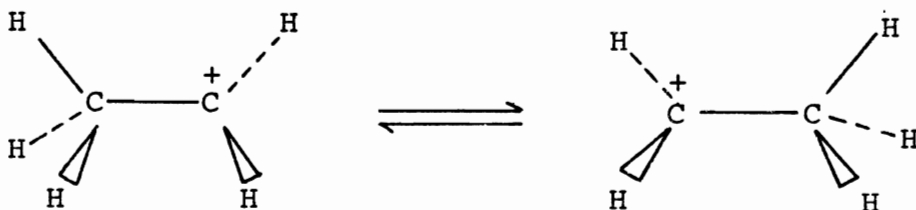
The lowest minimised sum (E_{\min}) was found to be for a rotamer having the hydrogen perpendicular to the trigonal plane of the sp^2 hybridised carbon, in agreement with experimental evidence.

3. Molecular rearrangements.

Intramolecular rearrangement was anticipated to be the area in which the use of PLM would be most appropriate, since no atoms have to be neglected, and the effect of external reagents should be negligible.

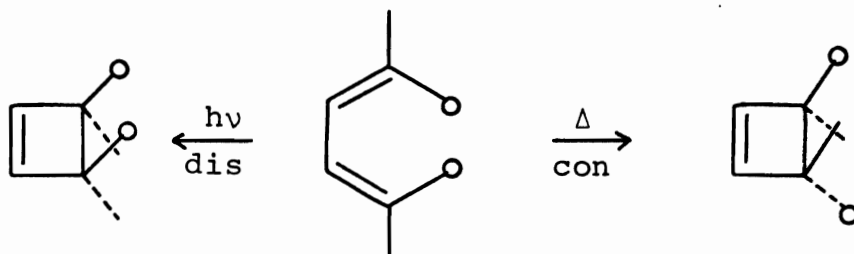
One of the examples chosen was the interconversion of species of the type AX_5 having a trigonal bipyramidal structure. The calculations predicted that, of the five conceivable alternatives, pseudorotation should be the preferred path of interconversion.

PLM was also applied to a 1,2-hydride shift in ethyl cation. The results suggested that migration will preferentially occur when the migrating hydride ion is perpendicular to the trigonal planes of both the reactant and the product.



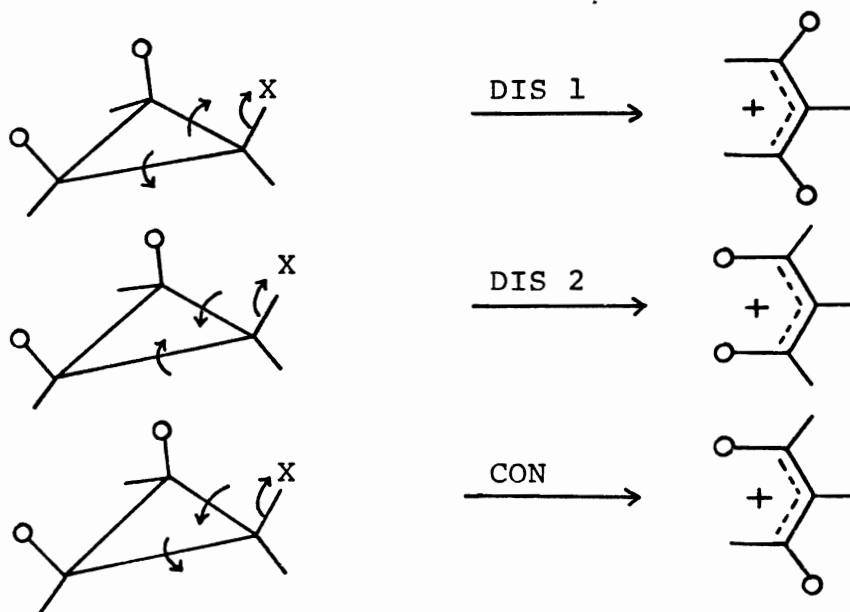
This finding is in agreement with arguments based on molecular orbital considerations.

The cyclisation of butadiene to cyclobutene was also studied and the conrotatory mode was predicted to be favoured



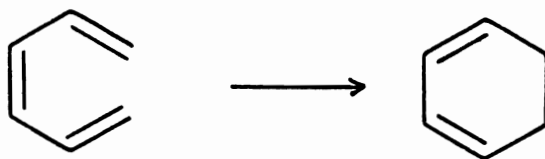
in accord with the Woodward-Hoffman rules¹. The same result was obtained later using more up-to-date molecular parameters³⁹, and varying the angle of twist about the central bond of butadiene.

The thermal ring opening of cyclopropyl cation to



form allyl cation was predicted by the PLM to occur in a disrotatory manner in accord with similar findings by other techniques⁴⁰. Moreover, in the case when the ring opening is concerted with the loss of the leaving group, and two disrotatory processes are distinguishable, both the calculations and the experiments⁴¹ preferred the DIS 2 mode.

For the transformation of 1,3,5-hexatriene to 1,3-cyclohexadiene the results obtained (preferred conrotatory ring closure) did not agree with either the experimental



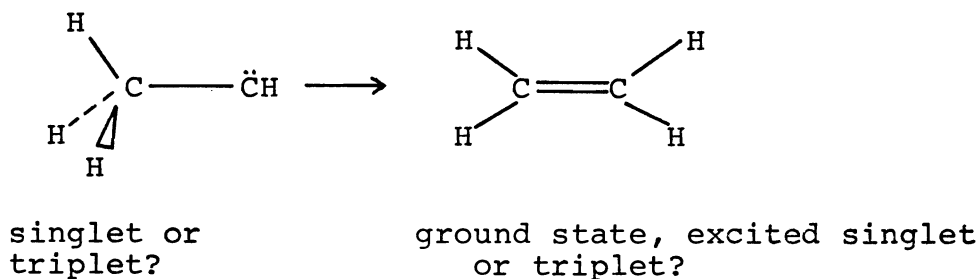
results or the predictions based on the conservation of orbital symmetry¹.

PLM calculations were carried out for the interconversion of various conformers of cyclohexane. The results agree with the currently held view that chair to chair interconversion occurs via the intermediacy of a twist conformer, and that the boat conformer represents the transition state between two twist forms.

Another interesting reaction studied using PLM was the Cope rearrangement. Conceivably, the transition state for this process could be either "chair-like" or

"book-like". The calculations, however, did not indicate a definite preference for either mode. Experimentally, it has been shown that a "chair-like" transition state is preferred⁴², although it was pointed out that certain cyclic molecules do react via a "book-like" transition state⁴³.

The migration of a hydrogen in methyl carbene to produce ethylene could be visualised as occurring in several ways, depending upon the electronic state of the reactant and the product.



The results of PLM calculations emphasised that the ethylene will most probably be produced in an excited state of the same multiplicity as the reactant carbene. Orbital symmetry considerations also favour the formation of the product in an excited state. Furthermore, the calculations suggested the possible stereochemistry of the hydrogen migration.

METHOD OF CALCULATION

The procedure followed consisted of three parts:

Part 1. Calculation of the Atomic Coordinates.

- a) The Cartesian coordinates of the reactant and product were calculated in the most convenient fashion by the methods of analytical geometry, using the structural parameters either from literature or based on suitable estimates.
- b) Checking for errors in the calculation of the above was performed by recalculating the individual bond lengths using equation (1).

$$D_{ij} = \sqrt{(x_i - x_j)^2 + (y_i - y_j)^2 + (z_i - z_j)^2} \quad \dots (1)$$

where (x_i, y_i, z_i) are the coordinates of atom i and (x_j, y_j, z_j) are those of atom j .

Part 2. Calculation of E_{\min} .

E_{\min} is defined as the minimum sum of squares of the individual atomic displacements between the reactant and the product. The calculation was performed using the program LESMOT, the basis of which may be found in the literature³⁸.

The program requires as input:

- a) the number of atoms common to both the reactant and product,
- b) the (x,y,z) coordinates of the above
- c) the maximum number of iterations desired
- d) an initial estimate of the parameters C_j ($j= 1....6$) required for the minimisation of E (i.e. $C(1,2,3)$ are needed for translation and $C(4,5,6)$ for rotation)

The program functions as follows:

1. Using the data from b) above, it calculates the initial sum of the squares of the atomic distances.
2. With the aid of the initial C_j ($j= 4,5,6$) values from d) above the rotation matrices θ_x, θ_y and θ_z , are set up, where

$$\theta_x = \begin{pmatrix} 1 & 0 & 0 \\ 0 & \cos C_4 & -\sin C_4 \\ 0 & \sin C_4 & \cos C_4 \end{pmatrix}$$

$$\theta_y = \begin{pmatrix} \cos C_5 & 0 & \sin C_5 \\ 0 & 1 & 0 \\ -\sin C_5 & 0 & \cos C_5 \end{pmatrix}$$

$$\theta_z = \begin{pmatrix} \cos C_6 & -\sin C_6 & 0 \\ \sin C_6 & \cos C_6 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

3. The above matrices are multiplied to obtain the triple product: $\theta_x \theta_y \theta_z$.

4. Using the parameters C_j ($j=1,2,3$) the origin is translated:

$$Q_i = \begin{pmatrix} x_o \\ y_o \\ z_o \end{pmatrix} = \begin{pmatrix} x_i^p - C_1 \\ y_i^p - C_2 \\ z_i^p - C_3 \end{pmatrix}$$

5. The new coordinates are obtained by multiplication of 3. and 4. above:

$$\theta_x \theta_y \theta_z \begin{pmatrix} x_o \\ y_o \\ z_o \end{pmatrix} = \begin{pmatrix} x_i \\ y_i \\ z_i \end{pmatrix}$$

6. Utilising the new coordinates obtained from above, the program calculates the sum of the squares of the atomic displacements (E).

7. Next, it compares the E value from 6. to the original from 1. If the absolute value of the difference is less than 0.5×10^{-6} , then convergence is registered.

8. If there is no convergence, then by means of the parameters C_j ($j=4,5,6$), it evaluates the differentials of the matrices: θ'_x, θ'_y and θ'_z

9. Incorporating 3., 4. and 8., it evaluates the partial differentials $\partial x_i / \partial C_j = Fx_j^i$, $\partial y_i / \partial C_j = Fy_j^i$, etc., and sets up the matrix whose elements are:

$$F_1^i = \begin{pmatrix} Fx_1^i \\ Fy_1^i \\ Fz_1^i \end{pmatrix} = \theta_x \theta_y \theta_z \begin{pmatrix} -1 \\ 0 \\ 0 \end{pmatrix}$$

$$F_2^i = \theta_x \theta_y \theta_z \begin{pmatrix} 0 \\ -1 \\ 0 \end{pmatrix}$$

$$F_3^i = \theta_x \theta_y \theta_z \begin{pmatrix} 0 \\ 0 \\ -1 \end{pmatrix}$$

$$F_4^i = \theta'_x \theta_y \theta_z \cdot Q_i$$

$$F_5^i = \theta_x \theta'_y \theta_z \cdot Q_i$$

$$F_6^i = \theta_x \theta_y \theta'_z \cdot Q_i \quad (\text{Where } Q_i \text{ is defined as in 4.})$$

10. Using the obtained partial differentials, the column vector S_j ($j=1, \dots, 6$) is evaluated, where

$$S_j = \frac{\partial E}{\partial C_j}.$$

Next it calculates the error in S_j by evaluating the elements of a 6 x 6 matrix $A = (A_{lj})$ defined by:

$$A_{lj} = \sum_{l=1}^6 \left(\sum_{i=1}^n - (F x_j^i F x_l^i + F y_j^i F y_l^i + F z_j^i F z_l^i) \right)$$

(j= 1,.....6)

and inverting the matrix, after which it performs the multiplication:

$$A^{-1} S = \Delta C$$

The error vector ΔC contains estimates of the errors in C_j . Using it six new C-parameters are calculated which then may be used to perform translation, rotation, differentiation, etc., in an iterative fashion until the process registers convergence.

Normally the program converges rapidly, especially with respect to the displacements $C(1,2,3)$. It is less sensitive, however, to the angles of rotation ($C(4,5,6,))$. The initial parameters C_j should not be set to zero, since this results in the translation vector being zero, the rotation matrices being identity matrices and consequently the program registering false convergence.

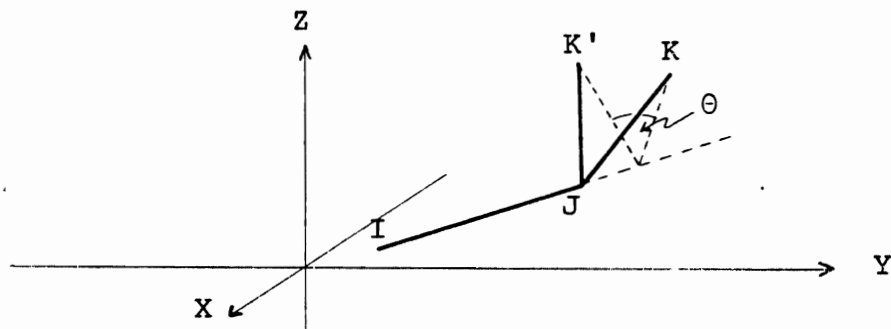
Part 3. Rotation About Bonds.

In some cases calculations were performed for a number of conformations of a molecule generated by

rotation about a bond by various dihedral angles. This was achieved by using the program LESMOT/2 which included a rotating program ROTCOR as a subroutine.

The basis for ROTCOR is the following³²:

If rotation of a point K about a bond IJ is desired, the simplest way is the transformation of the coordinates of I, J and K such that I, J lies along an axis. After the rotation is performed, the coordinates are transformed back such that I, J are at their original positions.



The step-by-step procedure to be followed is thus:

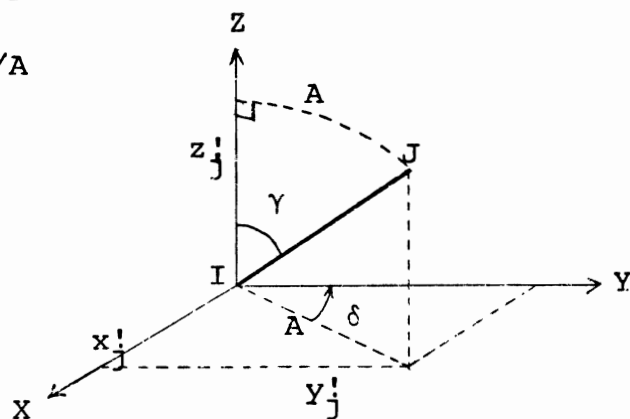
1. Translate I with coordinates $q_I = (x_I, y_I, z_I)$ to origin.

$$q' = q - q_I \quad \text{where } q = (x, y, z)$$

2. Next, rotate I, J (with K) about the Z-axis by an angle δ so that IJ lies in the YZ-plane:

$$\cos \delta = y'_j / \sqrt{(x'_j)^2 + (y'_j)^2} = y'_j / A$$

$$\sin \delta = -x'_j / A$$



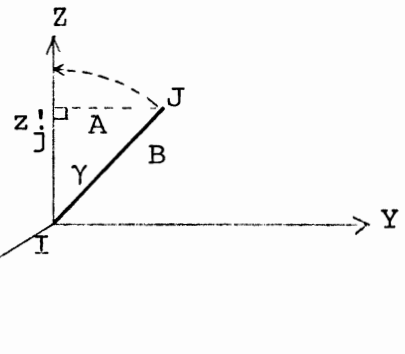
Rotation matrix $\Delta = \begin{pmatrix} \cos \delta & -\sin \delta & 0 \\ \sin \delta & \cos \delta & 0 \\ 0 & 0 & 1 \end{pmatrix}$

3. Now rotate IJ (with K) about the X-axis by an angle γ until IJ will lie on the Z-axis:

$$\cos \gamma = z'_j / B$$

$$\sin \gamma = A/B$$

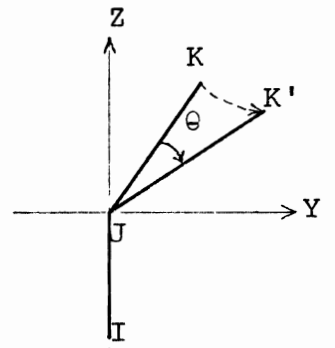
$$\text{where } B = IJ = \sqrt{A^2 + z_j'^2}$$



Rotation matrix $\Gamma = \begin{pmatrix} 1 & 0 & 0 \\ 0 & \cos \gamma & -\sin \gamma \\ 0 & \sin \gamma & \cos \gamma \end{pmatrix}$

4. Next rotate K about the Z-axis by the required angle θ :

Rotation matrix $\Theta = \begin{pmatrix} \cos \theta & -\sin \theta & 0 \\ \sin \theta & \cos \theta & 0 \\ 0 & 0 & 1 \end{pmatrix}$



The direction of rotation is defined anti-clockwise looking from J to I.

5. In order to place I and J back into their original positions, a reverse transformation has to be performed.

The rotational matrices are:

$$\Gamma' = \begin{pmatrix} 1 & 0 & 0 \\ 0 & \cos\gamma & \sin\gamma \\ 0 & -\sin\gamma & \cos\gamma \end{pmatrix}$$

$$\Delta' = \begin{pmatrix} \cos\delta & \sin\delta & 0 \\ -\sin\delta & \cos\delta & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

and the translation of I is:

$$q = q' + q_I$$

In summary, the overall transformation is:

$$q^K = q_I + \Delta' \Gamma' \theta \Gamma \Delta (q^K - q_I)$$

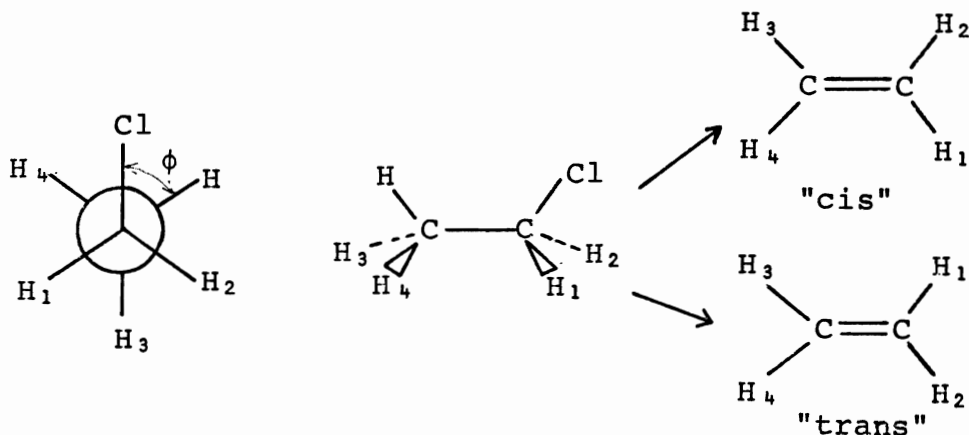
Note that if several atoms (in addition to K) are associated with J, then their coordinates may be rotated simultaneously.

RESULTS AND DISCUSSION

1.2-Eliminations.

Owing to the results of numerous experiments concerning reactions showing stereospecificity, it was concluded that bimolecular ionic eliminations (E_2) take place most readily when the four centres and the base lie in one plane, and that the atoms to be eliminated are trans to each other (anti-periplanar)⁴⁴. In open-chain compounds, whenever sterically feasible, the reactant molecule may adopt this required conformation⁴⁵.

Elimination from ethyl chloride. Earlier workers have studied the E_2 elimination from ethyl chloride using the PLM method^{33,38}. It was pointed out³⁸ that, since the hydrogens are specifically labelled, the elimination could yield either a "cis"- or a "trans"- product which might be formed from a number of rotational isomers of ethyl chloride.



Calculations on this system were extended to encompass

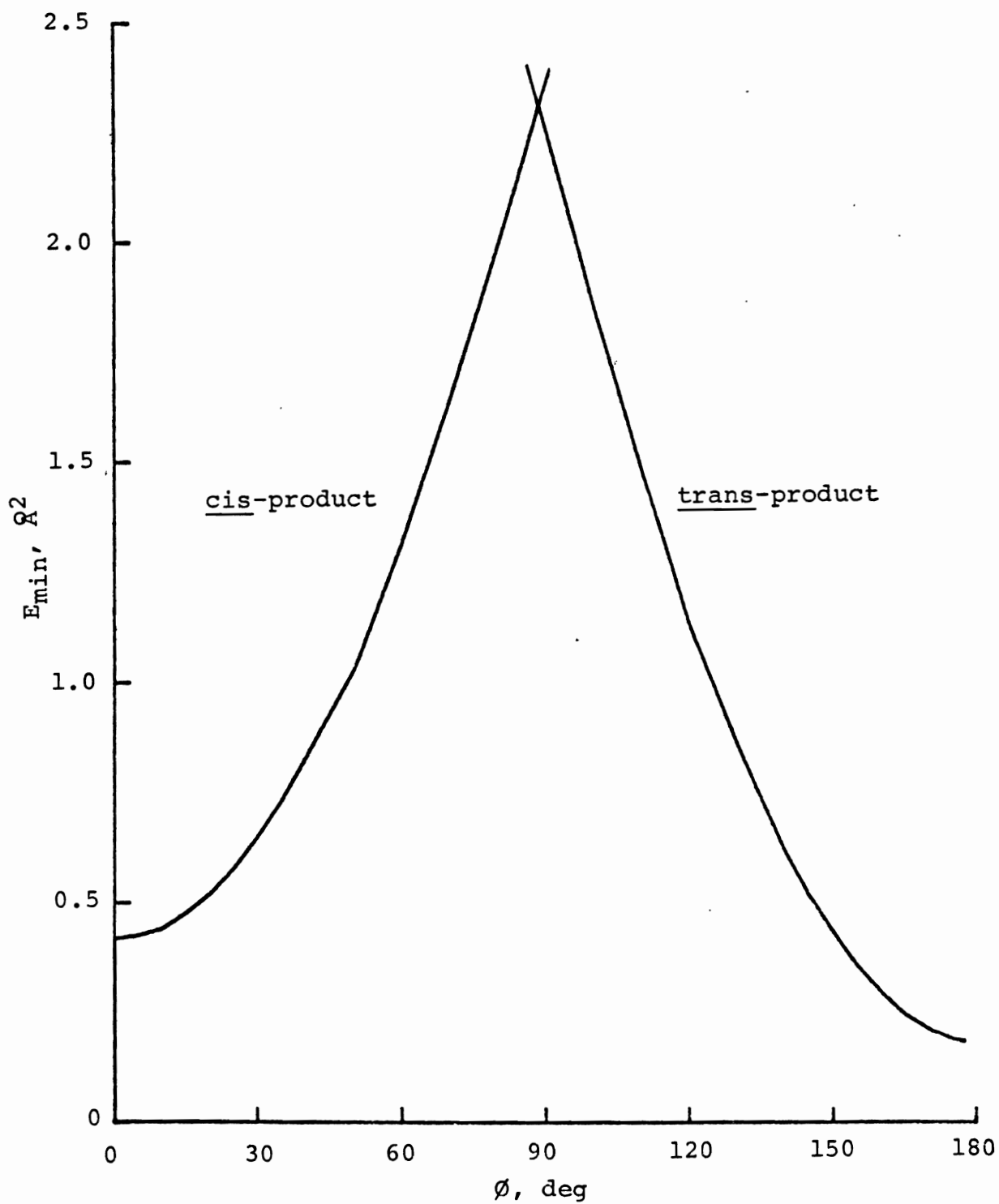
more values of the dihedral angle ϕ , in order to more closely define the relationship between the minimum sum of the squares of the atomic displacements (E_{\min}) and ϕ . The coordinates of the reactant and product were calculated from molecular parameters used earlier³³. Results are presented in Table II below.

Table II. Variation of E_{\min} with Dihedral Angle for β -Elimination from Ethyl Chloride.

<u>"cis"</u> -product		<u>"trans"</u> -product	
ϕ , deg	$E_{\min}, \text{\AA}^2$	ϕ , deg	$E_{\min}, \text{\AA}^2$
0	0.421	90	2.254
15	0.479	105	1.647
30	0.653	120	1.134
45	0.937	135	0.725
60	1.326	150	0.427
75	1.810	165	0.246
90	2.379	180	0.185

From the data in Table II and plotted in Fig.3(p 32) it is apparent that PLM favours the formation of ethylene from a conformer of ethyl chloride in which the leaving groups have an anti-periplanar³ relationship ($\phi = 180^\circ$,

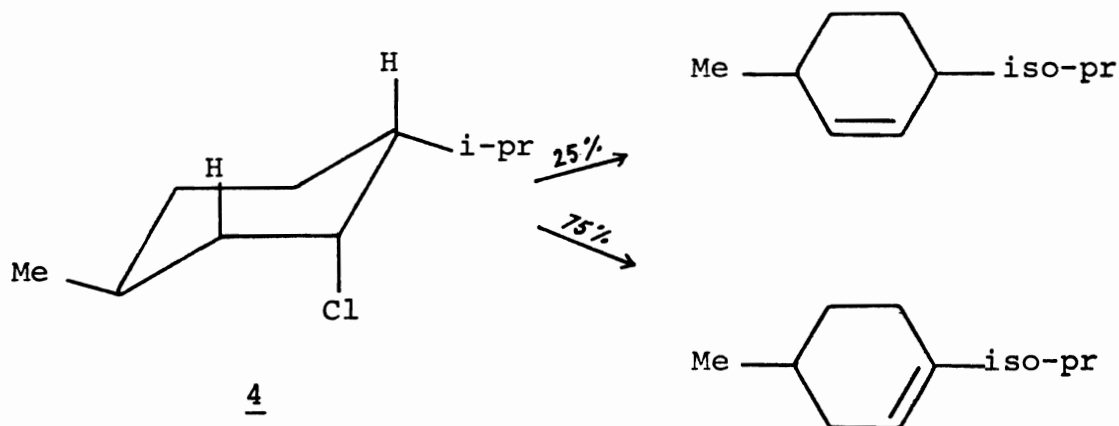
Figure 3. Variation of E_{\min} with the Dihedral Angle ϕ
for the 1,2-Elimination from Ethyl Chloride.



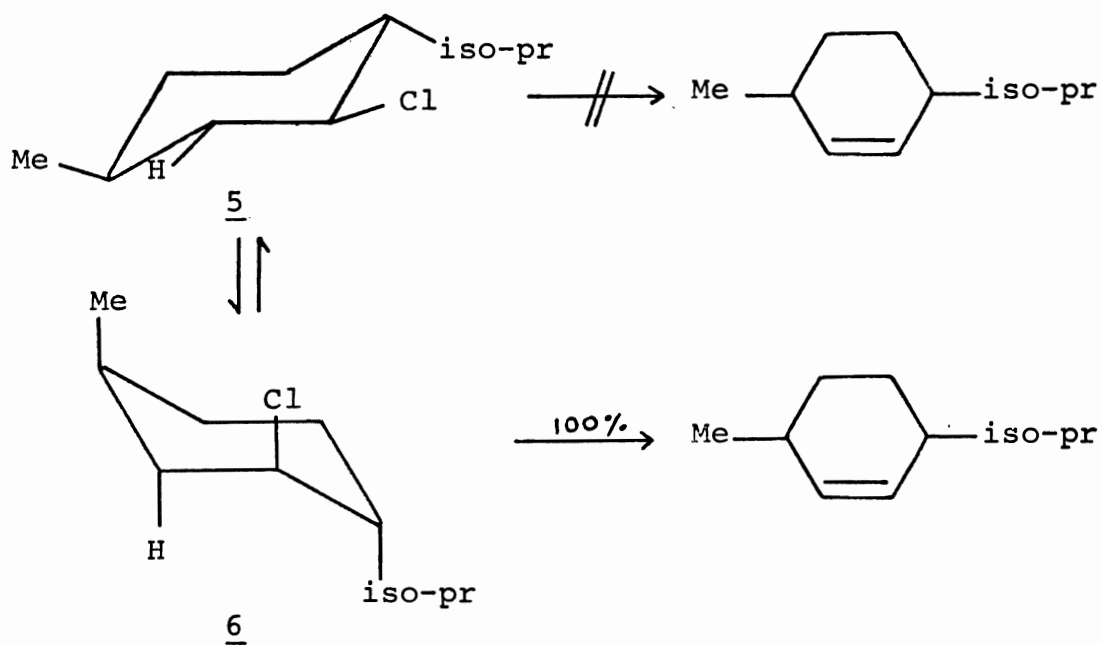
"trans"-product). The data suggest that a "cis"- product is only really feasible when the dihedral angle ϕ is close to 0° . Due to the sharp increase of both curves in Fig. 3 the chances of product formation should be very low for dihedral angles which differ markedly from either 0° or 180° . Not surprisingly, these conclusions are the same as those drawn earlier^{33,38}.

Elimination from cyclohexyl chloride. In cyclic systems an anti-periplanar arrangement of leaving groups is not always possible. For instance, in cyclohexane derivatives this relationship exists only where the groups are 1,2-diaxial. Compounds where the potential leaving groups are trans, but are held in equatorial positions, may undergo elimination but at a rate which is slower by many orders of magnitude. A number of suitable examples are provided by the debromination of steroid dibromides with iodide ion⁴⁶.

It is noteworthy that the requirement of the anti-periplanarity of the leaving groups prevails even if it necessitates the adoption of a conformation of higher energy. For example, the more stable chair conformation of neomenthyl chloride (4), in which both the bulky isopropyl and methyl groups are in equatorial positions, possesses two axial hydrogens available for anti-diaxial elimination, thus allowing the facile reactions below.



However, in the case of menthyl chloride, the more stable chair conformation (5) does not have the chlorine atom in a required axial position.



The achievement of coplanarity of the leaving groups requires conversion of (5) to the energetically less favourable conformation (6) prior to elimination. In consequence, menthyl chloride undergoes a much slower elimination than neomenthyl chloride⁴⁷. Many other examples demonstrating the strong preference towards anti-diaxial E_2 elimination from cyclohexane derivatives are known^{48,49,50}. In view of this, PLM calculations were performed for the conversion of a cyclohexane to cyclohexene by a synchronous elimination. In addition, it seemed necessary to test that the preference exhibited by the calculations for the ethyl chloride to ethylene conversion is also applicable to the cyclohexyl analogue.

Since there are three well known⁵¹ conformations of the cyclohexane, the interconversions of which were dealt with earlier³⁹, all of these were considered as the possible reactant in the elimination reaction. The molecular parameters used for the calculation of the coordinates of the reactants and the products are listed in Table III.

The coordinates of cyclohexyl chloride were taken to be those of cyclohexane³⁹, since the chlorine atom was not included in the computations of E_{\min} . For the chair conformation, D_{3d} ; for the boat, C_{2v} ; and for the symmetrical twist, D_2 symmetry was assumed⁵⁴.

Table III. Reported Bond Lengths and Bond Angles of Cyclohexane Derivatives.

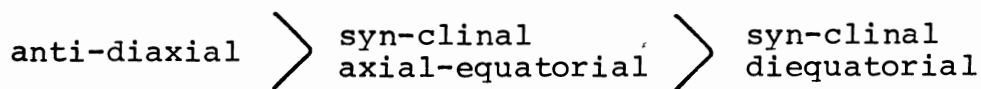
Molecule	Bond lengths, Å		Bond angles, deg		Ref.
Cyclohexyl chloride (chair, twist and boat conf.)	-C-C-	1.54	tetrahedral		39
	-C-H	1.10			
Cyclohexene boat conf.	-C-C-	1.533	-C=C-C-	117.7	52
	=C-C-	1.505	-C-C-C-	108.9	
	-C=C-	1.331			
	-C-H	1.108			
	=C-H	1.085			
Cyclohexene half-chair conformation	-C=C-	1.335	-C=C-C-	123.5	53
	=C-C-	1.504	=C-C-C	121.1	
	-C-C-	1.515	-C-C-C-	110.0	
	-C-C-	1.550*			
	-C-H _{av}	1.093			

* Long single bond corresponds to the one opposite to the double bond.

The molecular structure of cyclohexene in the half-chair conformation, which has been determined by electron diffraction to have C_2 symmetry⁵², was used as the product for those reactions which have the reactant either in a chair or in a symmetrical twist conformation.

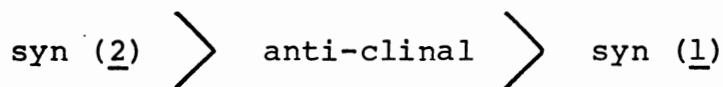
The product resulting from eliminations using the boat conformer as the reactant was assumed to have a similar boat conformation with a plane of symmetry.

Results are presented in Table IV (overleaf), which shows the different modes of eliminations for the chair, symmetrical twist and boat conformations respectively, and the corresponding E_{\min} values obtained by the PLM calculations. According to the above, for both the chair and the symmetrical twist conformations the order of preference in elimination reactions should be:



This order agrees with both the predictions based on the ease of achievement of coplanarity of the four atoms and the base involved, and the experimental results⁴⁶⁻⁵⁰.

For the boat conformation the results indicate the following order of preference:



The geometry of this conformation is such that both its

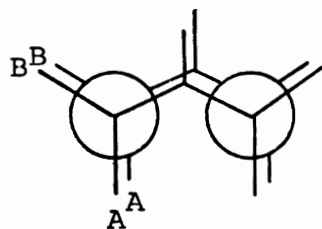
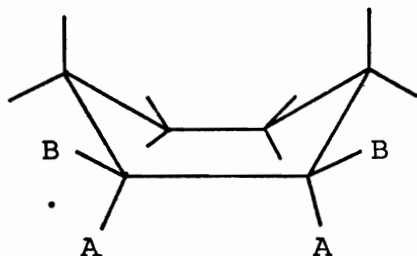
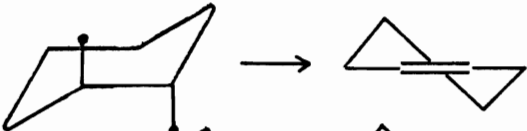
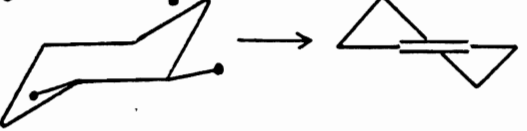
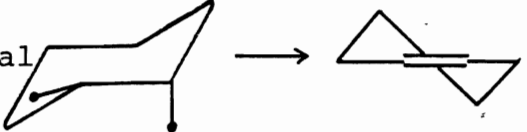
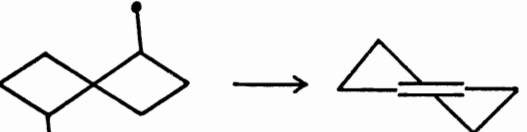
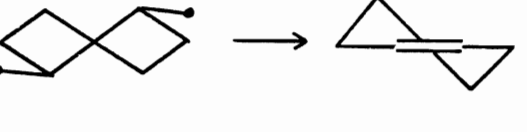
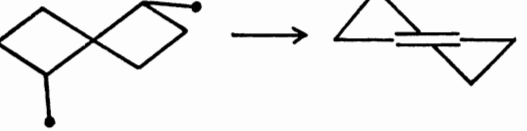
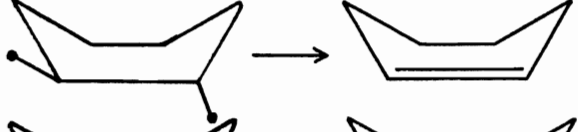

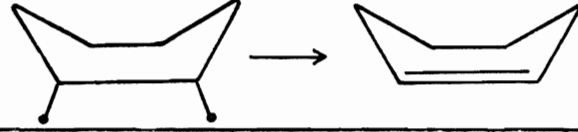


Table IV. Variation of E_{\min} with the Modes of Elimination from Cyclohexane Derivatives.

Elimination type	Reaction	$E_{\min}, \text{\AA}^2$
Anti-diaxial		0.610
Syn-clinal diequatorial		7.36
Syn-clinal axial-equatorial		3.64
Anti-clinal diaxial		0.938
Syn-clinal diequatorial		8.86
Syn-clinal axial-equatorial		4.64
Anti-clinal		2.20
Syn (1)		2.23
Syn (2)		1.10

pseudo-axial (A) and pseudo-equatorial (B) substituents are eclipsed. Owing to the non-coplanarity of the AC and CB bonds in the transition state, the anti-clinal elimination is not expected to be favoured. On the other hand, a priori similar E_{\min} values would be expected for the two syn-type eliminations, because the four atoms involved are coplanar in both. However, there are geometrical differences between these processes which can be best explained with the aid of Fig.4 (p. 40) presenting the X-Y plane projections of reactant and product for all three types of eliminations involving the boat conformer. The solid lines are used for the reactant and the dashed lines indicate the position of the product at E_{\min} . It is apparent from Fig.4 that the displacements of atoms 7 and 8 are much smaller in case (a) than they are in case (b). Furthermore, in the latter case minimisation of the 7-7' and 8-8' distances resulted in a fairly large increase of both the 12-12' and the 14-14' distances. Therefore (a) would be expected to have a lower E_{\min} than (b).

In Fig.4 (c) the displacements of atoms 7 and 8 are very similar to that in (b), but displacements of the other atoms in the molecule are somewhat smaller, thus the E_{\min} value is expected to be slightly lower than in (b).

In summary, the PLM results agree with the observations⁴⁶⁻⁵⁰ that concerted E_2 elimination occurs preferen-

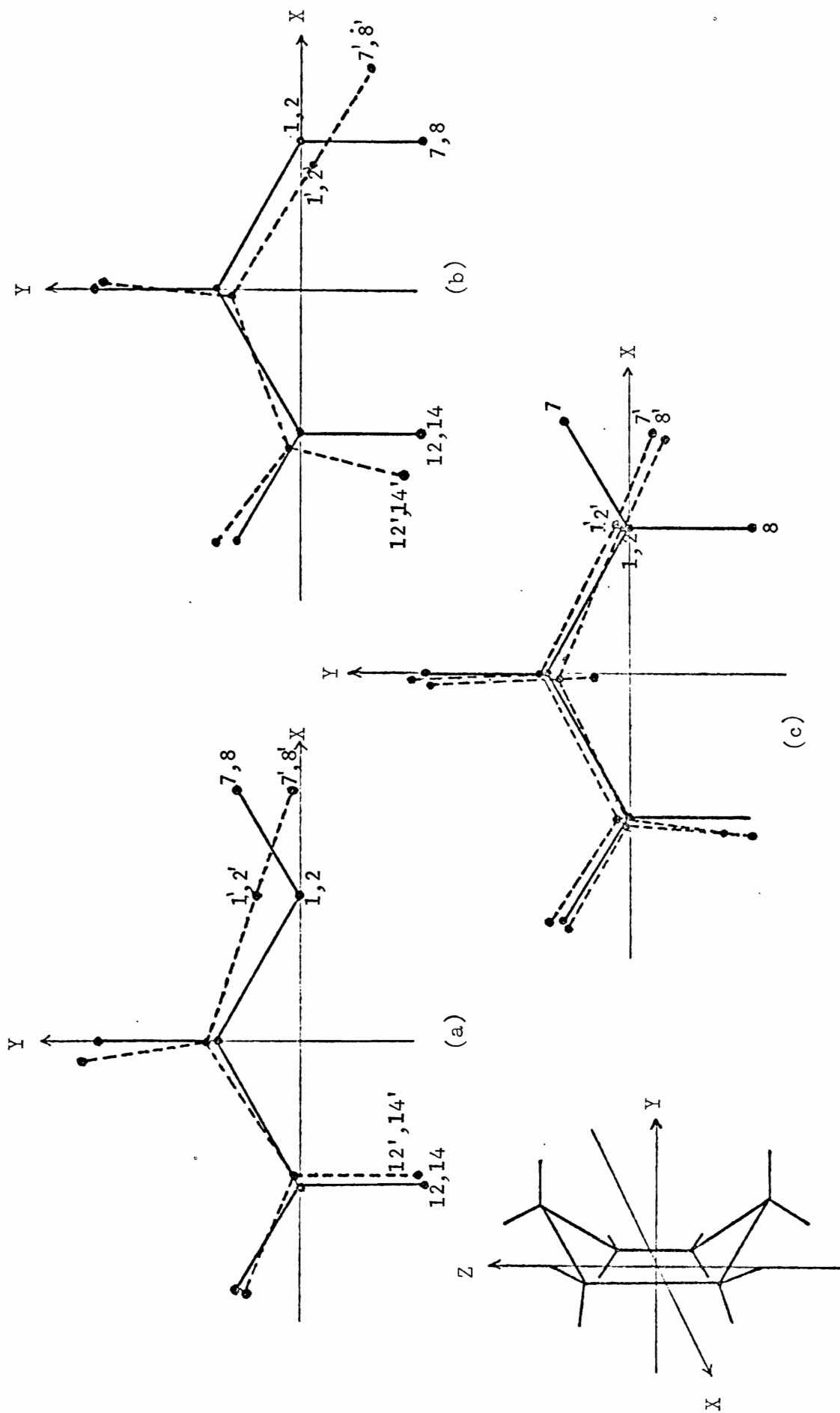
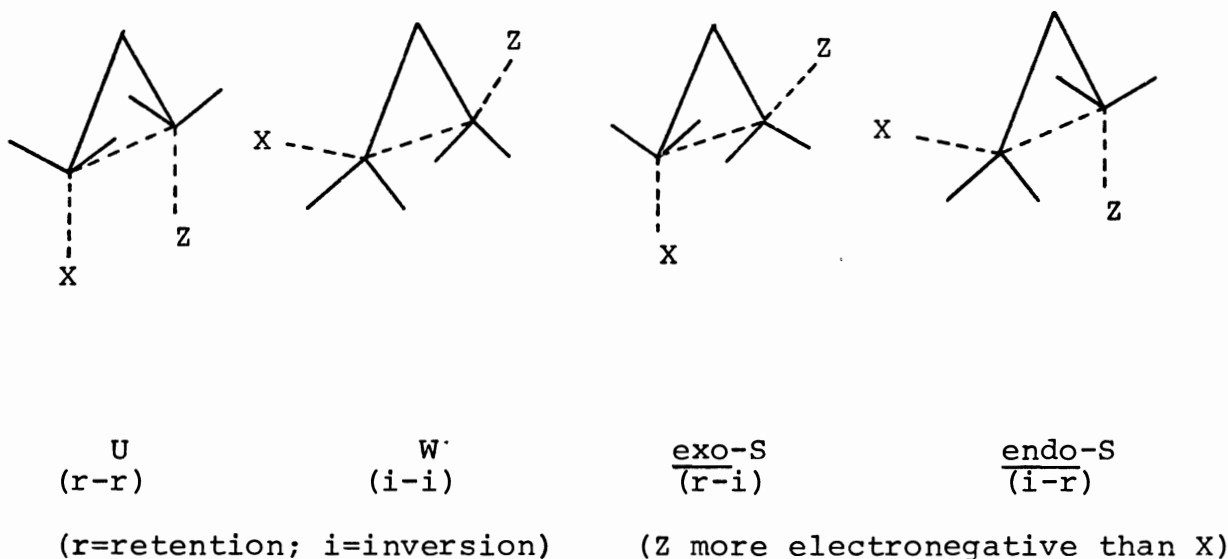


Figure 4. X-Y Plane Projections of the Reactant and the Product for (a) Syn (2), (b) Syn (1), and (c) Anti Mode of Elimination from the Boat Conformer.

tially from the anti-diaxial mode of the chair conformation of the cyclohexyl derivatives. Also the least motion preference suggested for the stereochemistry of the E_2 elimination from ethyl chloride seems to be applicable for cyclohexyl chloride. The E_{\min} values of the preferred mode of elimination from each conformation follow the same order as their stabilities⁵¹, that is the elimination would preferentially occur from the chair conformation and would very seldom be from the energetically unfavourable boat conformation, particularly since the latter represents the transition state between two twist forms⁵¹.

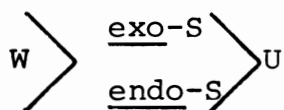
1,3-Eliminations.

The formation of a cyclopropane by a concerted 1,3-elimination from a substituted propane formally can occur with retention or inversion of configuration at the two reacting centres⁵⁵. Four basic possibilities therefore exist, which have been designated U,W,exo-S and endo-S by Nickon and Werstiuk⁵⁵ according to the geometries of the transition states. Eliminations having U-like transition states result in products showing retention of configuration at both reacting centres, whereas the W-like transition state is accompanied by inversion at these sites. In cases where the transition state is either exo-S or endo-S, the configuration of one of the reacting centres



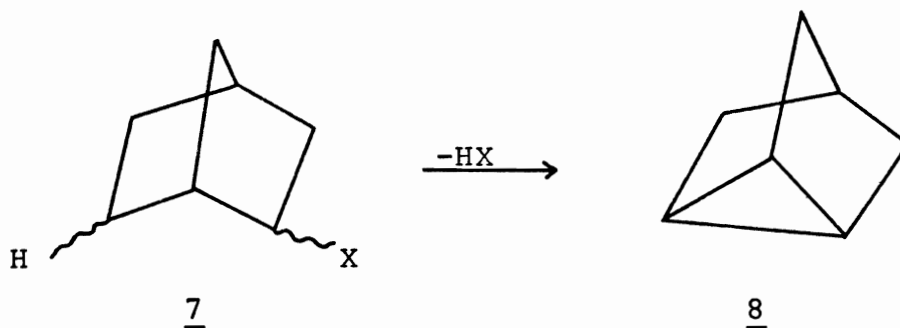
is retained and the other is inverted.

PLM calculations for the formation of cyclopropane from substituted propanes were carried out previously³², and the following order of preference of the transition states was found:

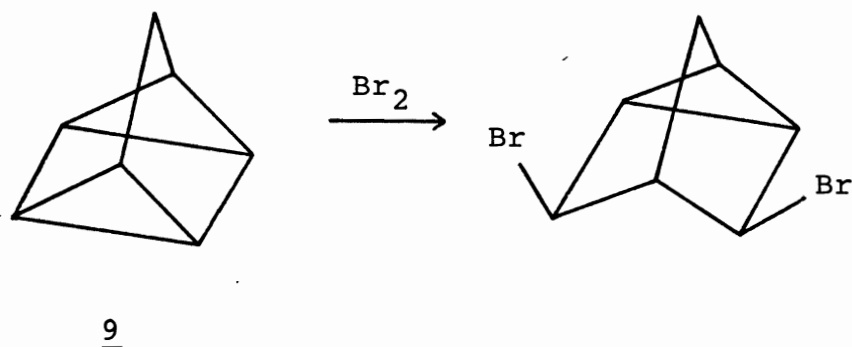


The preference for a W-like transition state agrees with the experimental evidence of Bordwell⁵⁷. On the other hand, Nickon and Werstiuk⁵⁸, in studying the conversion of 2-norbornyl tosylates (7) to nortricyclene (8), arrived at results contradictory to the predictions of the PLM. That this conflict might be due to the particular

geometry of the norbornyl system was considered.



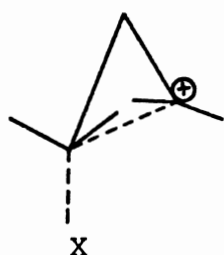
However, results of calculations added further support to the previously established order of preference. In an attempt to resolve this ambiguity, a third system was treated by the PLM approach. The reaction chosen was the addition of bromine to quadricyclene (9) which, according to the report of Cristol⁵⁹, proceeds via a W-like transition state.



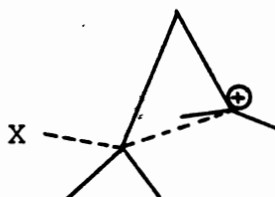
Since the order of preference, once more, remained unaltered, it was concluded that the findings of Nickon and Werstiuk constitute an exception for which further investigation is

necessary. The details of the latter are outlined in the next section.

Elimination from n-propyl cation. In those eliminations where a stepwise carbonium ion mechanism applies, the stereochemistry of one of the reacting centres is lost prior to the ring closure. Therefore, of the four geometrical arrangements considered previously only two remain as possible structures of the transition state involved in the ring forming step⁵⁵.



semi-U



semi-W

PLM calculations were performed for the conversion of n-propyl carbonium ion to cyclopropane. The coordinates of the reactant and the product were calculated from the data summarised in Table V.

E_{\min} values were calculated for a number of conformations arising from the rotation about the C-C bonds by the dihedral angles α & β defined below. Results for the retention of configuration are shown in Table VI (p 46).

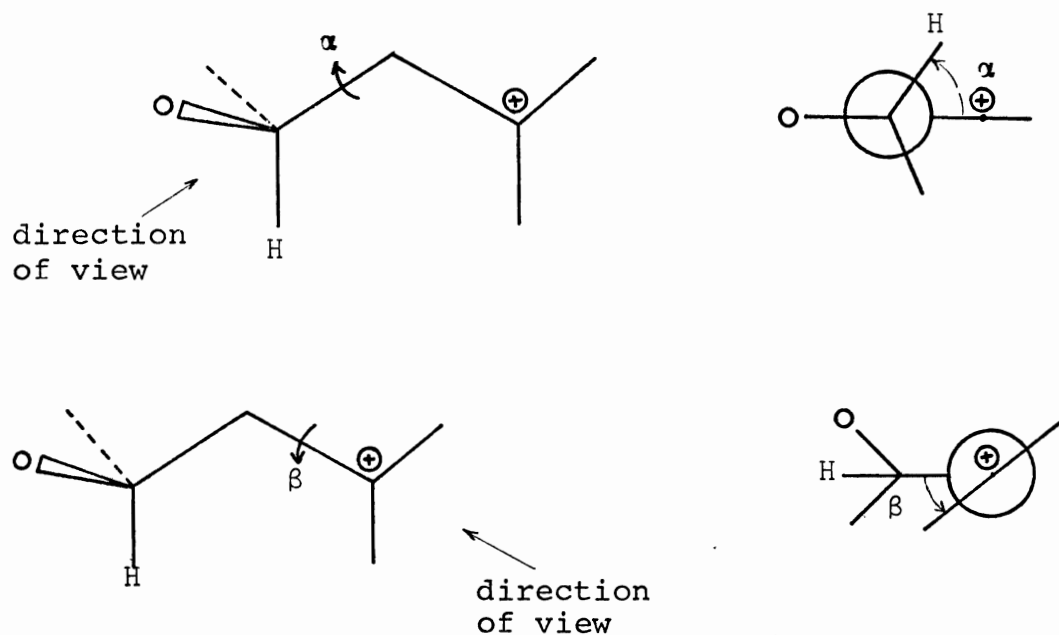


Table V. Structural Parameters of n-Propyl Carbonium Ion and of Cyclopropane.

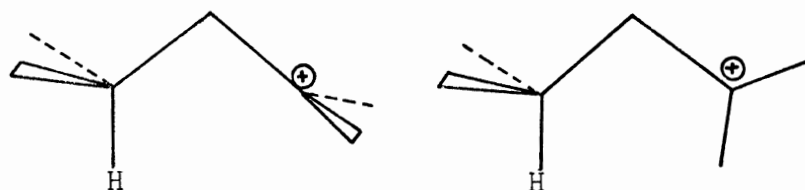
Name	Bond length, Å		Bond angle, deg		Ref
n-propyl carbonium ion	-C ₁ -C ₂ -	1.54	tetrahedral		60
	-C ₂ -C ₃ -	1.50			"
	-C-H	1.10			"
	-C ₃ -H	1.09	HC ₃ C	120	"
cyclopropane	As in literature				61

Table VI. Variation of E_{\min} with Dihedral Angles α & β for the 1,3-Elimination from n-Propyl Carbonium Ion. Retention of Configuration.

β/α	$E_{\min} (\text{\AA}^2)$						
	0°	30°	60°	90°	120°	150°	180°
-90°	7.53	5.96	4.94	4.64	5.10	6.25	7.87
-60°	6.39	4.80	3.74	3.42	3.87	5.01	6.64
-30°	5.66	4.05	2.95	2.59	3.02	4.16	5.80
0°	5.46	3.82	2.70	<u>2.30</u>	2.70	3.82	5.46
30°	5.79	4.16	3.02	2.59	2.96	4.05	5.66
60°	6.64	5.01	3.87	3.42	3.74	4.80	6.39
90°	7.87	6.25	5.10	4.64	4.94	5.96	7.53

The above results indicate that, for retention of configuration involving a semi-U transition state, the PLM prefers the conformation in which the hydrogens of the trigonal centre are perpendicular to the plane of the carbon atoms (10) over that conformation in which they are coplanar with those atoms (11).

For those conformations leading to inversion of configuration, the PLM results are summarised in Table VII.



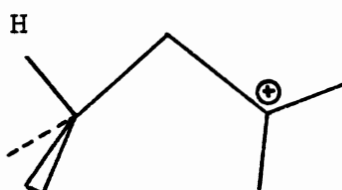
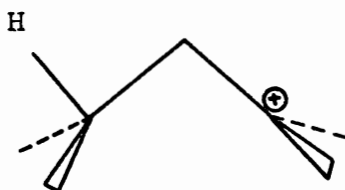
	<u>10</u>	<u>11</u>
α	0°	0°
β	90°	0°
$E_{\min}(\text{\AA}^2)$	2.30	5.46

Table VII. Variation of E_{\min} with Dihedral Angles α & β
for the 1,3-Elimination from n-Propyl Carbonium Ion.
Inversion of Configuration.

		$E_{\min}(\text{\AA}^2)$						
β/α	0°	30°	60°	90°	120°	150°	180°	
90°	8.42	6.68	5.30	4.57	4.60	5.39	6.80	
120°	6.42	4.68	3.35	2.68	2.80	3.68	5.17	
150°	4.89	3.18	1.93	1.38	1.63	2.64	4.21	
180°	4.11	2.46	1.32	<u>0.92</u>	1.32	2.46	4.11	
210°	4.21	2.64	1.63	1.38	1.93	3.18	4.89	
240°	5.17	3.68	2.80	2.68	3.35	4.68	6.42	
270°	6.80	5.39	4.60	4.57	5.30	6.68	8.42	

From the above data it is apparent that the

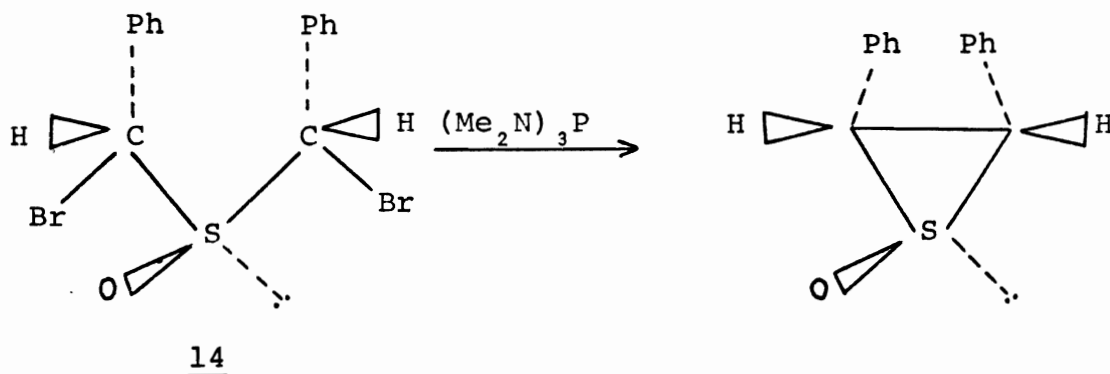
conformation favoured by the PLM is indeed a semi-W structure in which the hydrogens of the trigonal centre are perpendicular to the CCC plane (12), in contrast to (13) in which the latter are in that plane.



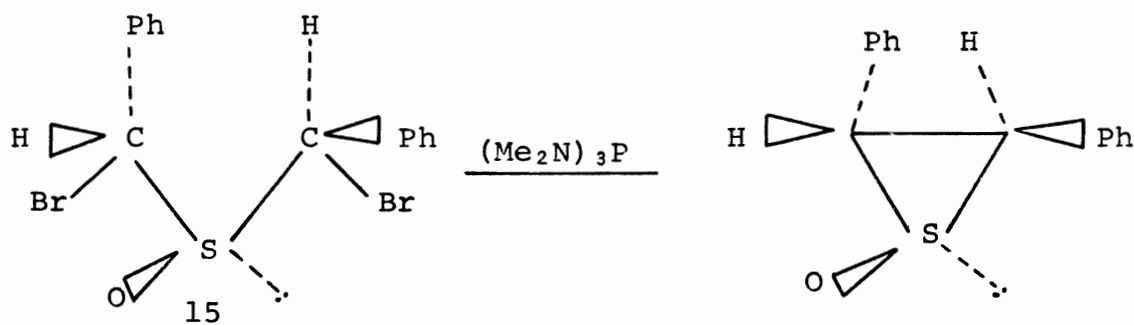
	<u>12</u>	<u>13</u>
α	180°	180°
β	90°	0°
$E_{\min}(\text{\AA}^2)$	0.92	4.11

Comparison for the alternative types of transition states results in the conclusion that the PLM prefers the semi-W geometry which is associated with inversion of configuration at the tetrahedral centre and a 90° twist at the trigonal centre (12).

Recently, Jarvis, Dutkey and Ammon⁶² presented direct evidence for a W-like transition state in the debromination



of the dibromo sulfoxides (14) and (15) with hexamethyl phosphoric triamide, $(\text{Me}_2\text{N})_3\text{P}$.



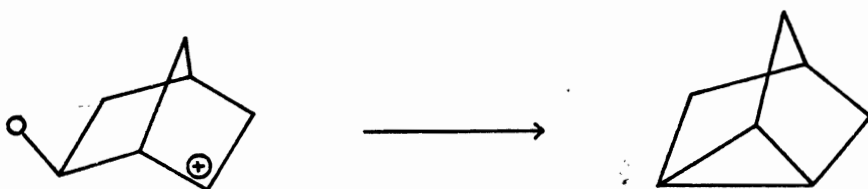
The structures of both 14 and 15 were determined by single crystal X-ray diffraction analysis and the reaction products were identified by NMR. It was remarked that the above reactions appear to occur via a stepwise mechanism, forming a carbanion intermediate followed by loss of bromide ion to give the closed-ring product.

Several other cases exhibiting preferences for W-type transition states in 1,3-elimination reactions are known⁶³⁻⁶⁶. Some of these, however, cannot be considered conclusive because the systems studied were rigid polycycles in which the leaving groups had no choice but to assume the W conformation^{65,66}.

Elimination from 2-norbornyl cation. PLM calculations were also carried out for the formation of nortricyclene from the 2-norbornyl carbonium ion. The coordinates of the reactant were calculated using the geometry of norbornane determined by electron diffraction⁶⁷, with the

exception of the hydrogen at the cationic centre which was calculated separately. The coordinates of nortricyclene were calculated utilising its C_{3v} symmetry and the appropriate bond lengths and bond angles given in the literature^{68,69}.

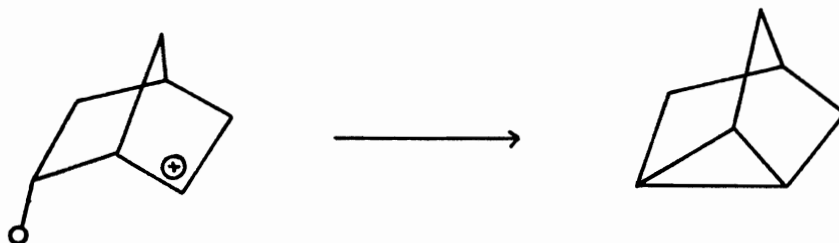
E_{\min} values were calculated for the elimination from both the exo and endo position corresponding to a W-like transition state for the former and a U-like for the latter reaction. The results are as follows:



Elimination of exo-hydrogen.

$$E_{\min} = 4.59 \text{Å}^2$$

W-like transition state.



Elimination of endo-hydrogen.

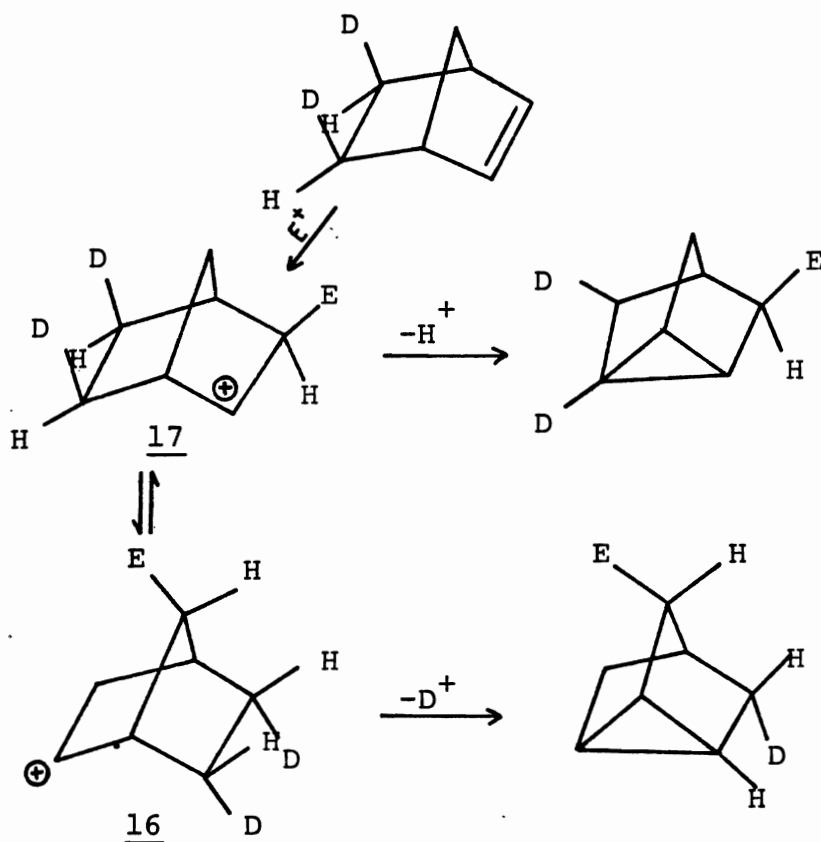
$$E_{\min} = 8.05 \text{Å}^2$$

U-like transition state.

It is apparent that, as in the previous case, PLM prefers the W-like transition state.

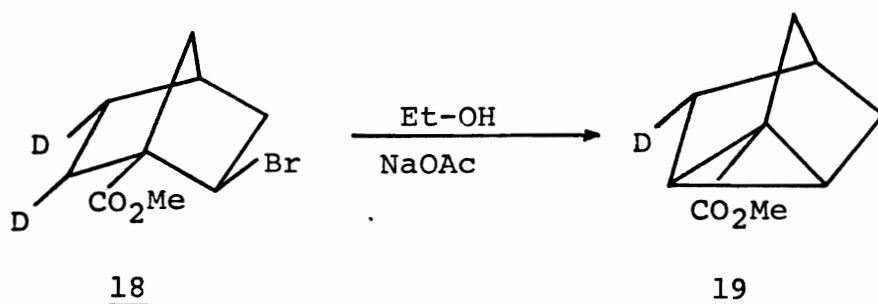
Nickon and Werstiuk⁷⁰ studied the behaviour of the exo and endo-norbornyl tosylates in alkaline media and found evidence that in low base concentrations ionization to norbornyl cation precedes the formation of the 3-membered ring. Deuterium labeling at the 6-exo or 6-endo position resulted in formation of identical products with a primary isotope effect of approximately 2, suggesting that the ionization (most probably to a non-classical carbonium ion) removes the stereochemical distinction between the exo and endo hydrogens, thus giving no information as to the nature of the transition state in the ring forming step.

Recently it was reported⁷¹ that, when Br_2 or Cl_2 is



added to exo-exo-5,6 or endo-endo-5,6-dideuterio norbornene, analysis of the resulting nortricyclene indicates that loss of proton(deuteron) occurs predominantly from 16 when the reagent is Br_2 , and from 17 when the reagent is Cl_2 . Although at first glance each cyclization step appears to have a U-like transition state, the authors suggest that the possibility of proton loss via an unsymmetrical norbornyl cation should not be overlooked.

Another experiment⁷² involving the solvolysis of endo-endo-5,6-dideuterio-exo-2-bromonorbornane-1-carboxylic acid methyl ester (18) gave predominantly (19), indicating the preference for an exo-S rather than a W transition state.



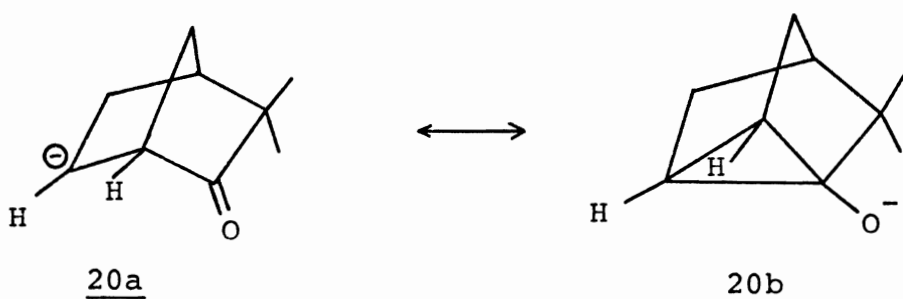
From the above evidence one may conclude that the 1,3-elimination from the norbornyl system either proceeds via a non-classical norbornyl cation intermediate, in which case the stereochemistry of the process cannot be determined, or involves a transition state other than the W-like favoured by the least motion considerations. This behaviour is by no means unique, since the peculiarity of the system

has been suggested by many workers in the past.

Homoenolisations.

Homoenolisation may be defined as a base-catalysed process by which abstraction of a proton situated remote from a carbonyl group is facilitated by homoconjugation, and leads to the formation of a corresponding homoenolate anion⁷³.

The concept was originated by Nickon and Lambert⁷³ who offered an explanation for the base-induced racemisation of (+)-camphenilone by postulating a non classical "homoenolate" ion (20),



whose charge is stabilised by delocalization to the carbonyl group. Following this, various homoenolisation reactions have been reported⁷⁴⁻⁷⁸, either to explain certain observed rearrangements^{74,75,77,78}, or to demonstrate the potential usefulness of homoenolisation in synthesis⁷⁶.

Homoenolisation of propionaldehyde. The simplest molecule

which may be used as a model for the study of the stereochemistry of this process is propionaldehyde, the reaction of which results in the formation of cyclopropanolate ion. The ring closure may occur with retention or inversion of configuration at the reacting centre, depending on the geometry of the transition state involved (Fig. 5).

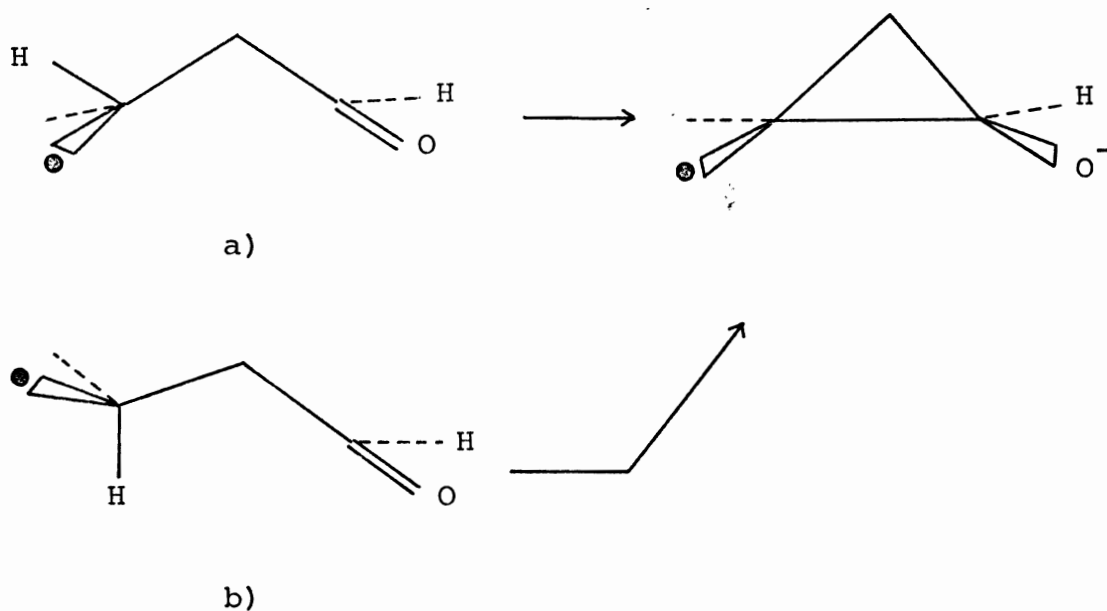


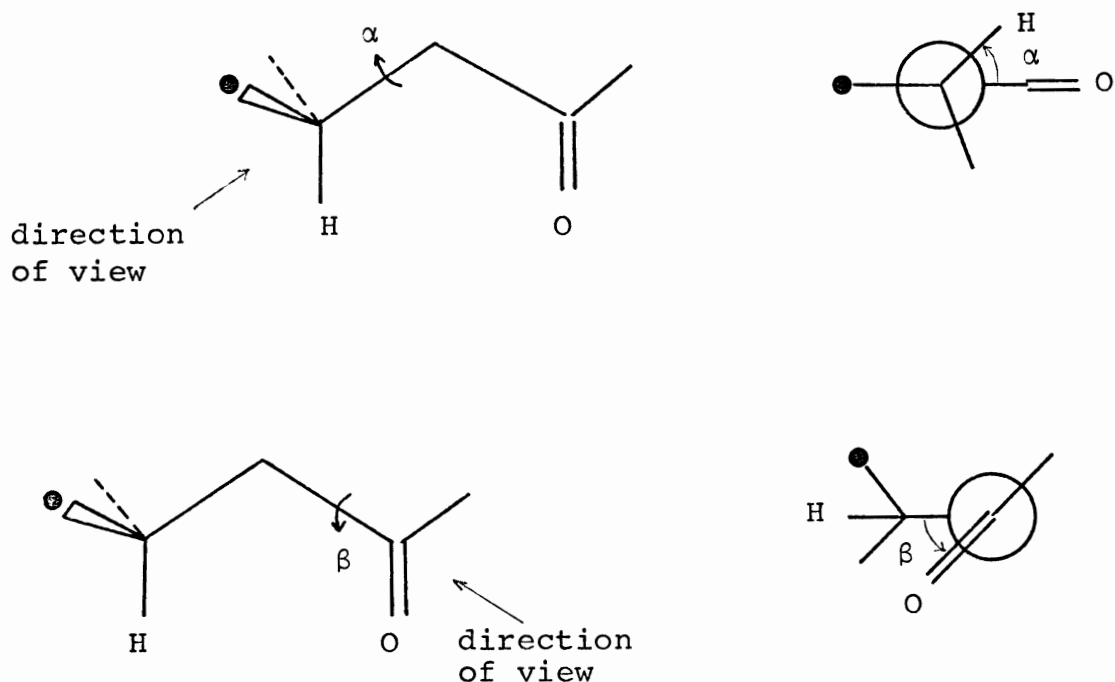
Fig. 5. a) W-like transition state accompanied by inversion of configuration.

b) U-like transition state accompanied by retention of configuration.

PLM calculations were carried out for both of the

possibilities above. The coordinates of propionaldehyde are similar to those of propylcarbonium ion calculated earlier (p 45), with the exception of the oxygen whose coordinates were calculated using 1.22 \AA^{060} as the length of the carbon-oxygen bond. Similarly, for the product the coordinates of cyclopropane were used, with the exception of the oxygen for which the C-O bond length was taken to be 1.42 \AA^{060} .

Values of E_{\min} were calculated for a number of conformations arising from the rotation about the carbon-carbon single bonds by various dihedral angles, α & β , whose definitions are shown below.



Results of the calculations are summarised in Tables VIII (a) and (b).

TableVIII. Variation of E_{\min} with the Dihedral Angles α and β for the Homoenolisation of Propionaldehyde.

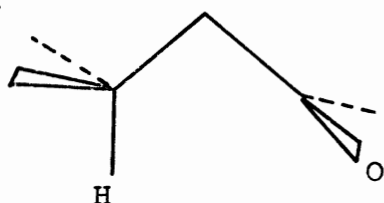
(a) Retention of Configuration.

β/α	$E_{\min} (\text{\AA}^2)$						
	-90°	-60°	-30°	0°	30°	60°	90°
0°	8.21	7.03	6.23	5.93	6.18	6.96	8.15
30°	6.41	5.21	4.40	4.10	4.37	5.17	6.38
60°	5.23	4.01	3.17	2.85	3.10	3.90	5.11
90°	4.87	3.62	2.75	<u>2.40</u>	2.62	3.39	4.58
120°	5.37	4.12	3.22	2.83	3.01	3.73	4.88
150°	6.67	5.42	4.50	4.07	4.21	4.88	5.98
180°	8.54	7.29	6.37	5.92	6.01	6.63	7.70

(b) Inversion of Configuration.

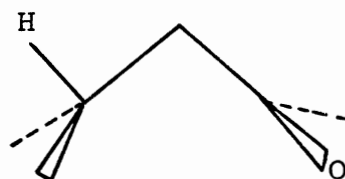
β/α	$E_{\min} (\text{\AA}^2)$						
	90°	120°	150°	180°	210°	240°	270°
0°	9.21	7.17	5.54	4.64	4.61	5.46	7.02
30°	7.21	5.19	3.60	2.77	2.84	3.80	5.46
60°	5.64	3.66	2.16	1.46	1.69	2.80	4.57
90°	4.80	2.88	1.51	<u>0.97</u>	1.37	2.63	4.51
120°	4.81	2.98	1.75	1.38	1.94	3.33	5.29
150°	5.68	3.94	2.85	2.63	3.31	4.79	6.80
180°	7.27	5.61	4.62	4.47	5.21	6.73	8.74

The lowest E_{\min} value in Table VIII(a) appears for $\alpha = 0^\circ$ and $\beta = 90^\circ$ whereas that in Table VIII(b) may be located at $\alpha = 180^\circ$ and $\beta = 90^\circ$.



Retention of
configuration

$$E_{\min} = 2.40 \text{ Å}^2$$



Inversion of
configuration

$$E_{\min} = 0.97 \text{ Å}^2$$

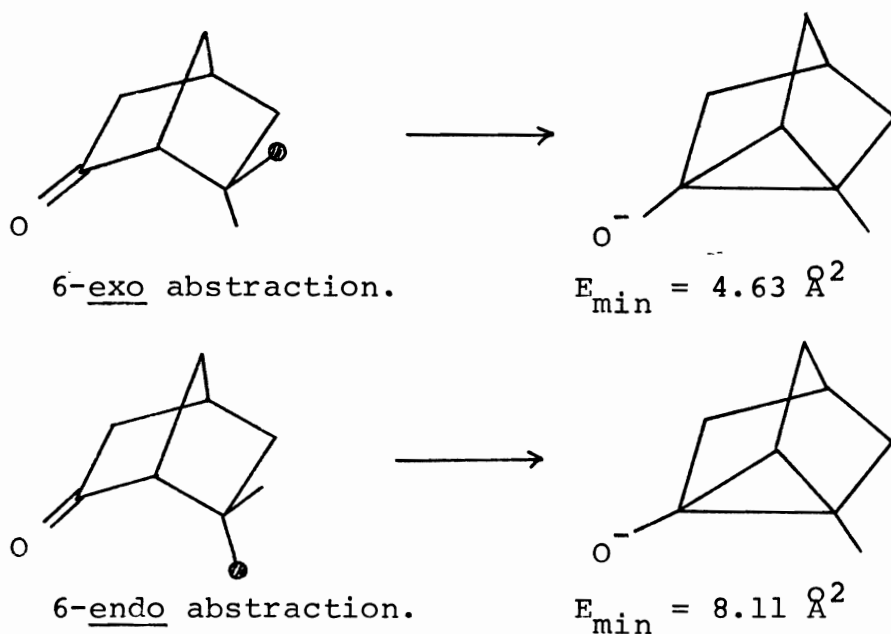
From the above it is clear that the PLM favours a W-like transition state with inversion of configuration (cf. elimination from n-propyl carbonium ion).

Due to the free rotation of the C-C bonds it is rather difficult to design an experiment which is suitable to gain insight into the stereochemistry of homoenolization of open-chain compounds. However, the stereochemistry of the reverse reaction has been investigated⁷⁹, and it was found that in alkaline media the ring opening proceeded with inversion of configuration. This means that protonation occurred from the remote side of the carbanion, or conversely, proton was abstracted from that side during cyclisation, leading to the conclusion that a W-like transition state prevails in the latter case, in accord with

the predictions of the PLM approach.

Homoenolisation of 2-norbornanone. From the stereochemical point of view, the abstraction of the proton from 2-norbornanone may occur either from the 6-exo or 6-endo position. The former corresponds to a semi-W and the latter to a semi-U transition state.

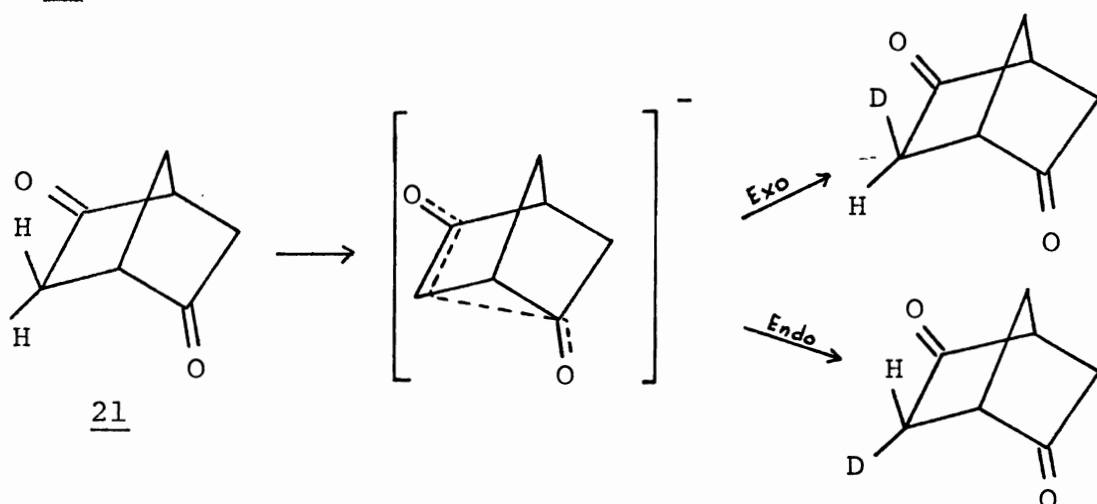
E_{\min} values were calculated for the abovementioned possibilities. The coordinates used for the reactant and product were calculated earlier (p 49) with the exception of the carbonyl group in the reactant, which was computed using 1.215 Å as the length of the carbon-oxygen bond⁶⁰, and the enol group in the product, for which a C-O bond length of 1.426 Å was used⁶⁰. The results of the calculations are as follows:



Clearly, the results demonstrate a substantial preference for the abstraction of the 6-exo hydrogen.

Nickon and coworkers⁸⁰ studied both the acid and base catalysed homoketonizations of labeled 1-acetoxynortricyclene and observed that in alkaline media the reaction produced an exo C-D bond at the 6-position with high stereospecificity. Consequently, it was suggested⁸⁰ that the reverse reaction (i.e. homoenolisation) of 2-norbornanone and the previously studied camphenilone⁷³ very likely involve preferential abstraction of the 6-exo hydrogen.

Recently, investigations⁸¹ of base-catalysed protium-deuterium exchange in bicyclo [2.2.1]-heptanones revealed that the rate of exchange is enhanced considerably when a second carbonyl group is arranged 1,3 from the enolizable centre. Furthermore, it was found⁸¹ that in these systems (21)



the exo-exchange is much faster than the endo, thus providing further evidence that in homoenolization the abstraction

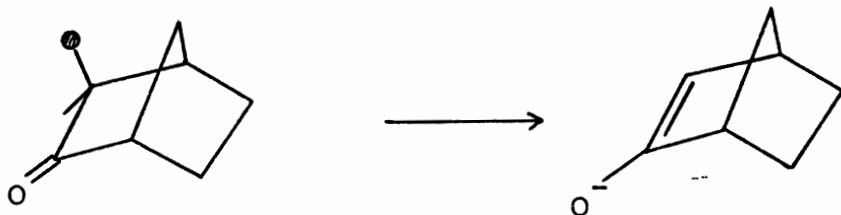
of the exo-hydrogen is favoured.

In summary, the PLM preference for the abstraction of a 6-exo-proton is supported by the available experimental evidence^{80,81}.

Enolisation of 2-Norbornanone.

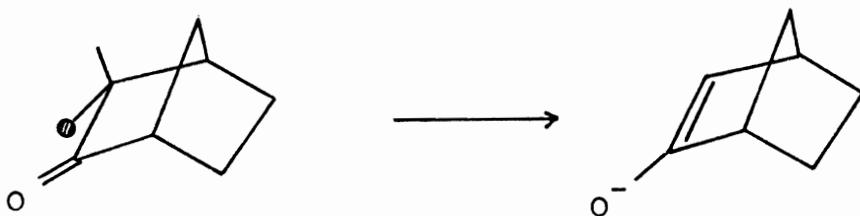
Least motion calculations have previously been performed for the stereochemistry of proton abstraction from acetaldehyde³⁸ and acetone³². The results favoured abstraction from a conformation in which the C-H bond is perpendicular to the trigonal plane at the carbonyl centre.

The stereochemistry of enolisation can best be studied in cyclic systems where the relative positions of the hydrogens are fixed.



Exo abstraction.

$$E_{\min} = 2.46 \text{ Å}^2$$



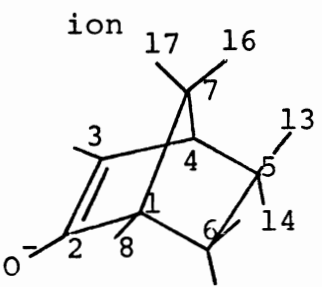
Endo abstraction.

$$E_{\min} = 5.94 \text{ Å}^2$$

A molecule particularly amenable to such a study is 2-norbornanone in which proton abstraction may occur from the 3-exo or 3-endo position.

E_{\min} values were obtained for both of these possibilities, which are illustrated above. The coordinates of the reactant were calculated earlier (p 57), and the coordinates of the product were arrived at using the parameters summarised in Table IX.

Table IX. Structural Parameters of Norbornenolate Ion.

Name	Bond length, Å		Bond angle, deg	Ref
Norbornenolate ion 	-C ₁ -C ₂ -	1.51		83
	-C ₂ -C ₃ -	1.34		"
	-C ₁ -C ₆ -	1.56		"
	-C ₁ -C ₇ -	1.51		"
	-C ₅ -C ₆ -	1.56		"
			C ₁ C ₂ C ₃	108 84
			C ₇ C ₁ C ₂	100 "
			C ₁ C ₇ C ₄	97.6 calc'd
			C ₁ C ₆ C ₅	103.2 "
			H ₁₆ C ₇ H ₁₇	92.0 67
	C-H	1.11		60
	C-O	1.426		"

From the values of E_{\min} obtained one may predict that the

enolisation of 2-norbornanone proceeds predominantly via the abstraction of the 3-exo hydrogen.

This prediction is in agreement with the recent work of Tidwell^{82,85} and other workers⁸⁶, who investigated the base-catalysed deuterium-exchange of a series of bicyclo [2.2.1] heptanones and found that for 2-norbornanone the relative rate of exchange at 3-exo/3-endo is 715/1.

Rearrangements of Carbenes.

A carbene is defined as a neutral intermediate having a divalent carbon with two nonbonded electrons. The latter may be spin-paired or spin-free corresponding to a carbene electronic state of singlet or triplet, respectively.

The structure of the singlet carbene has been determined experimentally as bent, and although the reported⁸⁷ HCH angle was 103° , other workers⁸⁸ considered it to be sp^2 hybridised with the lone pair in an sp^2 lobe and the p_z orbital being vacant.

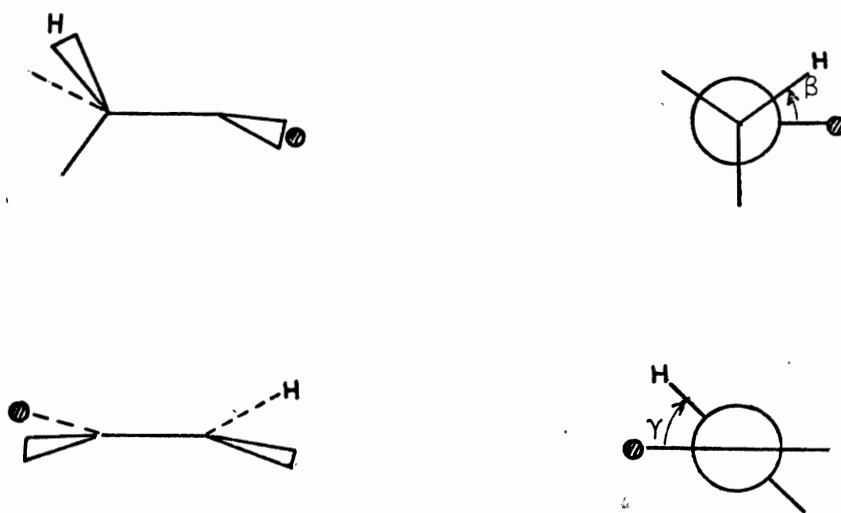
Triplet carbene was believed to be linear (sp hybridised) with one electron in both p_x and p_z orbitals^{88,89}. However, recent electron-spin resonance work⁹⁰ and theoretical considerations⁹¹ as well as the reinterpreted UV results of Herzberg⁹² strongly suggest a non-linear geometry.

There is no simple method of generalisation regarding the ground state of a carbene, since it is suspected that it is greatly dependent on substituents, steric factors, etc. Nevertheless, extended Huckel type Molecular Orbital calculations⁹³ and the results of ESR experiments^{94,95,96} for several different systems imply that most carbenes have a triplet ground state.

Methyl carbene. The stereochemistry of hydrogen migration has various possibilities depending upon the electronic state of both the carbene and the olefin formed. These were considered earlier by the PLM approach³⁹ using methyl carbene as a model. For the conversion of both the singlet and the triplet carbene to the corresponding excited singlet and triplet ethylene, the migrating hydrogen was predicted to be syn-periplanar to the carbenic hydrogen. Furthermore, the favoured geometry of the products was such that the trigonal centres were perpendicular to each other. Since these predictions arose from calculations utilising a linear triplet carbene, the recent reassessment of this geometry necessitated the recalculations for the triplet-triplet conversion.

The coordinates of both the reactant and the product were taken from the previous calculations³⁹ with the exception of the carbenic hydrogen for which a C-H bond length of 1.078 Å and a CCH angle of 136° were used⁹².

The reactant conformations were obtained via rotations about the C-C bond by the dihedral angle β defined below.



The corresponding product conformers were generated through variation of the angle between the trigonal planes by different values of γ (see definition above). The results are summarised in Table X below.

Table X. Variation of E_{\min} with Dihedral Angles β and γ for the Migration of Hydrogen in Methyl Carbene.

γ/β	0°	30°	60°	90°	120°	150°	180°
0°	4.82	5.22	5.61	5.90	6.03	6.00	5.79
30°	3.72	4.01	4.31	5.55	4.68	4.67	4.52
60°	3.01	3.19	3.39	3.58	3.72	3.77	3.71
90°	<u>2.77</u>	2.81	2.92	3.08	3.25	3.39	3.44
120°	3.01	2.92	2.95	3.09	3.32	3.55	3.71
150°	3.72	3.52	3.48	3.63	3.92	4.25	4.52
180°	4.82	4.54	4.48	4.65	5.01	5.43	5.79

Table X. Continued.

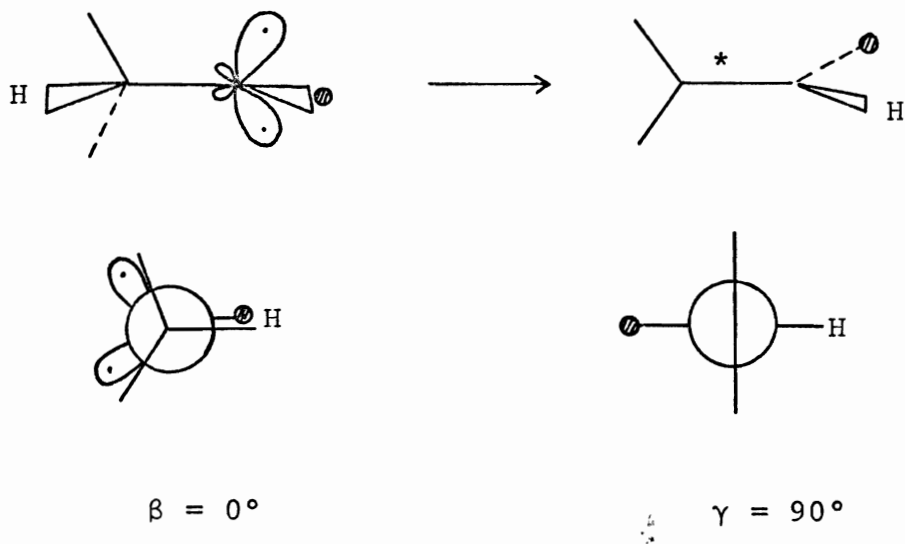
γ/β	0°	5°	10°	15°	20°	25°
88°	2.776	2.778	2.783	2.790	2.798	2.809
89°	2.775	2.777	2.781	2.787	2.795	2.805
90°	<u>2.774</u>	2.776	2.779	2.784	2.791	2.801
91°	2.775	2.776	2.777	2.782	2.789	2.797
92°	2.776	2.776	2.777	2.780	2.786	2.794

Table X. Continued.

γ/β	0°	1°	2°	3°	4°
88°	2.7756	2.7760	2.7764	2.7769	2.7775
89°	2.7748	2.7750	2.7753	2.7757	2.7761
90°	<u>2.7745</u>	2.7746	2.7747	2.7749	2.7752
91°	2.7748	2.7747	2.7747	2.7747	2.7749
92°	2.7756	2.7754	2.7752	2.7751	2.7750

The purpose of the refinement, as illustrated in the table above, was the exact location of the lowest value of E_{\min} . However, the insensitivity of the PLM approach towards minute changes in geometry is apparent.

The lowest E_{\min} value was obtained for $\beta = 0^\circ$ and $\gamma = 90^\circ$,



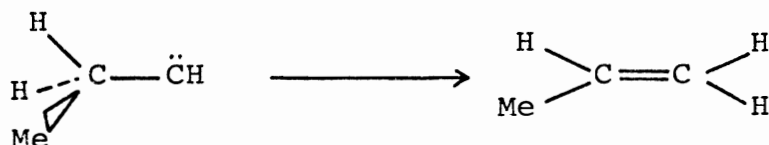
(The asterisk denotes an excited state.)

meaning that the hydrogen migrates syn to the carbenic H. Simultaneously, the excited ethylene takes up a conformation in which one trigonal centre is perpendicular to the other.

The use of a bent structure for the reactant did not markedly change the stereochemistry of the transition state involved. Furthermore, the E_{\min} value decreased, which indicates an increased preference for the triplet-triplet conversion.

Ethyl carbene. The effect of a simple substituent (Me) on

the stereochemistry of the H-migration in acyclic compounds was studied using the example of the conversion of ethyl carbene to propylene.



Four distinct possibilities were considered: a.) singlet carbene to ground state propylene, b.) triplet carbene to ground state propylene, c.) singlet carbene to excited singlet propylene and d.) triplet carbene to excited triplet propylene.

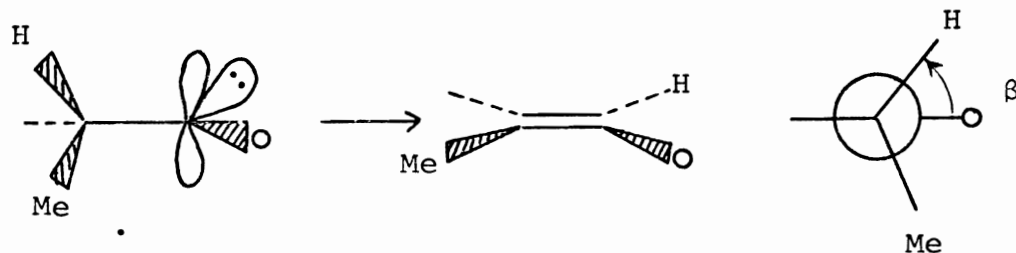
For the conversion of singlet ethyl carbene to ground state propylene the coordinates used for the reactant were identical to the ones calculated previously³⁹, with the exception of the methyl substituent for which a C-C bond length of 1.54 Å⁶⁰ and tetrahedral symmetry was assumed. The product geometry was taken to be that of ethylene³³ with a C_{sp}³-C_{sp}² bond length of 1.504 Å to a tetrahedral Me group.

PLM calculations were carried out for a number of conformations generated by rotation about the CH₃CH₂-CH bond with various dihedral angles β, and the results are presented in Table XI.

Table XI. Variation of E_{\min} with the Dihedral Angle β for the Rearrangement of Singlet Ethyl Carbene to Ground State Propylene.

β , deg	$E_{\min} (\text{\AA}^2)$	β , deg	$E_{\min} (\text{\AA}^2)$
10	5.80	100	5.51
20	5.62	110	5.64
30	5.48	120	5.79
40	5.37	130	5.95
50	5.29	140	6.11
60	<u>5.26</u>	150	6.27
70	5.27	160	6.44
80	5.32	170	6.60
90	5.40	180	6.76

A further search using one degree increments resulted in the exact location of the lowest E_{\min} to be at a β - value of 63° (compared to the value of 55° for the unsubstituted case).



From an electronic viewpoint it might be anticipated that migration towards the vacant p_z orbital ($\beta = 90^\circ$) or towards the sp^2 lone pair ($\beta = 180^\circ$) would be preferable. However, the requirement of an all-planar product seems to influence the least motion path in a compromising fashion.

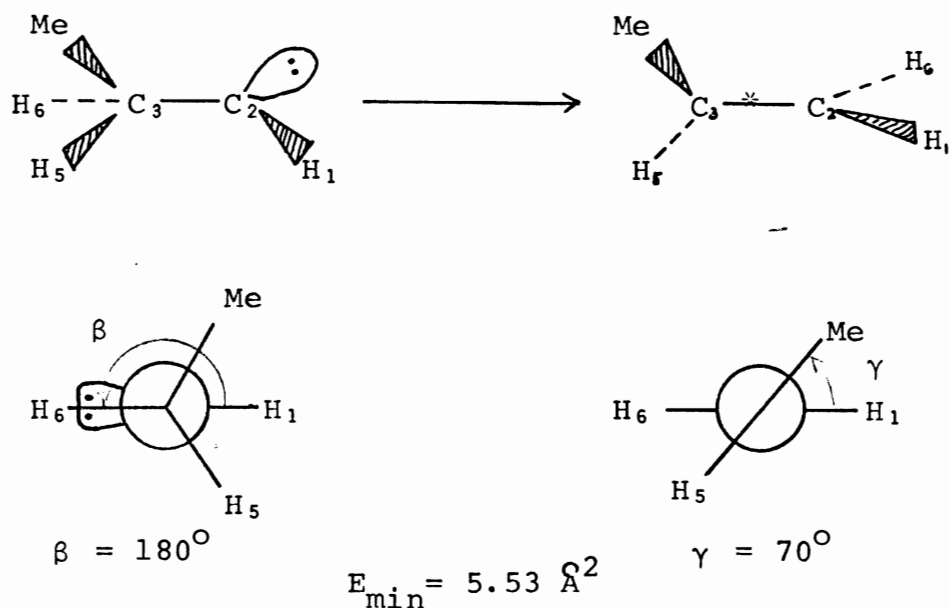
The migration of a hydrogen from triplet ethyl carbene to form ground state propylene is very unlikely, since it involves inversion of the spin. Nevertheless this case was considered for comparative purposes. The coordinates of the reactant were similar to those of the singlet with the exception of the carbenic centre for which a carbon-hydrogen bond length of 1.078 Å and an angle of bend of $136^\circ 92'$ was used as a basis for the calculations. E_{\min} values were calculated for a series of rotamers generated by varying the dihedral angle β defined as previously. After an initial wide search the calculations were expanded to one degree increments and the lowest E_{\min} of 5.49 Å² was located at $\beta = 69^\circ$. The similarity of this result to that of the singlet reflects the close resemblance of the two structures.

For the conversion of the singlet ethyl carbene to excited singlet propylene the geometry of the reactant was calculated earlier (p 67) and the coordinates of the product were taken to be those of singlet ethylene with $C_{sp^3}-C_{sp^2}$ bond length of 1.504 Å to a tetrahedral Me group. Calculations were carried out for various values of β defined

earlier. Simultaneously, the product was rotated about the $C_{sp^2}-C_{sp^2}$ bond by various values of γ , the dihedral angle between the trigonal planes. These angles were varied from 0° to 180° in ten degree increments and further refined to one degree increments around the minimum value.

Results were plotted and the surface obtained is presented in Fig.5, which shows the lowest E_{min} value of 5.53 \AA^2 to be located at $\beta = 180^\circ$ and $\gamma = 70^\circ$. This means that the PLM favours migration of the hydrogen to occur syn-periplanar to the carbene lone pair (see illustration on this page), in contrast to the previous calculations on methyl carbene³⁹, which favoured an anti-periplanar migration.

The shape of the surface in Fig.5 gives clear indication of a shift in the minimum from a low to a high β -value.



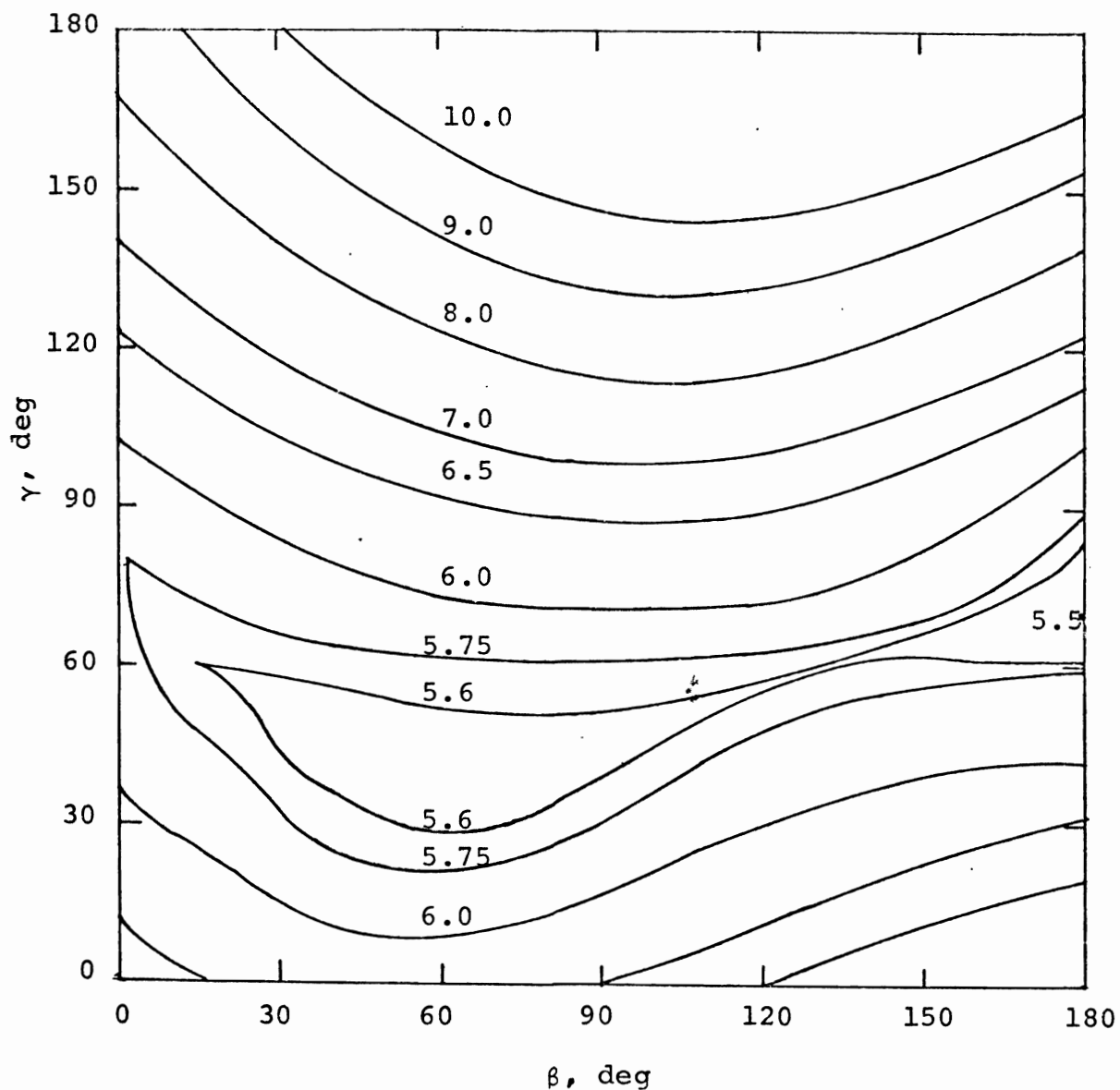


Figure 5. Variation of E_{\min} with the Dihedral Angles β (reactant) and γ (product) for the Rearrangement of Singlet Ethyl Carbene to Excited Singlet Propylene.

For a better understanding of this change of preference, a comparison may be made of the individual atomic displacements corresponding to the two modes of migration. Table XII (p 74) lists the data obtained.

Clearly, the largest displacement involves the migrating hydrogen (i.e. atom #6) and on this basis alone a large preference towards the anti-mode would be expected. Moreover, comparison of atoms 1-6 for methyl and ethyl carbene still would favour the anti-mode for both. Thus the difference lies in the displacements of atoms 7,8 and 9, which are the hydrogens of the methyl substituent. The E_{\min} values indicate that the changed preference is not very large, but remembering that 0.02 \AA^2 roughly corresponds to 1 kcal/mole^{22} , it is significant. A second methyl group at C_3 is expected to further enhance this preference.

The conversion of triplet ethyl carbene to excited triplet propylene was also investigated. The coordinates of the triplet carbene were calculated earlier (see p 69) and those of the excited propylene were calculated using $C_{sp^2}-C_{sp^2} = 1.54 \text{ \AA}$, the remaining parameters being identical to the ones used for the excited singlet. As before, calculations were carried out for a large number of conformations having different values of β and γ defined earlier. Results were plotted and the surface obtained is shown in Fig.6. The minimum of 4.73 \AA^2 at $\beta = 180^\circ$ and $\gamma = 71^\circ$ means

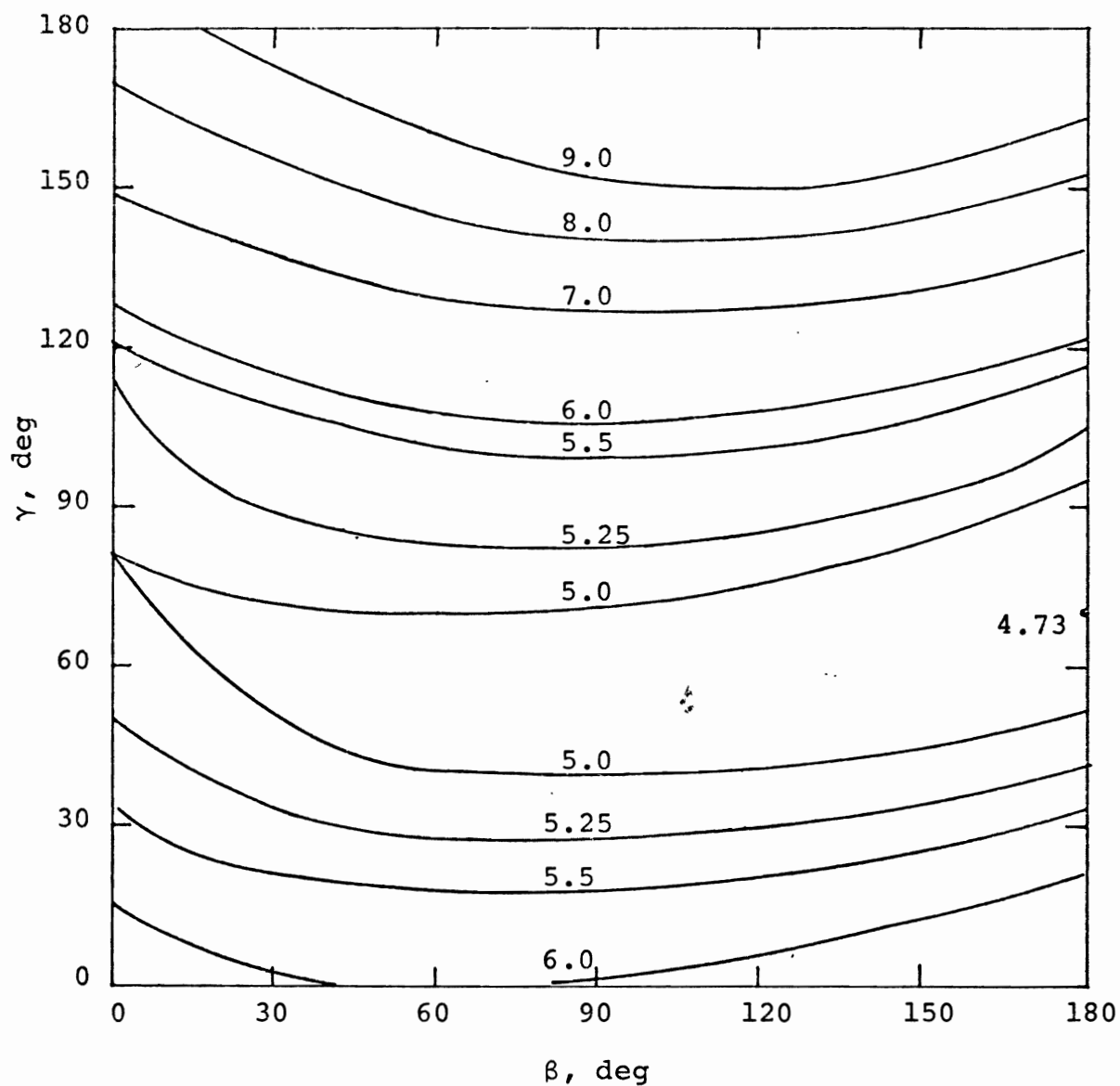
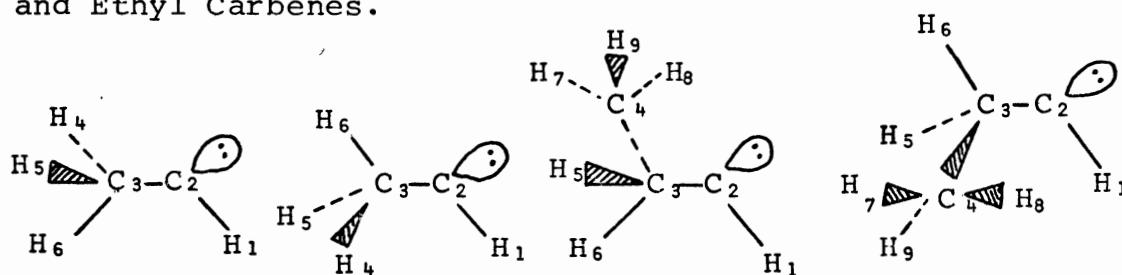


Figure 6. Variation of E_{\min} with the Dihedral Angles β and γ for the Rearrangement of Triplet Ethyl Carbene to Excited Triplet Propylene.

Table XII. Squares of the Atomic Displacements of Syn- and Anti-Periplanar Hydrogen Migration in Singlet Methyl and Ethyl Carbenes.



Atom _i	D_i^{2*}			
	<u>Syn</u> -periplanar		<u>Anti</u> -periplanar	
	Methyl carbene (<u>22</u>)	Ethyl carbene (<u>24</u>)	Methyl carbene (<u>23</u>)	Ethyl carbene (<u>25</u>)
1	0.470	0.490	0.051	0.522
2	0.212	0.143	1.06	0.906
3	0.448	0.267	0.285	0.151
4	0.295	0.111	0.200	0.052
5	0.295	0.497	0.200	0.316
6	2.32	3.32	1.32	2.20
7		0.309		0.643
8		0.265		0.601
9		0.138		0.301
$E_{\min} = \sum_i D_i^2$	4.04	5.53	3.12	5.69

* D_i represents the displacement of atom_i in Å.

that, once more, migration anti to the carbenic hydrogen is preferred. The similarity of this result to the previously discussed singlet case reflects the similarities in their geometries.

The lowest E_{\min} values for the various modes of conversion of ethyl carbene to propylene are summarised in Table XIII.

Table XIII. Lowest Values of E_{\min} for the Various Modes of Hydrogen Migration in Ethyl Carbene.

States		Angles*,deg		$E_{\min}, \text{\AA}^2$
carbene	propylene			
singlet	ground	63		5.26
singlet**	excited singlet	180	70	5.53
triplet	ground	69		5.49
triplet	excited triplet	180	71	4.73

* Angles were defined earlier in the text.

** The reversed preference in the case of the singlets is due to the unusually long (1.69 \AA) carbon-carbon bond of the excited singlet propylene.

In summary, for the singlet carbene, PLM slightly favours

the conversion to ground state propylene, whereas for the triplet there is a substantial preference towards its conversion to the excited triplet product.

Orbital symmetry considerations cannot be applied to the present study, since for conversions to a ground state product the number of orbitals in the reactant does not equal the number of orbitals in the product³⁹, and for the other cases there is not sufficient symmetry present for the correlation.

Experimentally, very little is known about the stereochemistry of hydrogen migration and even less about the initial state of the product formed.

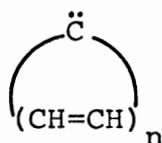
Recently, reactions of the type



in which both R_1 and R_2 are alkyl, aryl or carbethoxy groups, have been studied⁹⁷. Considering the cis/trans ratios of the olefins obtained, the stereochemical results indicated a singlet carbene precursor, but the state of the initially produced olefin was not reported. Other workers⁹⁸ generated anthronylidene in the triplet state, and have good reason to believe that the olefin formed via H-migration is also in the triplet state.

It was also postulated⁹⁹, that if there is p-orbital participation at the carbenic centre in a potentially

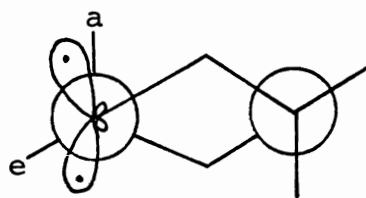
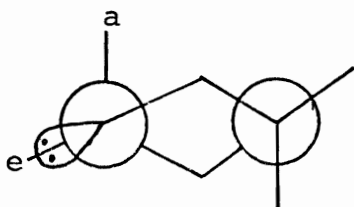
aromatic ring system



where $n = 1, 2, 3$

then a triplet ground state is stable, since one of the unpaired electrons may be delocalised in the π -system. In support of this postulate triplet phenalenylidene was generated and, although the state of the product formed by H-abstraction was not mentioned, an excited triplet product would be a reasonable assumption.

Cyclohexylidene. In the case of rigid cyclic molecules, the stereochemically feasible locations of the migrating moiety are known. Thus the electronic state of the carbene may be predicted by considering the least motion approach of the migrating moiety. For instance, in a cyclohexyl system, a singlet (sp^2 hybridised) carbene would intuitively be anticipated to abstract a hydrogen from the equatorial position. Alternatively, the triplet would most probably be sp^3 hybridised. However, due to the repulsion between the



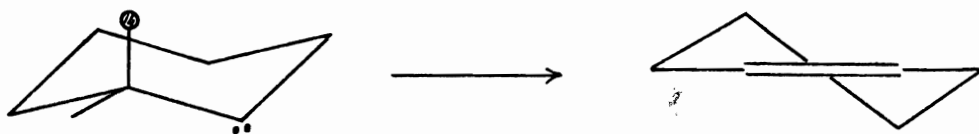
singlet, sp^2 hybridised

triplet, sp^3 hybridised

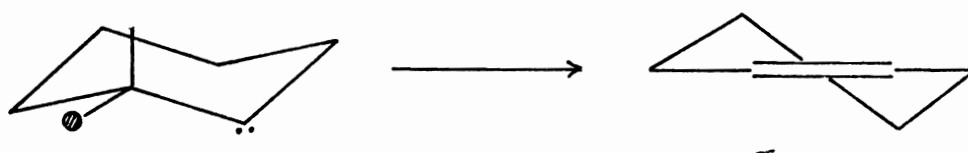
unpaired electrons in this case, the angle between the two

sp^3 lobes is expected to be larger than the usual tetrahedral value. As the angle increases, the distance between the sp^3 lobe and the axial hydrogen decreases and thus the migration towards that lobe appears to be the better choice.

PLM calculations were performed for the formation of cyclohexene from cyclohexylidene via migration of a hydrogen. The geometry of the reactant was evaluated from previous data³⁹ used for cyclohexane and the product con-



Migration of the axial hydrogen. $E_{\min} = 5.39 \text{ Å}^2$



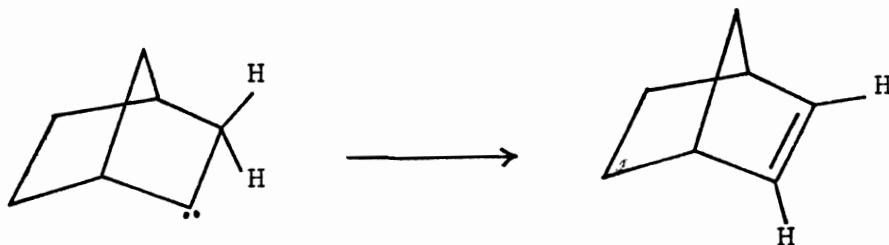
Migration of the equatorial hydrogen. $E_{\min} = 9.18 \text{ Å}^2$

dinates were readily available (see 1,2-eliminations p 31). The E_{\min} values obtained for both the axial and equatorial H-migration are reported above. These suggest large preference towards the migration of the axial hydrogen. The

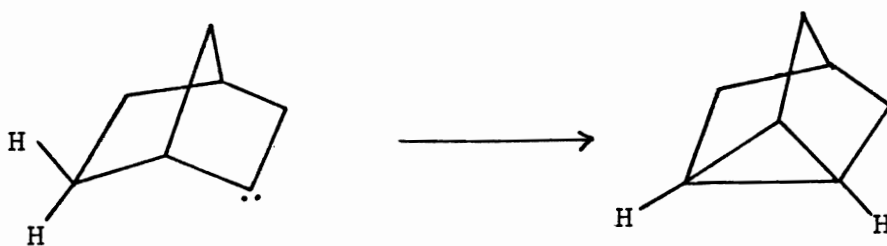
validity of the above prediction is not known, since experimental results are not available for comparative purposes.

2-Norbornylidene. The migration of a hydrogen in a bicyclic system was studied using norbornylidene as a model compound. Two different processes may be distinguished:

- (a) 1,2-migration, which results in the formation of norbornene,

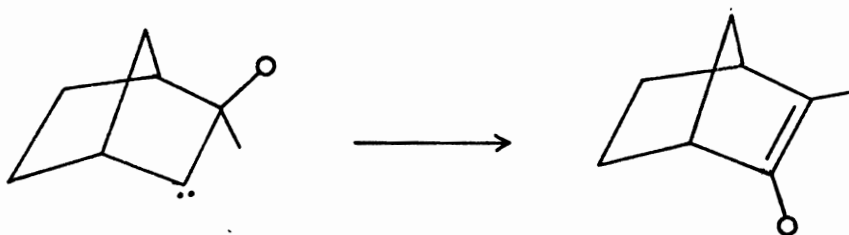


- (b) 1,3-migration, which formally may be regarded as an intramolecular insertion process resulting in the formation of nortricyclene.



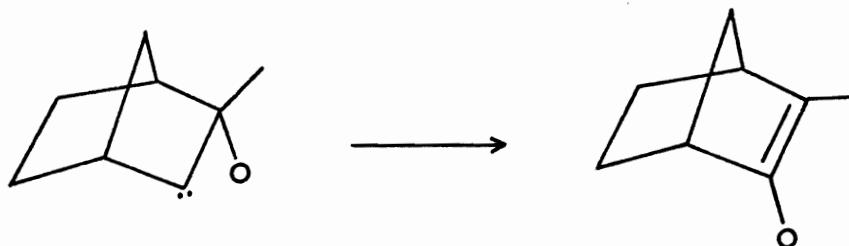
From the stereochemical point of view, both processes might involve the migration of either an exo or an endo hydrogen and values of E_{\min} were calculated for these possibilities.

For both cases the coordinates of the reactant were calculated from the parameters of norbornane⁶⁷. For norbornene the geometry was taken to be that of norbornenol (see Table IX p 61) less the hydroxyl group which was replaced by a hydrogen using a C-H bond length of 1.11 Å.



Exo-migration.

$$E_{\min} = 9.31 \text{ Å}^2$$



Endo-migration.

$$E_{\min} = 9.67 \text{ Å}^2$$

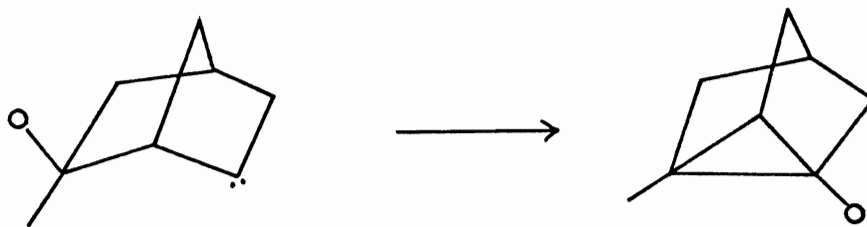
The results of the calculations show a slight preference for the migration of the exo hydrogen.

Experimental evidence¹⁰⁰ suggested however, that the formation of norbornene derivatives did not involve the intermediacy of a carbene, but proceeded via a protonated diazohydrocarbon (i.e. a diazonium ion) in solvents of high "protonating ability".

For the 1,3-migration process the geometry of the

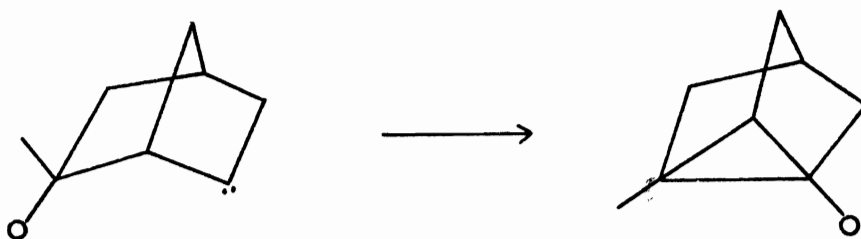
product was available from previous calculations (p 50).

The E_{\min} values obtained are shown below.



Exo-migration.

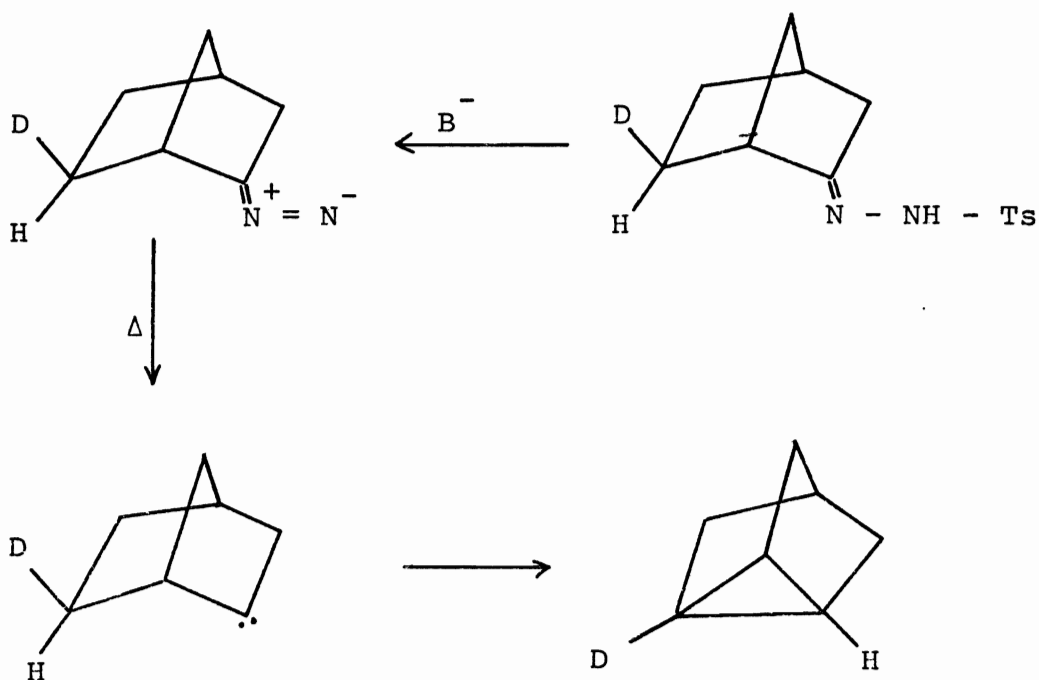
$$E_{\min} = 16.48 \text{ Å}^2$$



Endo-migration.

$$E_{\min} = 12.29 \text{ Å}^2$$

It may be observed, that the migration of the endo-



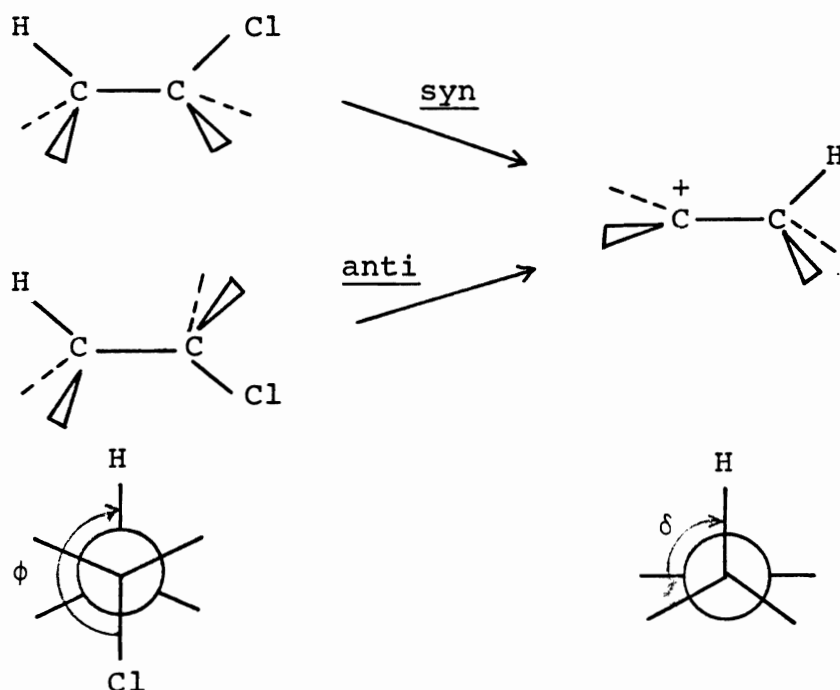
hydrogen is greatly favoured, which is in agreement with the conclusions reached¹⁰¹ from studies of the Bamford-Steven reaction of stereospecifically deuterated norbornan-2-one tosylhydrazone (see reaction p 81).

1,2-Hydride Shift in Ethyl Carbonium Ion.

The possible stereochemistry of a 1,2-hydride shift in ethyl carbonium ion has been considered from a PLM viewpoint earlier³⁸.

If the formation of the carbonium ion (i.e. the loss of leaving group) is concerted with the migration of the hydrogen, then two stereochemically different processes are conceivable depending on whether the migrating hydrogen is syn- or anti-periplanar to the leaving group. The above possibilities were considered by the PLM approach. The geometry of the ethyl chloride was available from previous work (p 31) and the coordinates of the ethyl cation were calculated using parameters from earlier work in the literature³⁸.

Calculations were performed for a number of conformations arising from the rotation in both the reactant and product about the C-C bonds by the dihedral angles ϕ and δ defined below.



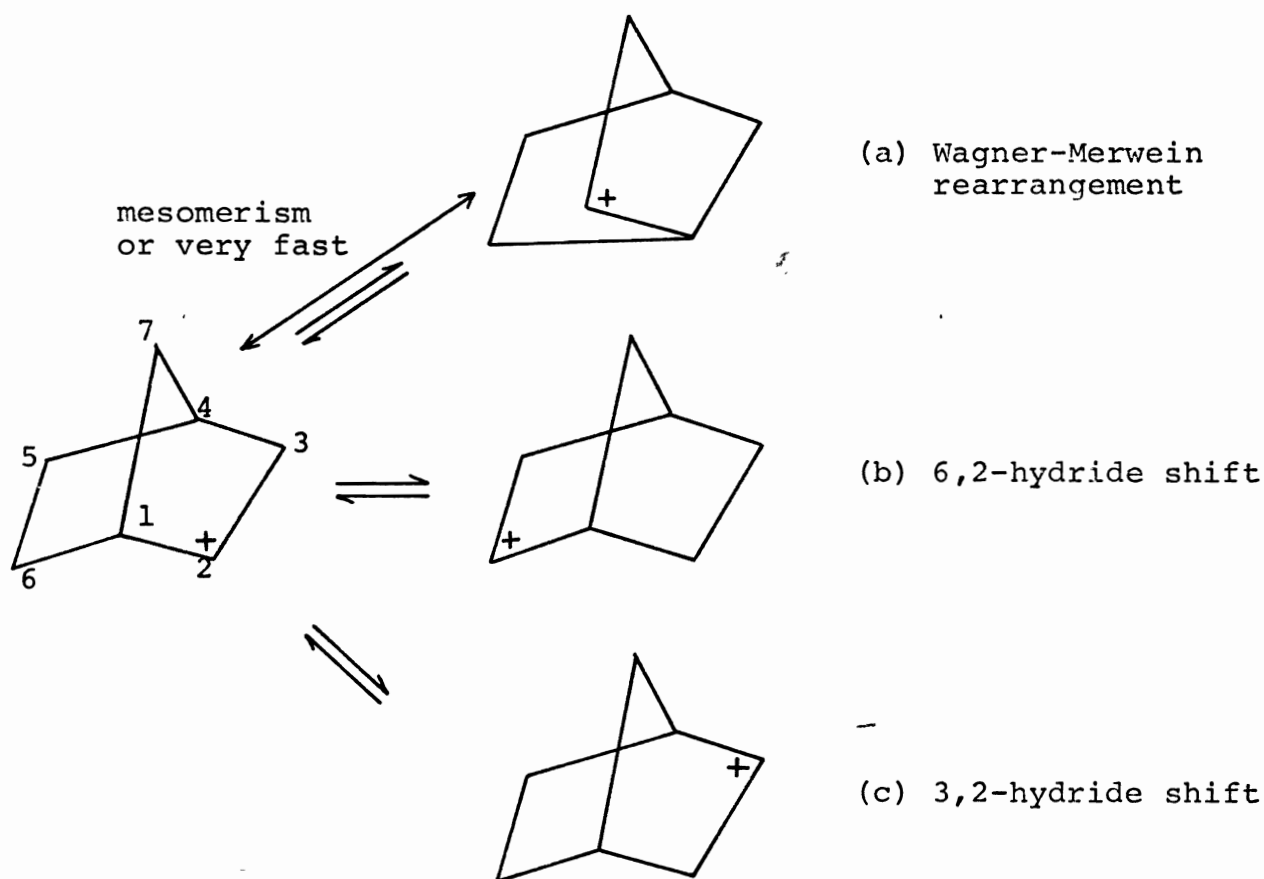
Results are summarised in Table XIV (Appendix). The lowest E_{\min} of 2.33 Å^2 was located at $\phi = 180^\circ$ and $\delta = 90^\circ$. Thus, of the two possible processes the PLM favours that in which the migrating hydrogen is strictly anti-periplanar to the leaving group.

At the present time no experimental evidence is available to confirm this prediction.

Vicinal Hydride Shift in the 2-Norbornyl Cation.

Over the last twenty years a remarkably intensive research effort has been devoted to the study of bi-

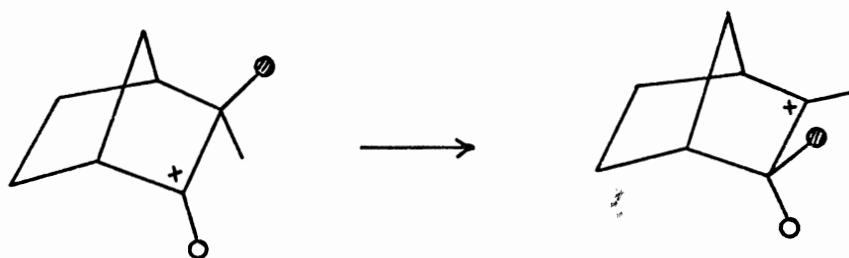
cyclo [2.2.1]-heptyl cations, their rearrangements, rates of formation and structure¹⁰². Experimental results suggested¹⁰³ three different types of rearrangement possibilities: (a) the Wagner-Meerwein rearrangement, (b) the 6,2 (or 1,3) hydride shift and (c) the 3,2 (or 1,2) hydride shift.



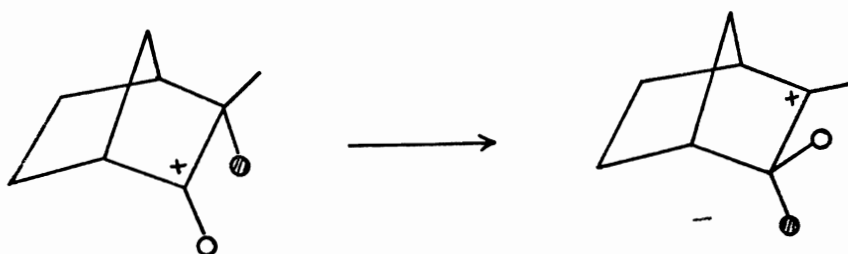
Quantitative rate analysis¹⁰³ resulted in the conclusion that route (c) is slower than the other two by a

minimum factor of $10^{8.8}$, thus permitting this process to be the most amenable to the study of its stereochemistry.

The two basic stereochemical possibilities, namely migration of either the exo- or the endo-hydrogen were considered. The geometry of the 2-norbornyl cation was that calculated earlier (see 1,3-eliminations). The E_{\min} values obtained are as follows:



Exo-shift. $E_{\min} = 5.69 \text{ Å}^2$



Endo-shift. $E_{\min} = 7.06 \text{ Å}^2$

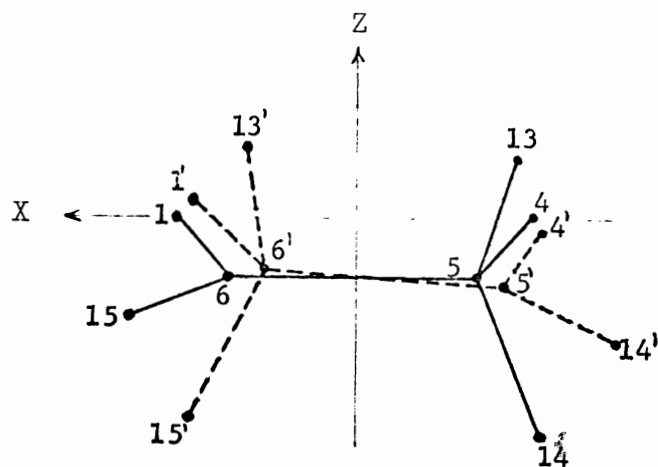
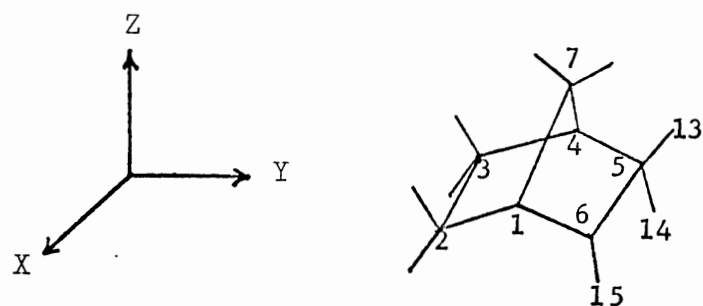
The high preference for the exo shift shown above can be best rationalised by considering the relative geometries

of the reactant and product at E_{\min} . Figure 7 illustrates the XZ plane projections of the above in the vicinity of the reaction centres for both of the stereochemical modes discussed. In Fig.7 (a), representing the exo case, minimisation of the 13-13' distance resulted in the reduction of both the 14-14' and 15-15' distances as well, whereas in the case of the endo-migration (shown in Fig.7 (b)), further minimisation of the above distances would have placed all the other atoms of the molecule away from their optimum position.

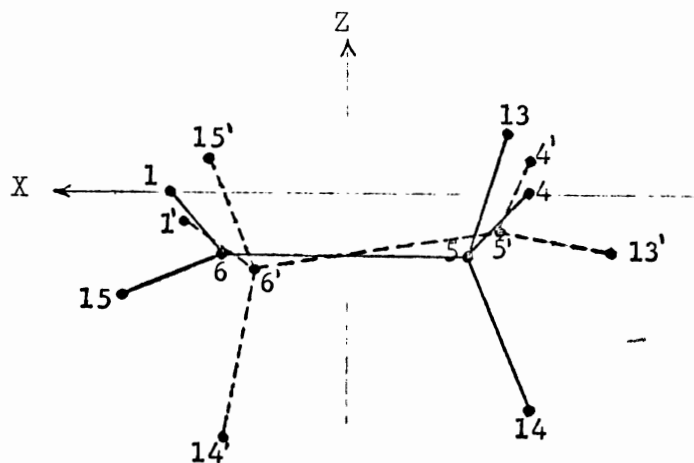
The above discussion may be supplemented by a numerical comparison of the individual displacements of the atoms displayed in Fig.7. These, as presented in Table XV, show

Table XV. Squares of the Atomic Displacements for the 1,2-Hydride Shift in 2-Norbornyl Cation.

Atom _i	D_i^2	
	<u>Exo</u>	<u>Endo</u>
1	0.031	0.044
4	0.031	0.044
5	0.047	0.063
6	0.047	0.063
13	3.134	1.043
14	0.905	4.061
15	0.905	1.043



(a) exo-migration



(b) endo-migration

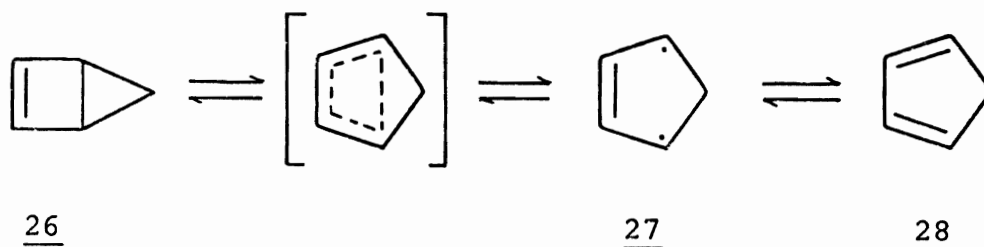
Figure 7. XZ Plane Projections of Reactant and Product at E_{\min} in the Vicinity of the Reaction Centres for the 1,2-Hydride Shift in 2-Norbornyl Cation. Solid lines represent the reactant and dashed lines represent the product.

that the displacement of the migrating atom₁₃ for the exo-migration is substantially smaller than that of atom₁₄ for the endo-migration, all others being of comparable magnitude.

Experiments performed^{104,105} on a series of bicyclo-[2.2.1]-heptyl cations also revealed an exo-preference for the vicinal hydride shift.

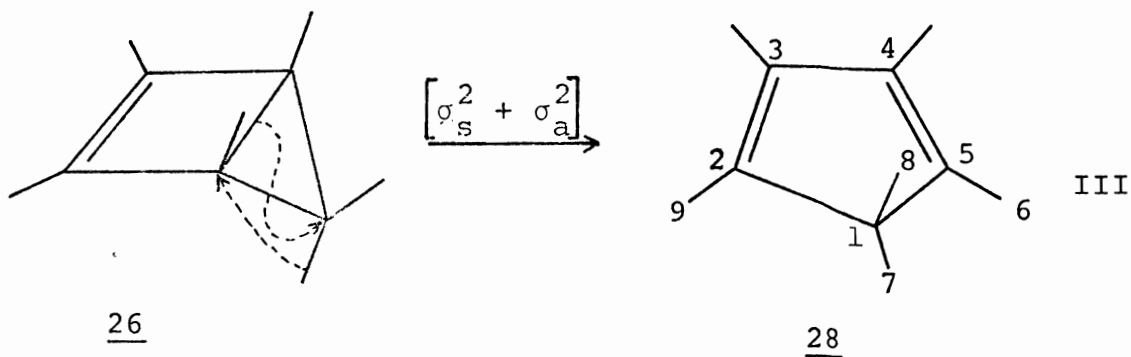
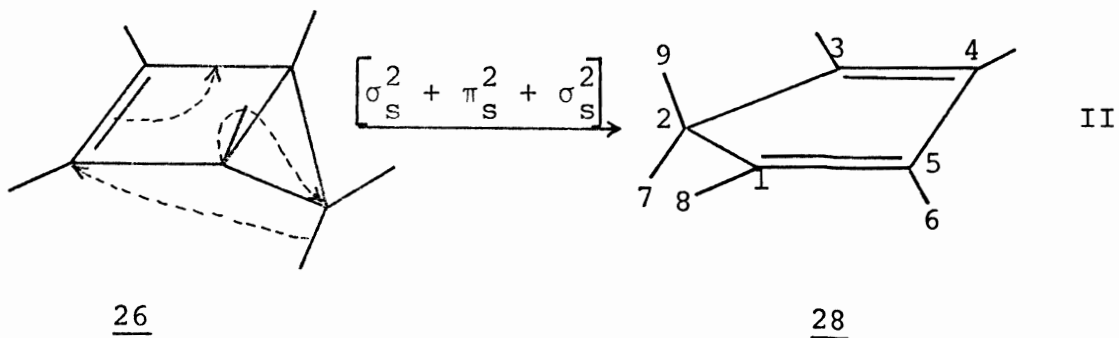
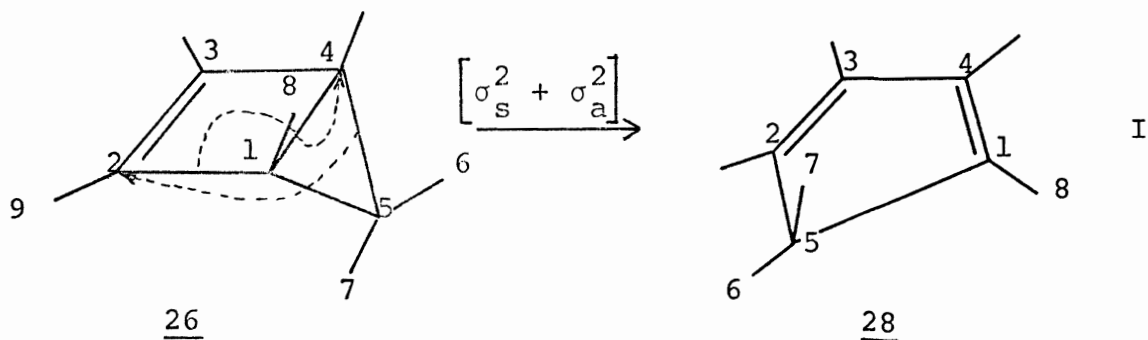
Rearrangement of Bicyclo [2.1.0] Pent-2-ene.

The stereochemistry of the facile thermal rearrangement of bicyclo [2.1.0] pent-2-ene (26) to cyclopentadiene (28) is the subject of much current interest^{106-109,114-117}. Based on the symmetry allowed conrotatory electrocyclic change of cyclobutene to butadiene, the Woodward-Hoffmann rules¹ predict that the rearrangement of its cis-fused homologue would result in the formation of a cyclic cis-trans-diene. However, the application of this symmetry-allowed route to 26 would lead to the sterically impossible cis-trans-1,3-cyclopentadiene. Thus, a disrotatory, symmetry forbidden process involving the diradical (27) has been



proposed¹⁰⁶⁻¹⁰⁸, since diradical models are well known to account for a wide variety of unimolecular ring openings¹⁰⁷.

Based on the above reaction scheme, theoretical estimates¹⁰⁶⁻¹⁰⁸ of the "energy difference between orbital



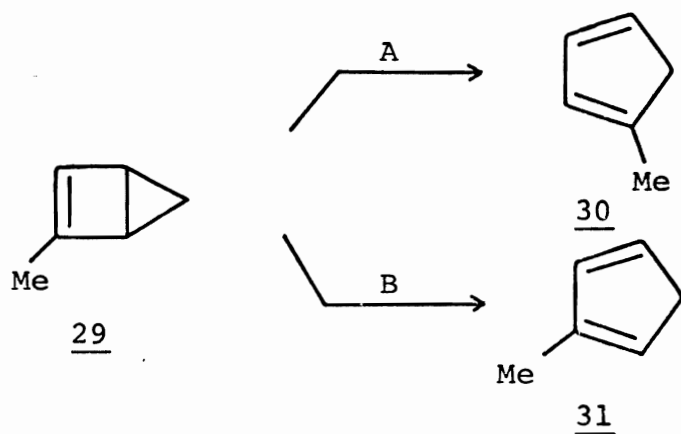
symmetry allowed and non-allowed processes"¹⁰⁶ indicated that the difference in activation energies involved is approximately 15 kcal/mole. These estimates, however, concern only the valence isomerisation of (26) involving the fission of its C₁-C₄ bond (see numbering p 89). Consequently, it was pointed out¹¹⁴ that there are other well known types of thermally allowed¹ concerted reactions which may possibly be operative in the transformation of bicyclopentene (26) to cyclopentadiene, as illustrated (p 89).

Reaction I is a symmetry-allowed $[\sigma_s^2 + \sigma_a^2]$ cycloaddition and it involves inversion of configuration at C₅.

Reaction II may be identified with the aid of the Woodward-Hoffmann nomenclature as an allowed $[\sigma_s^2 + \pi_s^2 + \sigma_s^2]$ process involving a hydrogen transfer.

Reaction III is a cyclopropane-to-propylene rearrangement and it is also accompanied by a hydrogen shift.

It was found experimentally^{115,116} that 2-methylbicyclo-pent-2-ene (29) also undergoes thermal isomerisation



at a similar rate as (26) giving exclusively (30) as the product. This result provided evidence that the reaction is concerted and follows one of the symmetry-allowed paths shown earlier. Identification of the actual mechanism was attempted by means of primary and secondary isotope effects¹¹⁴, and although the results do not appear conclusive, it was concluded that the reaction occurs via the $\left[\sigma_s^2 + \sigma_a^2 \right]$ cyclo-addition (I).

PLM calculations were carried out for all of the above reactions (I,II & III) as well as for the concerted non-allowed disrotatory ring opening process. The geometry of the reactant has recently been established by micro-wave spectroscopy¹⁰⁹ and the reported parameters were used for the calculation of its coordinates. For the product, bond lengths and bond angles of the carbon skeleton were taken from recent microwave data¹¹¹. Bond lengths and bond angles for the hydrogens of the product were obtained from recently published calculations¹¹³. The structural parameters of the reactant are shown in Table XVI and results of the calculations are presented in Table XVII.

It is apparent from Table XVII that the PLM favours the concerted $\left[\sigma_s^2 + \sigma_a^2 \right]$ cyclopropane-to-propylene type (III) of rearrangement. This result is in agreement with experimental evidence^{115,116} furnished for the concerted path A shown on page 90, but disagrees with the assumption of the

Table XVI. Structural Parameters of Bicyclo [2.1.0]

Pent-2-ene

Name	Bond length, Å		Bond angle, deg.		Ref.
Bicyclo pent-2-ene (26)	-C ₁ -C ₂ -	1.51	H ₈ C ₁ C ₄	128.5	109
	-C ₂ -C ₃ -	1.34	H ₉ C ₂ C ₃	126.0	"
	-C ₁ -C ₄ -	1.56	H ₆ C ₅ C ₃	126.0	"
	-C ₁ -C ₅ -	1.53	int.pl.*	114	"
	-C ₂ -H ₉	1.085			"
	-C ₁ -H ₈	1.071			"
	-C ₅ -H ₆	1.093			
			H ₈ C ₁ C ₂	119**	110

* The angle between the planes of the cyclobutene & cyclopropane rings.

** Obtained from data of bicyclo [2.1.0] pentane.

Table XVII. Variation of E_{min} with the Mode of Rearrangement of Bicyclo [2.1.0] Pent-2-ene (26).

Mode	E _{min} , Å ²	
Disrotatory ring opening	10.73	
$\left[\sigma_s^2 + \sigma_a^2 \right]$ cycloaddition (I)	17.69	
$\left[\sigma_s^2 + \pi_s^2 + \sigma_s^2 \right]$ process (II)	9.97	(a)
"	28.20	(b)
Cyclopropane-to-propylene type (III)	6.71	(a)
	22.09	(b)

(b) = exo hydrogen migrates

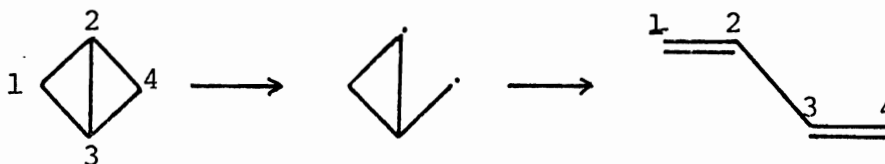
(a) = endo hydrogen migrates

$[\sigma_s^2 + \sigma_a^2]$ cycloaddition process (I). However, as it was mentioned earlier, the results of the isotope effect experiments were inconclusive and thus a decisive conclusion drawn¹¹⁴ could be incorrect. It should also be noted, that very recent experiments¹¹⁷ resulted in the trapping of (31) as the predominant product of the reaction, which would mean that path B (p 90) is operative. On the other hand, the authors¹¹⁷ do not believe that their results provide a decisive answer.

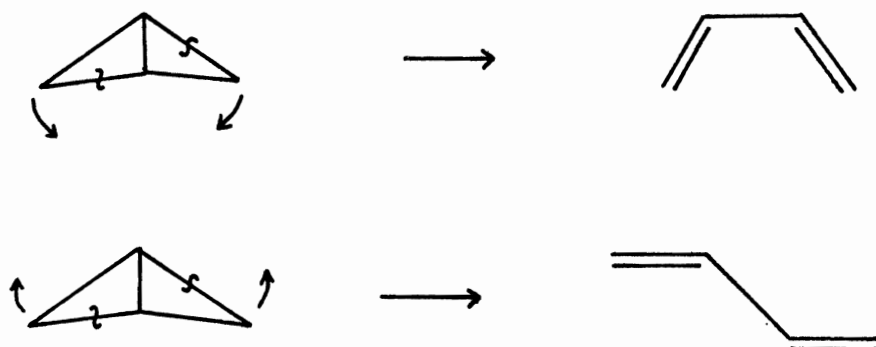
It seems that further experimental work is necessary to solve this ambiguity.

Rearrangement of Bicyclobutane.

The thermal rearrangement of bicyclobutane to butadiene may conceivably occur in a concerted manner or by a biradical intermediate.

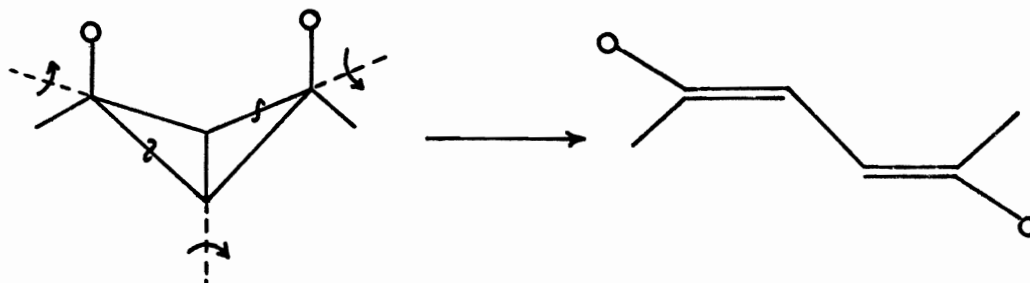


In the former case the reaction may lead either to cis- or trans-butadiene as the initial product.

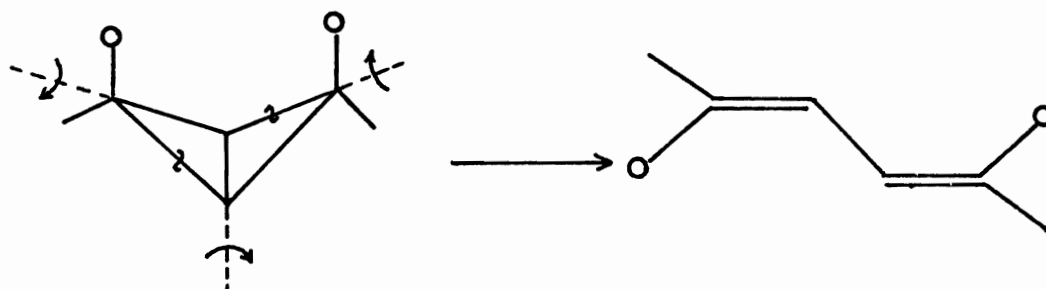


For each of these modes of reaction three stereochemically different paths can be envisioned:

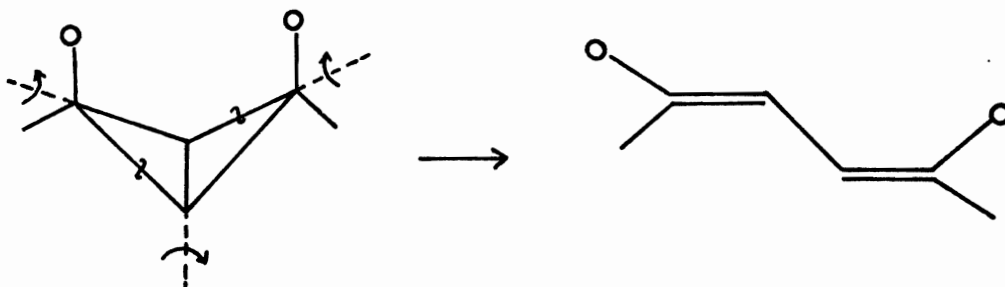
(a) Dis-dis



(b) Con-con



(c) Dis-con



Path (a) corresponds to a quasi-disrotatory opening of both rings, while path (b) requires a quasi-conrotatory motion. In path (c) one ring is opened disrotatory and the other conrotatory. The first two processes are not allowed by the Woodward-Hoffmann rules¹, since they would require the correlation of bonding with antibonding orbitals. Although the lack of common symmetry elements in reactant and product prevents a rigorous symmetry-orbital argument for part (c), qualitative overlap considerations¹ resulted in the conclusion that it should be an allowed $[\sigma_s^2 + \sigma_a^2]$ process.

Three similar processes leading to cis-butadienes are also possible. However, in subsequent discussion all possible rotamers of the product (about the formal C-C bond) are allowed for and therefore these possibilities are not considered explicitly.

PLM calculations were carried out for the three modes

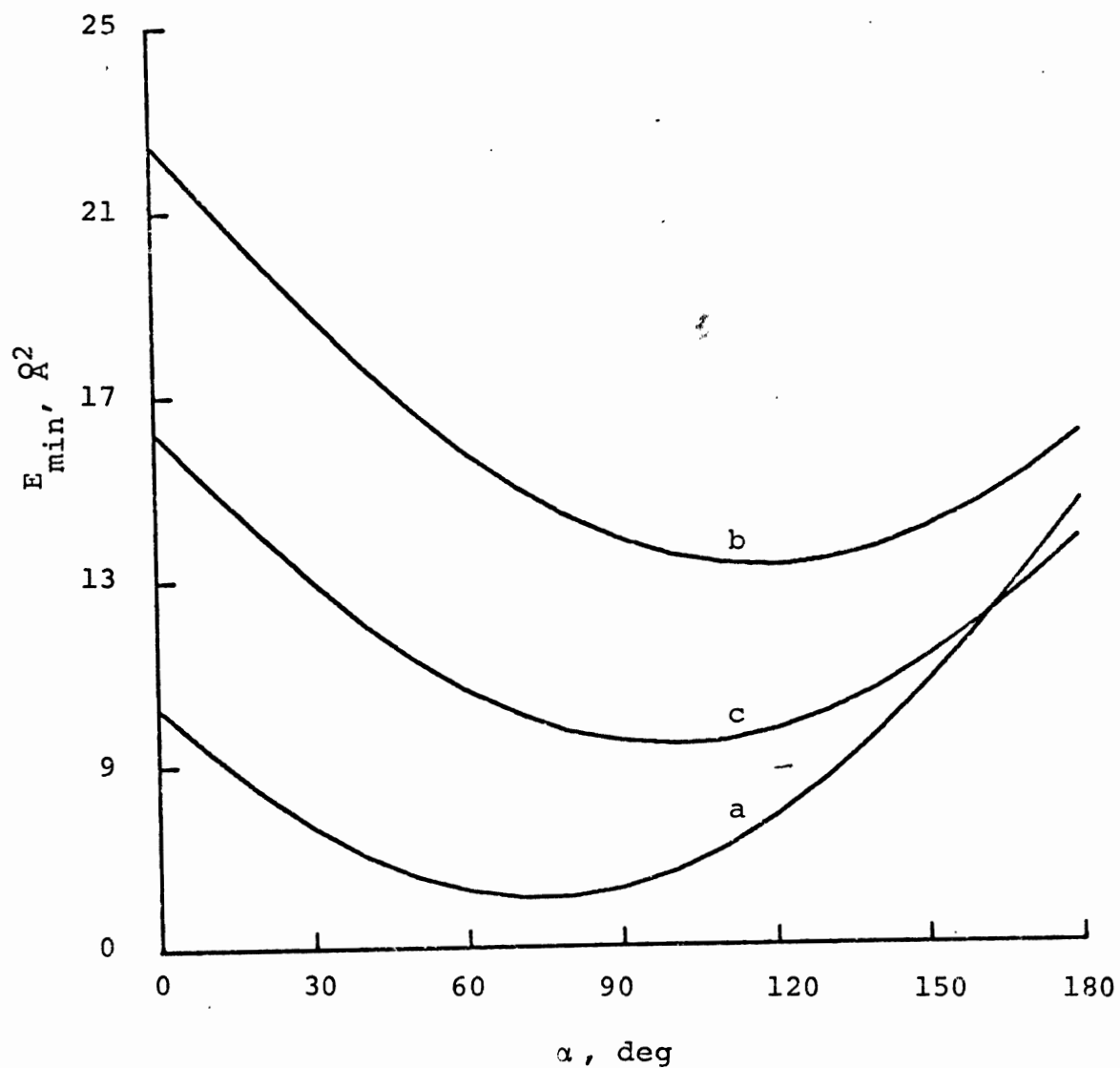
(a), (b) and (c) above. The structural parameters used for the calculations of bicyclobutane coordinates were obtained from microwave data¹¹⁸, and those utilised for the product were the results of electron diffraction studies¹¹⁹. The procedure used was the following: assuming cis-butadiene as the initial conformation of the product, the methylene groups of the butadiene were rotated about the central bond and E_{\min} values were calculated as the function of the dihedral angle α defined below.



Results are tabulated (see Appendix) and plotted in Fig.8. Several types of information may be obtained from these curves. Firstly, if the product is assumed to be planar ($\alpha = 180^\circ$, trans-butadiene), then the E_{\min} values favour rearrangement via the dis-con mode (path (c)). However, if the comparison is made for a cis-butadiene product ($\alpha = 0^\circ$), then the E_{\min} values favour the dis-dis mode (path (a)).

More realistically one should compare the lowest E_{\min} values for each mode which are:

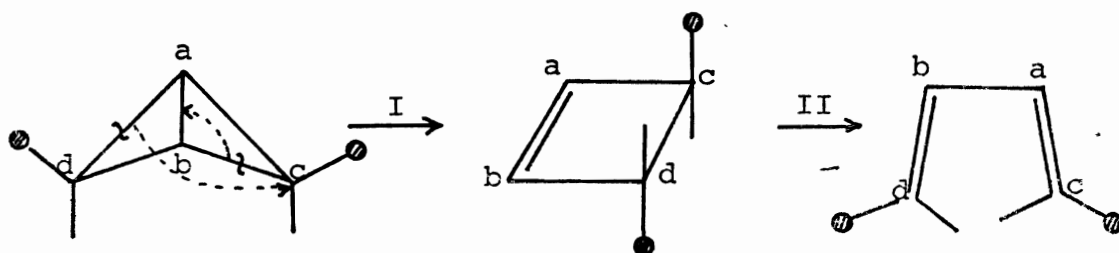
Figure 8. Variation of E_{\min} with the Dihedral Angle α for the Rearrangement of Bicyclobutane. Curve (a) represents dis-dis mode, curve (b) and curve (c) the con-con and dis-con mode, respectively.



Path (a)	<u>dis-dis</u>	Lowest $E_{\min} = 6.07 \text{ Å}^2$	at $\alpha = 78^\circ$
(b)	<u>con-con</u>	=13.3	=120°
(c)	<u>dis-con</u>	= 9.3	=110°

These again favour the dis-dis mode leading to a cisoid butadiene (since $\alpha < 90^\circ$). On the other hand, the interplanar angle of bicyclobutane is 122° ¹¹⁸ and thus it might be anticipated that the lowest values of E_{\min} for all three processes would occur when α is close to this value. This is the case for both the con-con and the dis-con modes. The unusually low angle value of the favoured process (a) required further investigation.

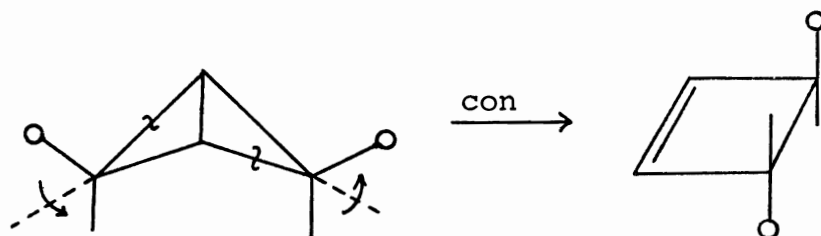
Orbital symmetry considerations¹ offer an alternative symmetry-allowed mechanism for the rearrangement of bicyclobutane.



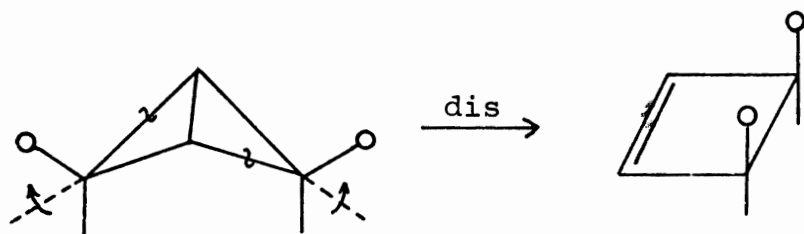
From the stereochemical point of view, step I may occur via conrotatory or disrotatory motion. Step II is the familiar conrotatory ring-opening of cyclobutene which

has already been considered by the PLM approach³⁹.

Calculations for step I resulted in the E_{\min} values shown below.



$$E_{\min} = 15.45 \text{ Å}^2$$



$$E_{\min} = 16.00 \text{ Å}^2$$

According to the results above, the PLM, in agreement with the qualitative overlap considerations¹, favours the conrotatory motion.

The effect of molecular size on the stereochemistry of the rearrangement was also studied by successive substitution of methyl groups for hydrogens. Calculations were performed for various conformations obtained by the simultaneous rotation of the methylene groups and the substituents. Results for both the monomethyl and the symmetrically substituted dimethyl derivative followed the same order as discussed earlier (p 98).

Results of CNDO calculations by Wiberg¹²⁰ led to the proposal of a vibrationally excited cyclobutene intermediate which rapidly rearranges to the final product. This was confirmed by experiment using stereospecifically deuterated bicyclobutane¹²⁰.

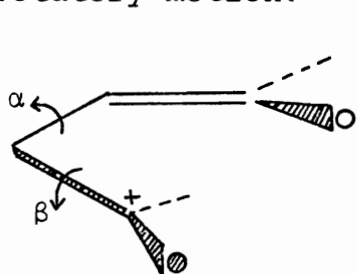
The rearrangement of a highly substituted bicyclobutane has also been studied¹²¹. It was reported, that at 140°C the reactant is in thermal equilibrium with a cyclobutene intermediate which, at 180°C rearranges to a butadiene derivative. However, more recent NMR data obtained¹²² for the intermediate was found not to be compatible with the previous structure, and a bicyclic molecule was offered as an alternative.

Other experimental results from the thermal rearrangement of symmetrically substituted dimethyl bicyclobutanes suggested a concerted dis-con mechanism (c)¹²³.

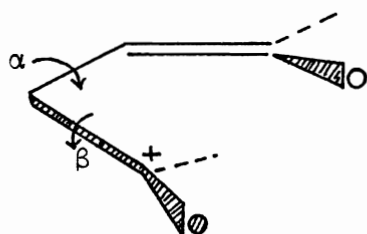
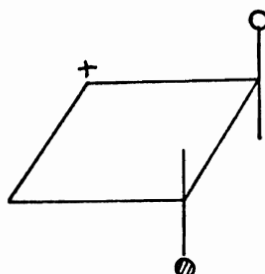
In summary, for the concerted thermal rearrangement of bicyclobutane and its monomethyl and symmetrically substituted dimethyl derivative to a trans-planar butadiene derivative, the PLM, in accord with experiment¹²³, favours the unsymmetrical dis-con mode. On the other hand, if the reaction involves a cyclobutene intermediate (as it was reported by some workers^{120,121}), then the PLM predicts its formation to be by means of conrotatory ring opening of the reactant. This prediction agrees with the qualitative arguments of Woodward and Hoffmann¹.

Cyclisation of the Syn-Allylcarbinyl Cation.

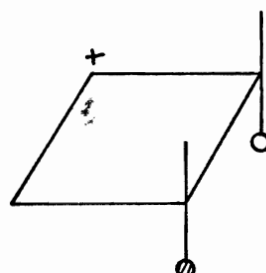
The thermal cyclisation of the syn-allylcarbinyl cation may, in principle, occur via a conrotatory or a disrotatory motion.



Disrotatory cyclisation

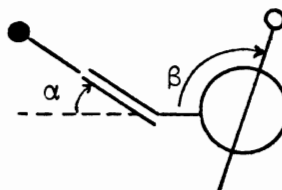
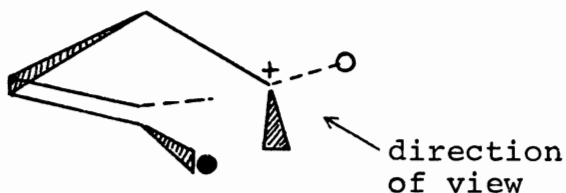


Conrotatory cyclisation



These alternatives were considered by the PLM method. The coordinates of both the reactant and product were calculated using structural parameters obtained from the literature¹²⁴. E_{\min} values were calculated for various conformations obtained by simultaneous rotation of the single bonds of the reactant by several values of α and β . The former is defined as the dihedral angle the trigonal centre forms with the plane of the molecule and the latter involves the angle between the carbonium ion centre and the molecular plane. Initially a wide scan was performed which later was expanded around the lowest value. The tabulated results are presented in Appendix I.

The lowest E_{\min} for the disrotatory mode was located at $\alpha = 12^\circ$ and $\beta = 98^\circ$

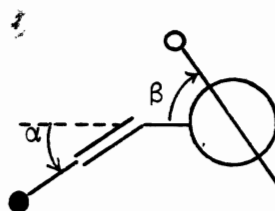
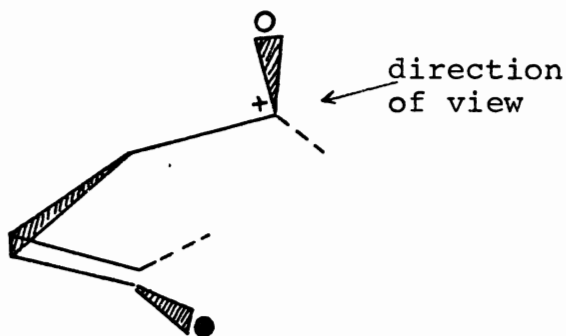


$$E_{\min} = 4.5028 \text{ Å}^2$$

$$\alpha = 12^\circ$$

$$\beta = 98^\circ$$

and for the conrotatory mode that value appeared at $\alpha = 12^\circ$ and $\beta = 82^\circ$.



$$E_{\min} = 4.5049 \text{ Å}^2$$

$$\alpha = 12^\circ$$

$$\beta = 82^\circ$$

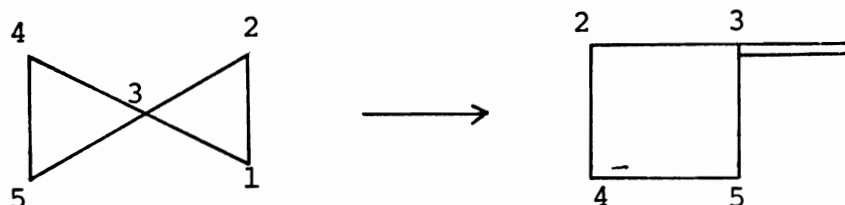
It was also noticed that the above values are invariant to the direction of the rotation. This was expected, since the product has a plane of symmetry. As is apparent from the above values, the PLM exhibits a negligible preference for the disrotatory mode. This is perhaps due to the fact that a planar product was assumed. The geometry of the reactant at the lowest E_{\min} suggests that the cyclisation could lead to a product having a bent structure. This is not at all unlikely, since cyclobutane itself is known to have a

puckered conformation. Furthermore, the observed solvolytic behaviour of cyclobutane derivatives¹²⁵ and also the CNDO calculations of Wiberg concerning the positional reactivity of cyclobutane¹²⁰ gave strong indication that the bent cyclobutyl ion is more stable than the planar form, and there is appreciable cross-ring binding in the bent form.

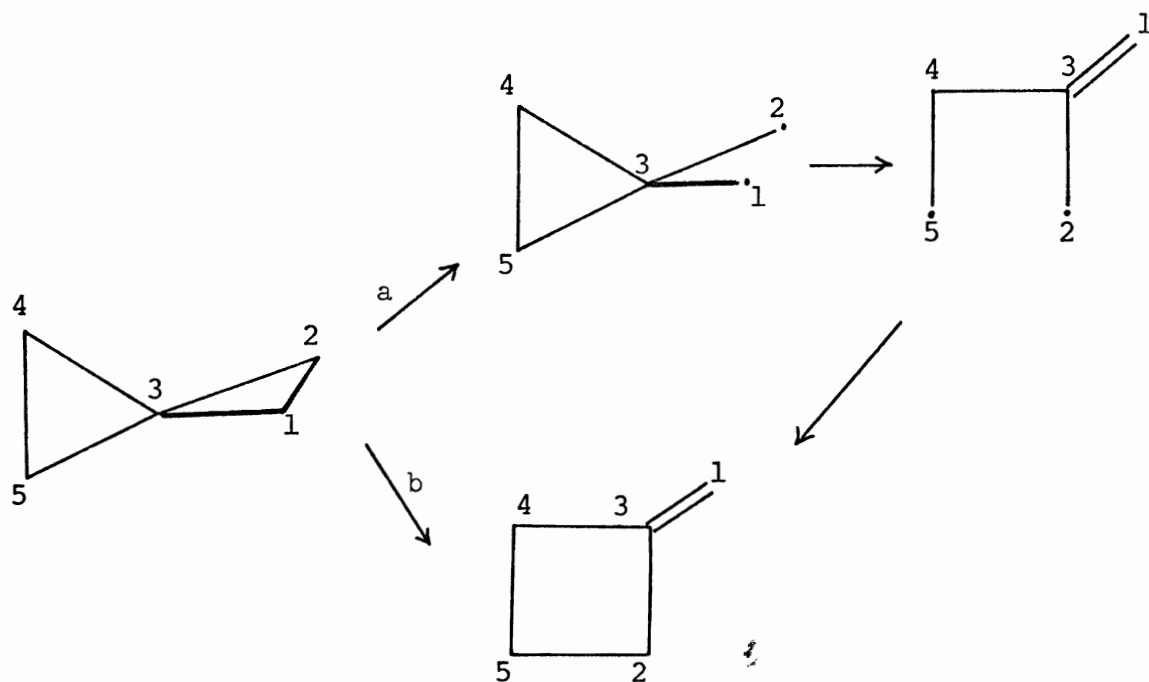
Both the localised molecular orbital approach of Trindle and Sinanoglu¹²⁴ and the conservation of orbital symmetry considerations¹ predict a disrotatory ring closure.

Rearrangement of Spiropentane.

The thermal rearrangement by spiro~~pentane~~ to methylene cyclobutane was first studied by Burkhardt¹²⁶ and by Frey¹²⁷. The latter furnished evidence that above 13.5 mm pressure the transformation is unimolecular and first order.



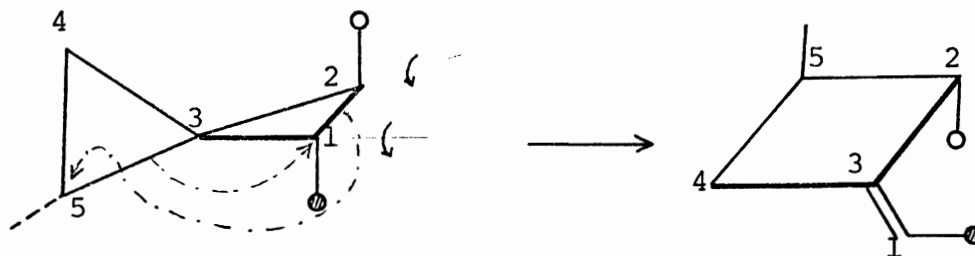
Two types of mechanism may be envisioned: the first (path "a") involves an initial (1,2) peripheral bond fission followed by a vicinal alkyl shift, and the second (path "b") is a concerted process.



The former has been found operational in the case of isopropenylspiropentane, its axially dissymmetric 4-methyl derivatives¹²⁸, and in trans-dimethyl-1,1-dicyanospiropentane¹²⁹. Other results¹³⁰, however, suggested that the mechanism of the rearrangement is dependent upon the stereochemistry of the methyl substituents at the 4-and 5-positions.

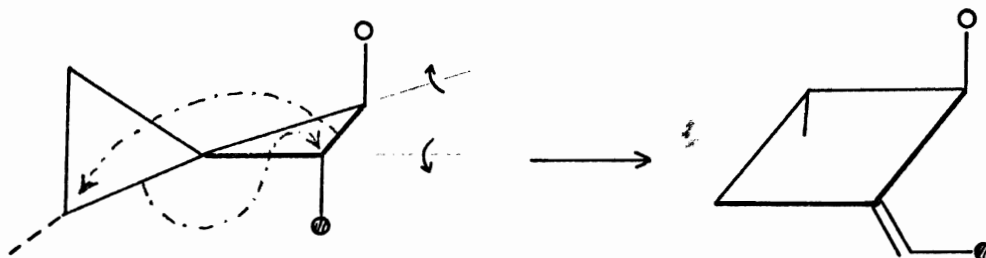
Of the two types of mechanisms ("a" and "b" above) only the concerted process is amenable to study by the present PLM method. Three distinct cases were considered, each corresponding to a different stereochemical result.

Case 1.



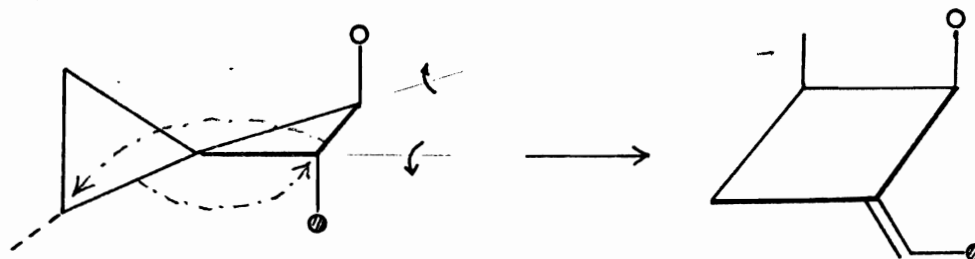
Conrotatory ring opening at C_1-C_2 with retention of configuration at both C_2 and C_5 . $[\sigma_s^2 + \sigma_a^2]$ process.

Case 2.



Disrotatory ring opening at C_1-C_2 with inversion of configuration at both C_2 and C_5 . $[\sigma_a^2 + \sigma_s^2]$ process.

Case 3.



Disrotatory ring opening at C_1-C_2 with inversion at C_2 and retention at C_5 . $[\sigma_s^2 + \sigma_s^2]$ process.

The coordinates of the reactant were calculated from electron diffraction data¹³¹ and those of the product were computed using cyclobutanone as a model¹³², with the exception of the double bond for which a literature⁶⁰ value was used.

Results obtained are as follows:

Case 1.	$E_{\min} = 27.34 \text{ Å}^2$
2.	$= 27.27 \text{ Å}^2$
3.	$= 30.11 \text{ Å}^2$

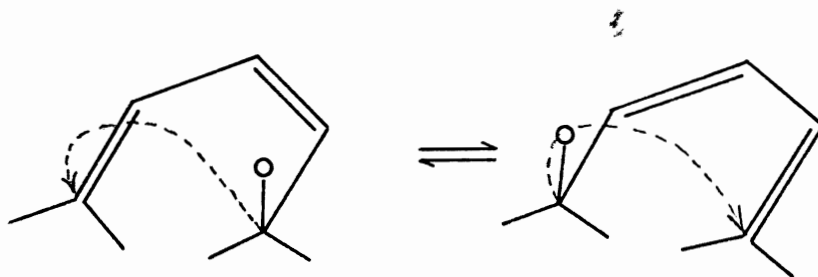
As it was shown above, the first two processes are controlled by the conservation of orbital symmetry and the products formed are enantiomers, whereas the last reaction is not "allowed". All of these facts are reflected in the results above; the former "allowed" processes have substantially lower E_{\min} values than the latter, and due to the mirror plane symmetry of the products, their modes of formation require almost identical nuclear motion (E_{\min} values are very close). There is, however, a small observable preference towards the inversion-inversion path.

Recent experimental observations¹³⁰ concerning the rearrangement of 2,4-dimethyl-1-carbethoxyspiropentanes suggested partial stereoselectivity. The predominating product was one of the two possible enantiomers discussed above. Further experiments revealed that the retention-retention path is favoured over the inversion-inversion

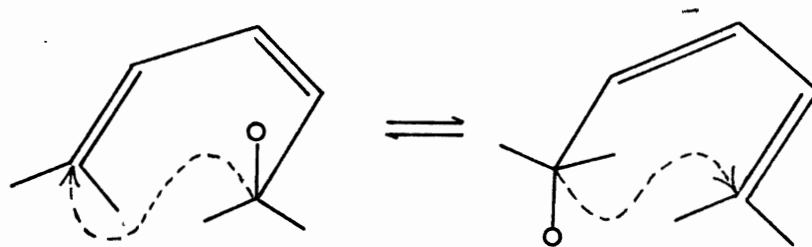
route. However, owing to the extremely poor product recovery (7%), the high temperature (385°C) of the reaction, along with the reported multiple product recovery, the above assignment is not convincing.

Sigmatropic Rearrangements.

[1,5] Shift in 1,3-pentadiene. The simplest case of a sigmatropic shift is the migration of a hydrogen atom. A suitable example for this process is the sigmatropic [1,5] shift in 1,3-pentadiene which, according to the conservation of orbital symmetry, should be suprafacial.



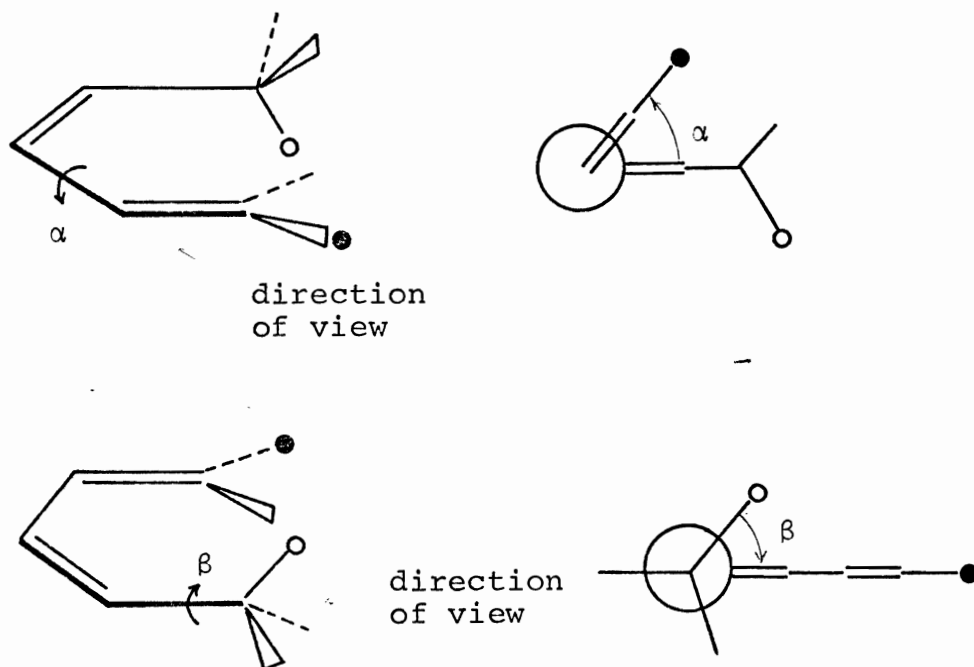
Suprafacial migration.



Antarafacial migration.

Considering this problem with the least motion approach in mind, it is clear that the favoured path will be the one in which both the reactant and product achieve the most advantageous conformation for the hydrogen transfer. Thus the objective was the location of that conformation.

The geometries of both the reactant and product were assumed to be that of butadiene¹¹⁹ with a $C_{sp^2}-C_{sp^3}$ bond length of 1.50 Å to a tetrahedral methyl group. Conformations were generated by the simultaneous rotation about the formal carbon-carbon single bonds in the reactant and the product by the angles α and β defined below.



Initially 10° increments were used for the rotation and this was further expanded to 1° increments around the critical point. The results obtained define a surface which is presented in Fig. 9 and 10. From the surface for the antarafacial migration shown in Fig.9 it appears that the E_{\min} values exhibit a slightly increased sensitivity towards the rotation of the trigonal centre. On the other hand, in Fig.10 representing the surface for the suprafacial migration, there is a marked increase in sensitivity towards the rotation of the tetrahedral centre. As was expected, the lowest E_{\min} of 2.97 Å^2 for the antarafacial mode was located at $\alpha = 38^\circ$ and $\beta = 50^\circ$, meaning that each centre has to move approximately half-way to best accommodate the migration. In contrast to this, is the suprafacial mode, where the lowest E_{\min} value of 2.34 Å^2 was found for a rotamer having $\alpha = 13^\circ$ and $\beta = 36^\circ$ suggesting that the tetrahedral centre need not bend extensively in order to minimise the motion. Comparing the lowest values for each mode of migration it is clear that the least motion approach favours the suprafacial mode, in agreement with the predictions of the orbital symmetry considerations¹. Experimental evidence^{133,134,135} confirms the above predictions.

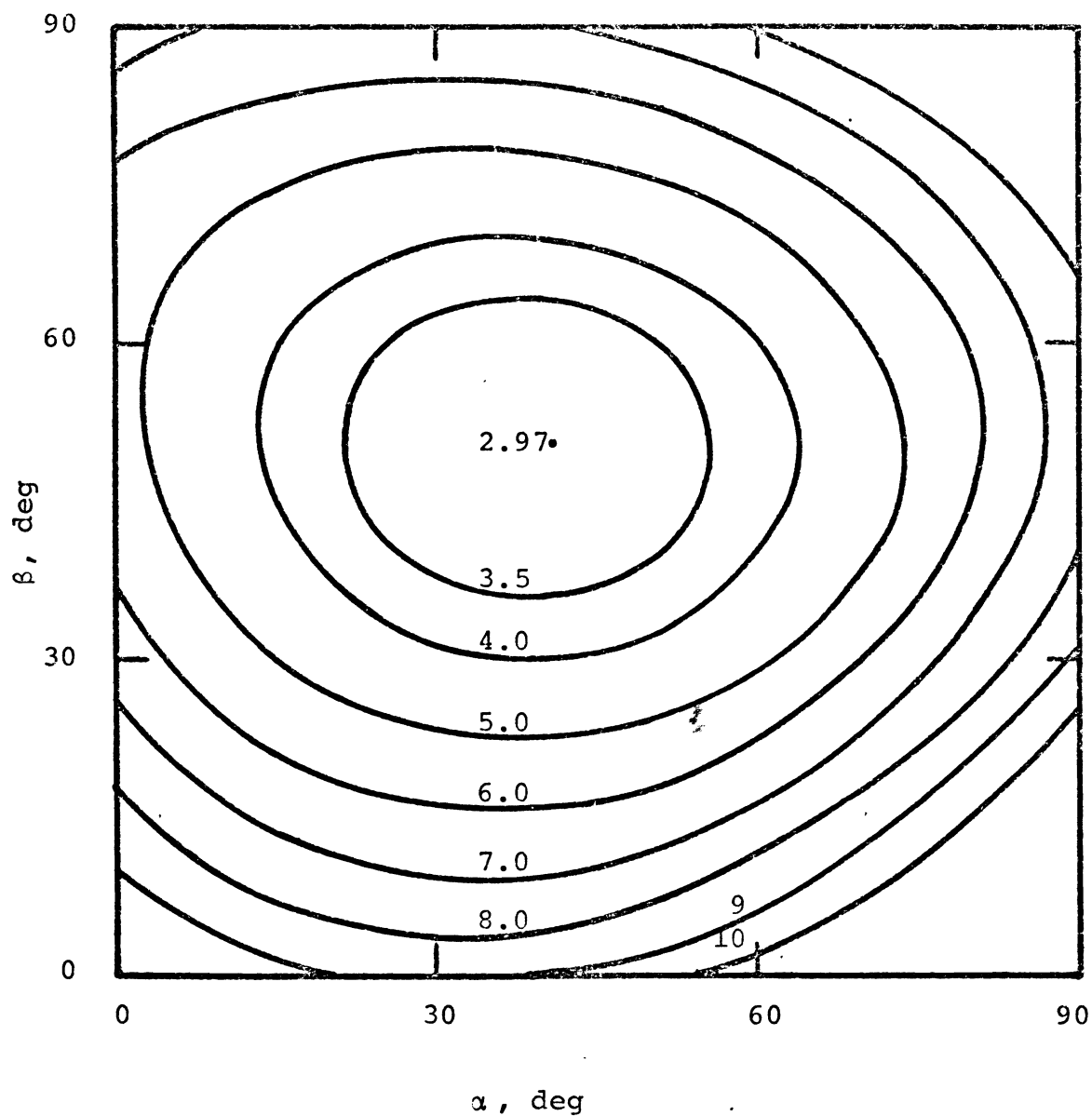


Figure 9. Variation of E_{\min} with the Dihedral Angles α and β for the Antarafacial $[1,5]$ Migration of a Hydrogen in 1,3-Pentadiene.

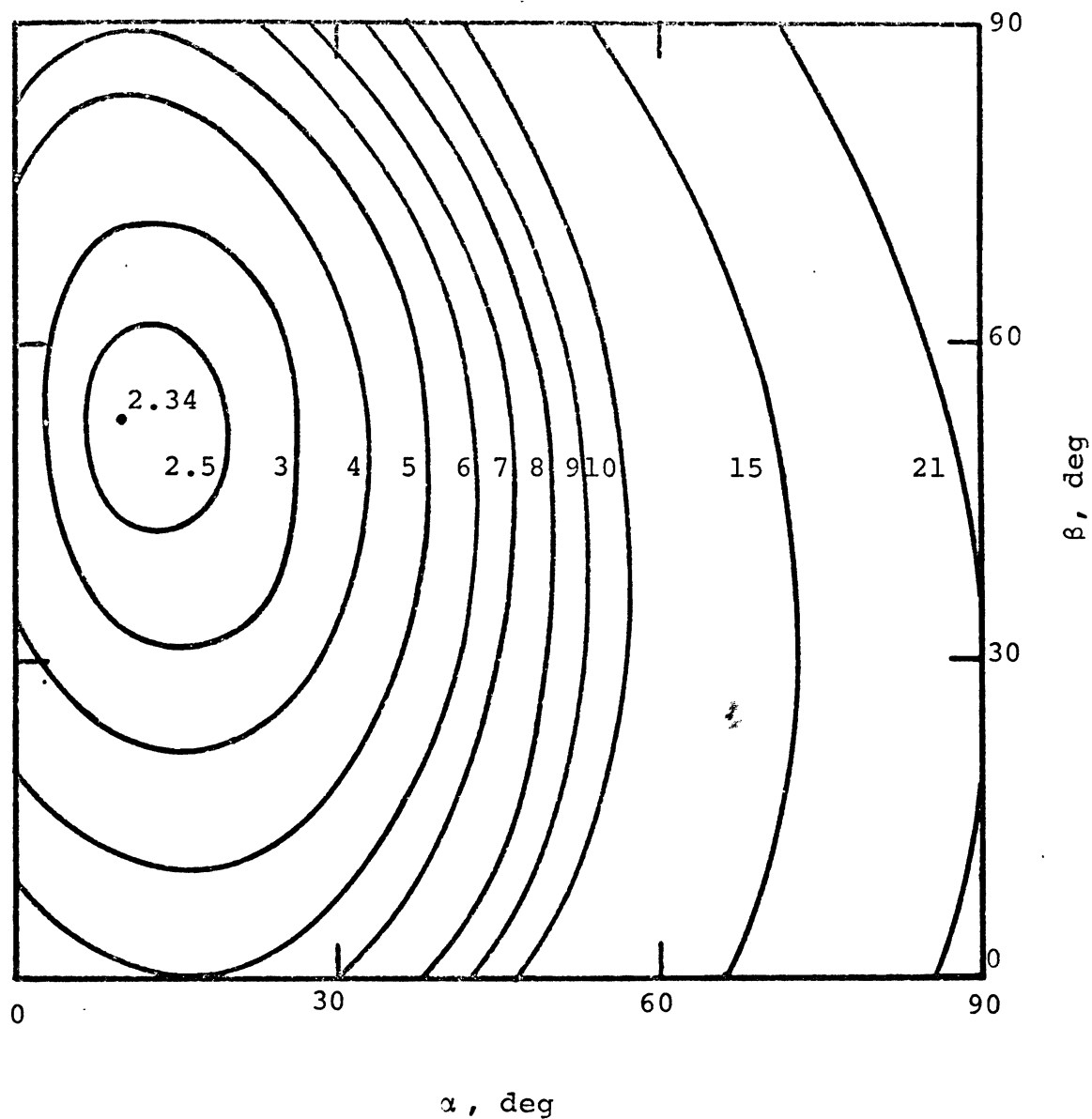


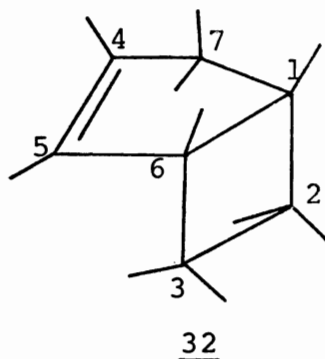
Figure 10. Variation of E_{\min} with the Dihedral Angles α and β for the Suprafacial [1,5] Migration of a Hydrogen in 1,3-Pentadiene.

[1,3] shift in bicyclo [3.2.0] hept-2-ene. According to the Woodward-Hoffmann rules¹, a concerted thermal [1,3]-sigmatropic rearrangement should be antarafacial. This rule is based on the assumption that the migrating atom is restricted to the use of a symmetric orbital (e.g. hydrogen) for bonding interactions in the transition state. Migrating atoms of higher atomic number, such as carbon, however, might use both lobes of an antisymmetric orbital and thereby achieve a suprafacial process with concomitant inversion of configuration at the migrating atom¹.

From the least motion point of view, if a suitable rigid system is chosen in which the migration is necessarily suprafacial, the stereochemistry of the migrating atom may be predicted. This requirement is satisfied by the bicyclo [3.2.0] hept-2-ene molecule. The rearrangement of the former to norbornene may occur with retention or inversion of configuration at the migrating carbon. These possibilities were considered by the PLM method.

Since no experimental results were available for the structure of the reactant, it had to be estimated. The model parameters were based on the structures of cyclopentene¹¹³ and cyclobutane¹³⁶, and are listed in Table XXV. The coordinates of the product (norbornene) were calculated earlier (see p 61). Results of the calculations are shown on page 114.

Table XXV. Structural Parameters of Bicyclo [3.2.0] hept-2-ene

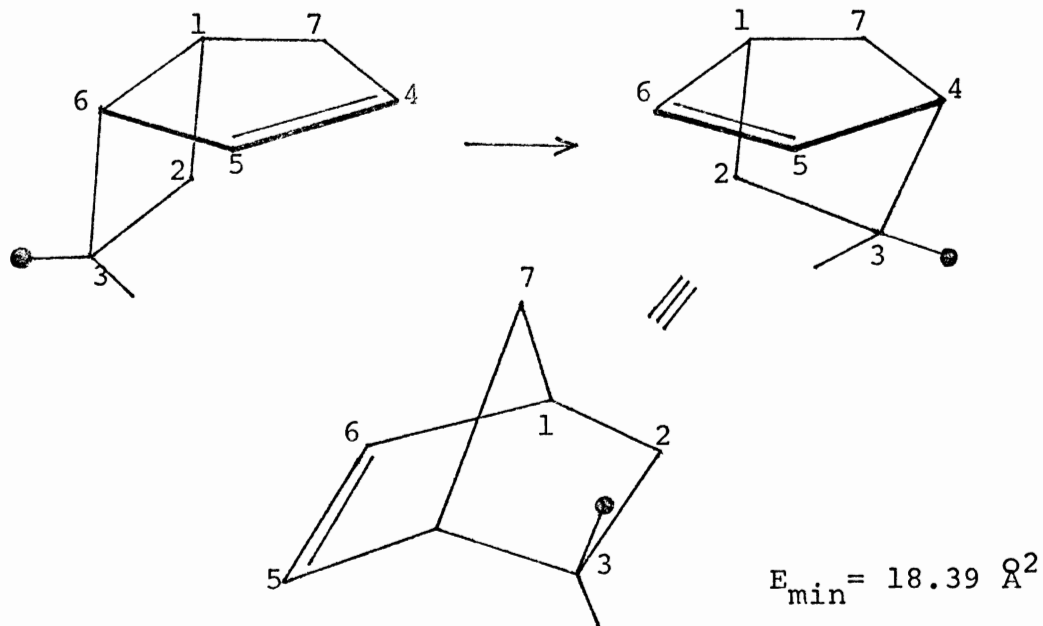


Structure	Bond length, Å		Bond angle*, deg		Ref.
<u>32</u>	-C=C-	1.333	C=C-C	112.2	135
	-C ₄ -C ₇ -	1.50	C ₄ C ₇ C ₁	104.1	"
	-C ₅ -C ₆ -	"	C ₇ C ₁ C ₆	107.4	"
	-C ₁ -C ₆ -	1.535			"
	-C ₁ -C ₇ -	"			"
	-C ₁ -C ₂ -	"	**		
	-C ₂ -C ₃ -	"	**		
	-C ₃ -C ₆ -	"	**	-	
	=C-H	1.08			135
	-C-H	1.11			"
			C ₃ C ₆ C ₅	115.0	136

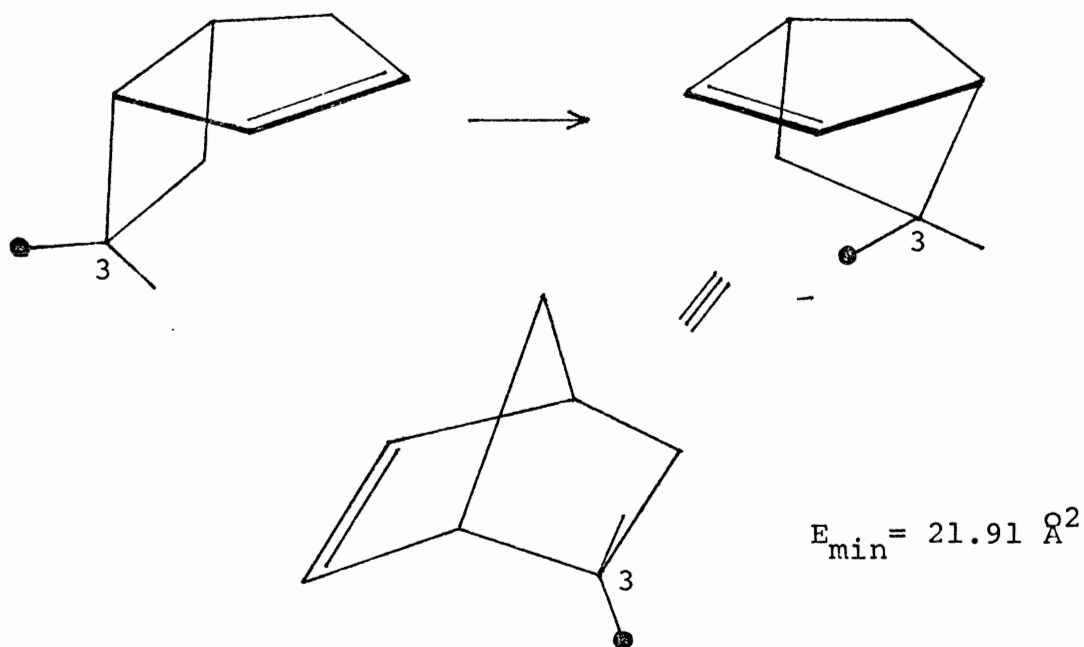
* Bond angles of the cyclobutane ring were assumed to be 90°.

** All bond lengths of the cyclobutane ring were assumed to be equal.

- 1) Suprafacial[1,3]-shift with inversion of configuration at C_3 .

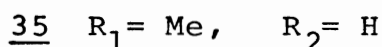
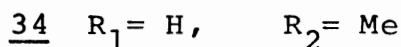
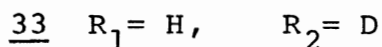
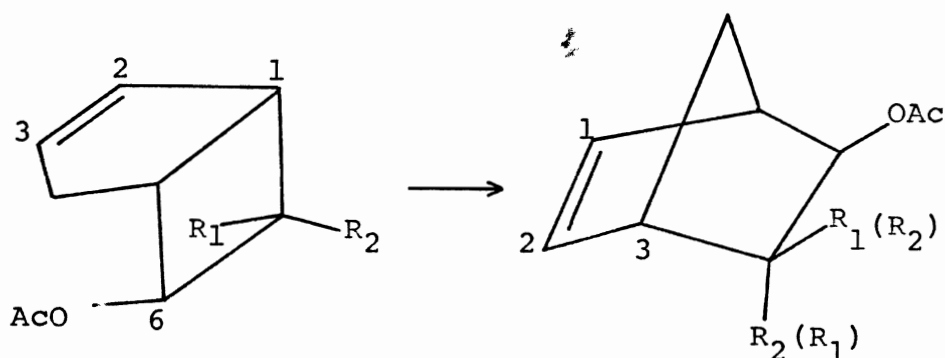


- 2) Suprafacial[1,3]-shift with retention of configuration at C_3 .



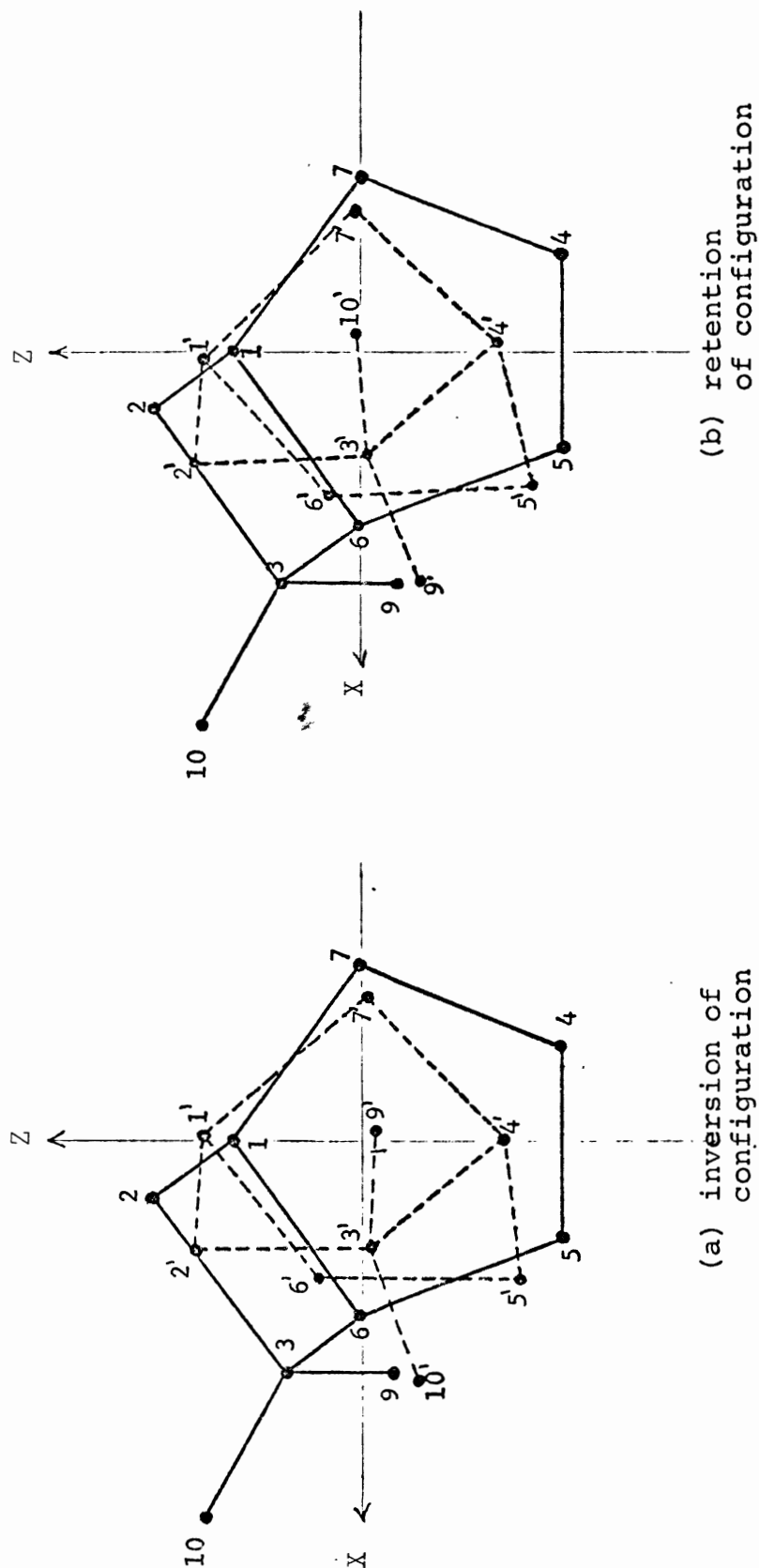
The results obtained clearly favour the inversion pathway, whereas intuitively the retention path was expected to be preferred. However, examination of the XZ projection of the reactive portion of the molecules at E_{\min} quickly reveals that in the latter case minimisation with respect to the atoms in the carbon framework brings about the maximisation of the 10-10' distance (see illustration in Fig.11).

The thermal suprafacial [1,3]-sigmatropic rearrangement of endo-bicyclo [3.2.0] hept-2-en-6-yl acetate was studied by Berson and co-workers^{56,137-139}. It was reported that the



reaction of (33) and (34)^{137,138} occurred with inversion of configuration. Further work, however, furnished evidence that^{56,139} the rearrangement of (35) took place with retention of configuration. This led to the conclusion that the configuration-inverting transition state from (35)

Figure 11.XZ Plane Projection of the Reactant and Product for the 1,3-Migration in Bicyclo [3.2.0] hept-2-ene. Note that only the carbon skeletons and hydrogens attached to the migrating carbon are shown. Solid lines represent the reactant and dashed lines the product.



is sterically too strained to permit the electronically "allowed" concerted process to occur, and thus a biradical mechanism was proposed.

SUMMARY

Within the framework of this thesis the PLM technique was applied to eliminations, homoenolisations, enolisations and various types of rearrangements.

Altogether twenty-four reactions were investigated, three of which were cases where no experimental evidence was available for comparison. The remainder, with the exception of one reaction, were in satisfactory agreement with either the predictions of the conservation of orbital symmetry (COS) or with experimental evidence, or both.

The one instance where the PLM approach resulted in an erroneous prediction was the 1,3-elimination from the norbornyl system. However, whether this should be attributed to the imperfection of the method used or the peculiarity of the norbornyl system, remains to be established.

It is noteworthy, that although in eliminations, homoenolisations and enolisations only the nuclear motions of atoms common to both the reactant and the product were considered, the results obtained correlated remarkably well with experimental findings. This suggests that the relaxation of the residual portion of the molecule to the final geometry of the product directs the stereochemical route of a reaction.

It was observed that substitution of a methyl group for a hydrogen atom may change the preferred path of a

reaction (eg. see ethyl carbene). This was rationalised by considering the additional motion due to the presence of the methyl hydrogens. An alternative explanation would be offered on steric grounds. Under these circumstances the COS approach, in contrast to the PLM method, is incapable of predicting the course of the reaction.

Another observation concerning the utility of the PLM technique is that it permits a reasonable estimation of transition state geometry which may be of value in the better understanding of those reactions where both concerted and stepwise mechanisms result in identical products, and in which the trapping of a possible reactive intermediate may be exceptionally difficult. For instance, for the rearrangement of bicyclobutane, consideration of the relative geometries of the reactant and product at the lowest E_{\min} value generated, suggested the possible existence of a reactive cisoid-conformation, although the reaction product is trans-butadiene. Remarkably, similar conclusions were arrived at by the use of a more sophisticated theoretical treatment.

Despite its usefulness, the PLM approach is fully applicable only to those reactions where the number of atoms in the reactant equals those in the product. Thus in this respect it is most suited for the study of molecular rearrangements.

In summary, the PLM proved to be a useful technique for predicting the stereochemistry of various organic

reactions.

The remarkable coincidence of the predictions of PLM with those derived from orbital symmetry and other considerations for those reactions studied, suggests that the least motion pathway parallels that of minimum energy. It thus appears that a correlation between these two factors, insofar as the prediction of the stereochemical course of organic reactions is concerned, might indeed be possible.

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APPENDIX I

Table XIV. Variation of E_{\min} with the Dihedral Angles δ and ϕ for the Formation of Ethyl Cation from Ethyl Chloride in which the Loss of Leaving Group is Concerted with H-Migration.

(a) Syn-Periplanar.

$E_{\min}, \text{\AA}^2$							
\varnothing, deg	δ, deg						
	0	30	60	90	120	150	180
-90	5.33	4.76	4.73	5.26	6.30	7.77	9.51
-60	5.02	4.12	3.80	4.09	4.96	6.33	8.04
-30	5.18	3.99	3.35	3.34	3.96	5.15	6.76
0	5.78	4.35	3.41	<u>3.09</u>	3.41	4.35	5.78
30	6.76	5.15	3.96	3.34	3.35	3.99	5.18
60	8.04	6.33	4.96	4.09	3.80	4.12	5.02
90	9.51	7.77	6.30	5.26	4.73	4.76	5.33

Table XIV. Continued.

(b) Anti-Periplanar

ϕ, deg	$E_{\min}, \text{\AA}^2$						
	δ, deg						
	0	30	60	90	120	150	180
90	6.13	5.38	5.09	5.30	6.00	7.17	8.70
120	5.21	4.20	3.69	3.72	4.32	5.44	6.97
150	4.79	3.56	2.83	2.69	3.16	4.19	5.68
180	4.94	3.54	2.64	<u>2.33</u>	2.64	3.54	4.94
210	5.68	4.19	3.16	2.69	2.83	3.56	4.79
240	6.97	5.44	4.32	3.72	3.69	4.20	5.21
270	8.70	7.17	6.00	5.30	5.09	5.38	6.13

Table XVIII. Variation of E_{\min} with the Dihedral Angle α for the Rearrangement of Bicyclobutane.

Dis-dis Mode

α , deg	$E_{\min}, \text{\AA}^2$	α , deg	$E_{\min}, \text{\AA}^2$
0	10.24	100	6.63
10	9.26	110	7.14
20	8.38	120	7.81
30	7.62	130	8.63
40	7.00	140	9.59
50	6.53	150	10.68
60	6.22	160	11.88
70	<u>6.07</u>	170	13.19
80	6.09	180	14.60
90	6.28		

Table XIX. Variation of E_{\min} with the Dihedral Angle α for the Rearrangement of Bicyclobutane.

Con-con Mode.

α , deg	$E_{\min}, \text{\AA}^2$	α , deg	$E_{\min}, \text{\AA}^2$
0	22.45	100	13.44
10	21.20	110	13.25
20	19.97	120	<u>13.22</u>
30	18.78	130	13.34
40	17.66	140	13.60
50	16.64	150	14.01
60	15.72	160	14.56
70	14.93	170	15.24
80	14.29	180	16.05
90	13.79		

Table XX. Variation of E_{\min} with the Dihedral Angle α
for the Rearrangement of Bicyclobutane.

Dis-con Mode

α , deg	$E_{\min}, \text{\AA}^2$	α , deg	$E_{\min}, \text{\AA}^2$
0	16.22	100	<u>9.36</u>
10	15.08	110	9.44
20	13.99	120	9.68
30	12.97	130	10.06
40	12.04	140	10.58
50	11.24	150	11.23
60	10.56	160	11.99
70	10.03	170	12.86
80	9.65	180	13.83
90	9.43		

Table XXI. Variation of E_{\min} with the Dihedral Angles α and β for the Conrotatory Cyclisation of Syn-Allylcarbinyll Cation.

		$E_{\min}, \text{\AA}^2$				
β , deg		α , deg				
		11	12	13	14	15
79		4.5129	4.5096	4.5090	4.5109	4.5154
80		4.5100	4.5071	4.5068	4.5090	4.5138
81		4.5082	4.5056	4.5055	4.5081	4.5132
82		4.5072	<u>4.5049</u>	4.5052	4.5080	4.5135
83		4.5071	4.5052	4.5058	4.5089	4.5147
84		4.5080	4.5063	4.5072	4.5107	4.5168
85		4.5097	4.5084	4.5096	4.5135	4.5198

Table XXII. Variation of E_{\min} with the Dihedral Angles α and β for the Disrotatory Cyclisation of Syn-Allylcarbinyl Cation.

$E_{\min}, \text{\AA}^2$					
β , deg	α , deg				
	11	12	13	14	15
95	4.5077	4.5066	4.5082	4.5123	4.5189
96	4.5058	4.5044	4.5056	4.5094	4.5158
97	4.5048	4.5031	4.5040	4.5075	4.5135
98	4.5048	<u>4.5028</u>	4.5033	4.5065	4.5122
99	4.5056	4.5033	4.5036	4.5064	4.5118
100	4.5074	4.5048	4.5047	4.5072	4.5123
101	4.5101	4.5071	4.5068	4.5089	4.5137

Table XXIII. Variation of E_{\min} with the Dihedral Angles α and β for the Suprafacial [1,5] Shift of a Hydrogen in 1,3-Pentadiene.

β, deg	α, deg										$E_{\min}, \text{\AA}^2$
	0	10	20	30	40	50	60	70	80	90	
0	5.31	4.92	5.54	7.14	9.64	12.93	16.85	21.21	25.81	30.43	
10	4.19	3.67	4.14	5.57	7.88	10.97	14.67	18.82	23.19	27.61	
20	3.48	2.85	3.18	4.45	6.59	9.49	12.98	16.91	21.07	25.28	
30	3.16	2.44	2.66	3.79	5.77	8.48	11.77	15.48	19.42	23.42	
40	3.20	<u>2.42</u>	2.54	3.56	5.39	7.93	11.03	14.53	18.26	22.04	
50	3.54	2.72	2.78	3.70	5.41	7.79	10.50	14.01	17.53	21.11	
60	4.13	3.31	3.33	4.18	5.78	8.03	10.79	13.90	17.21	20.59	
70	4.91	4.11	4.13	4.94	6.46	8.50	11.20	14.14	17.26	20.44	
80	5.82	5.08	5.13	4.92	7.39	9.43	11.91	14.69	17.64	20.63	
90	6.82	6.17	6.27	7.08	8.52	10.50	12.87	15.51	18.29	21.11	

Table XXIV. Variation of E_{\min} with the Dihedral Angles α and β for the Antarafacial [1,5] Shift of a Hydrogen in 1,3-Pentadiene.

β, deg	α, deg									
	0	10	20	30	40	50	60	70	80	90
0	10.59	9.59	8.97	8.76	8.95	9.57	10.62	12.10	14.00	16.31
10	8.94	7.86	7.15	6.81	6.87	7.35	8.24	9.55	11.27	13.40
20	7.56	6.43	5.65	5.23	5.19	5.55	6.31	7.48	9.04	11.00
30	6.47	5.33	4.52	4.06	3.96	4.24	4.90	5.94	7.38	9.20
40	5.71	4.60	3.81	3.34	3.22	3.45	4.04	4.99	6.32	8.01
50	5.30	4.26	3.52	3.09	<u>2.97</u>	3.19	3.74	4.64	5.88	7.47
60	5.26	4.33	3.67	3.30	3.24	3.48	4.08	4.90	6.08	7.00
70	5.59	4.79	4.25	3.99	4.00	4.30	4.88	5.75	6.91	8.36
80	6.27	5.64	5.25	5.12	5.25	5.63	6.27	7.17	8.32	9.74
90	7.29	6.85	6.64	6.66	7.00	7.42	8.14	9.10	10.28	11.69

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PROGRAM LESMOT2(INPUT, OUTPUT, TAPE 5=INPUT, TAPE 6=OUTPUT)
LESMOT/2 - - LESMOT CALCULATION FOR VARIOUS CONFORMERS

THIS PROGRAM INCORPORATES THE PREVIOUS PROGRAM LESMOT AS A
SUBROUTINE, AND HAS THE ADDED FACILITY THAT, GIVEN THE INITIAL
COORDS OF THE REACTANT AND PRODUCT, IT WILL WORK OUT THE COORDS
OF ANY DESIRED CONFORMATION OF THE REACTANT AND/OR PRODUCT AND
THEN CARRY OUT A PLM CALCULATION USING THEM.

DIMENSION XR(50),YR(50),ZR(50),XP(50),YP(50),ZP(50),C(6)
DIMENSION XXR(50),YYR(50),ZZR(50),XYP(50),YYP(50),ZZP(50)
DIMENSION BLR(50,50),BLP(50,50),TITLE(20)
DIMENSION IIR(6),JJR(6),IIP(6),JJF(6),KKKF(6,10),NAROTR(6)
DIMENSION KKKR(6,10),NAROTP(6),ANGR(6),ANGP(6)
INTEGER TITLE

1000 READ (5,101) TITLE
IF(TITLE(1).EQ.4HSTOP) STOP
READ (5,106) NATS,NITS,NCONF,NANGR,NANGP,MISS
READ (5,102) (XR(I),YR(I),ZR(I),I=1,NATS)
READ (5,102) (XP(I),YP(I),ZP(I),I=1,NATS)

NATS IS THE NUMBER OF ATOMS. NITS IS THE MAXIMUM NUMBER OF
ITERATIONS THAT THE LESMOT CALCULATION SHOULD GO TO. NCONF IS THE
NUMBER OF CONFORMATIONS FOR WHICH CALCULATIONS ARE DESIRED---
EFFECTIVELY IT IS THE NUMBER OF JOBS FOR A GIVEN SET OF INITIAL
COORDS. NANGR IS THE NUMBER OF ANGLES IN THE REACTANT FOR WHICH
ROTATIONS ARE REQUIRED. NANGP IS THE SAME FOR THE PRODUCT.
MISS IS A CONTROL. IF IT EQUALS ZERO THE INITIAL VALUES OF C(I)
ARE SET BY THE PROGRAM. IF IT EQUALS ONE THEY ARE READ IN.
THE ARRAYS XR,YR,ZR CONTAIN THE INITIAL GEOMETRY OF THE REACTANT.
THE ARRAYS XP,YP,ZP CONTAIN THE INITIAL GEOMETRY OF THE PRODUCT.

WRITE (6,201) TITLE
WRITE (6,202)
WRITE (6,203) (I,XR(I),YR(I),ZR(I),XP(I),YP(I),ZP(I),I=1,NATS)

CALL BONLEN(XR,YR,ZR,NATS,BLR)
CALL BONLEN(XP,YP,ZP,NATS,BLP)

WRITE(6,204)
CALL MATOUT(BLR,NATS)
WRITE(6,205)
CALL MATOUT(BLP,NATS)

BOND LENGTHS (BLR,BLP) ARE CALCULATED BY THE SUBROUTINE BONLEN,
AND THEN WRITTEN OUT. THIS ASSISTS CHECKING THAT THE INITIAL COORDS
ARE CORRECT.

IF(NANGR.EQ.0) GO TO 1002
DO 1001 I=1,NANGR
READ (5,103) IIR(I),JJR(I),NAROTR(I)
NR=NAROTR(I)
1001 READ (5,104) (KKKR(I,J),J=1,NR)

1002 CONTINUE

C
C NARCTR IS THE NUMBER OF ATOMS THAT ARE TO BE ROTATED BY THE
C DIHEDRAL ANGLE ANGR ABOUT THE BOND IIR,JJR. THE ANGLE IS DEFINED
C ANTI-CLOCKWISE LOOKING FROM JJR TO IIR. KKKR IDENTIFIES THOSE ATOMS
C THAT ARE TO BE ROTATED ABOUT IIR,JJR.
C NAROTF, IIP,JJP,KKKP,ANGP ARE DEFINED AS ARE NAROTR, ETC.

IF(NANGP.EQ.0) GO TO 1004

DO 1003 I=1,NANGP

READ (5,103) IIP(I),JJP(I),NAROTF(I)

NP=NAROTF(I)

1003 READ (5,104) (KKKP(I,J),J=1,NP)

1004 CONTINUE

ICONF=C

C
1005 WRITE(6,201) TITLE

IF(NANGR.NE.0) GO TO 1006

IF(NANGP.NE.0) GO TO 1007

GO TO 1008

C
1006 READ (5,105) (ANGR(I),I=1,NANGR)
IF(NANGP.EQ.0) GO TO 1008

1007 READ (5,105) (ANGP(I),I=1,NANGP)

1008 CONTINUE

IF(MISS.EQ.1) READ (5,105) (C(I),I=1,6)

C
C ANGR,ANGP ARE ARRAYS CONTAINING THE VARIOUS ANGLES OF ROTATION
C REQUIRED TO DEFINE A PARTICULAR CONFORMATION.
C THE ARRAY C CONTAINS THE PARAMETERS REQUIRED FOR THE MINIMISATION
C IN LESMOT. ONLY IN VERY SPECIAL CASES NEED GOOD ESTIMATES BE READ
C IN. IF MISS EQUALS ZERO,THE PROGRAM WILL ASSUME VALUES OF C(I).---
C -- SEE DO 1012

ICONF=ICONF+1

DO 1009 I=1,NATS

XXR(I)=XR(I)

YYR(I)=YR(I)

ZZR(I)=ZR(I)

XXP(I)=XP(I)

YYP(I)=YP(I)

1009 ZZP(I)=ZP(I)

C
C XXR,YYR,ZZR ARE ARRAYS TO HOLD THE TRANSFORMED COORDS OF THE
C REACTANT, AND XXP,YYP,ZZP ARE FOR THE PRODUCT.

IF(NANGR.EQ.0) WRITE(6,206)

IF(NANGR.EQ.0) GO TO 1010

C
C WRITE (6,207)
C CALL CCNFOR (XXR,YYR,ZZR,IIR,JJR,ANGR,KKKR,NANGR,NAROTR)

C
C THE SUBROUTINE CONFOR CALCULATES THE COORDS OF DESIRED CONFORMERS
C

```
1010 CONTINUE
C
  IF(NANGP.EQ.0) WRITE(6,208)
  IF(NANGP.EQ.0) GO TO 1011
C
  WRITE (6,209)
  CALL CCNFOR (XXP,YYP,ZZP,IIF,JJP,ANGP,KKKP,NANGP,NAROTP)
C
1011 CONTINUE
  IF(MISS.EQ.1) GO TO 1013
  DO 1012 I=1,3
    J=I+3
    C(I)=0.1
1012 C(J)=1.0
1013 CONTINUE
C
C   THE ACTUAL PLM CALCULATION IS CARRIED OUT BY THE SUBROUTINE LESMCT
C
  CALL LESMCT(XXR,YYR,ZZR,XXP,YYP,ZZP,NATS,NITS,C)
C
  IF(ICCNF.NE.NCONF) GO TO 1005
C
101 FORMAT (20A4)
102 FORMAT (3F10.0)
103 FORMAT(3I3)
104 FORMAT(10I3)
105 FORMAT (6F10.0)
106 FORMAT (6I3)
C
201 FORMAT (1H1,20X,20A4//)
202 FORMAT (30X,38HINITIAL COORDS OF REACTANT AND PRODUCT/5X,4HATCH,10
1X,5HXR(I),7X,5HYR(I),7X,5HZR(I),17X,5HXP(I),7X,5HYP(I),7X,5HZP(I))
203 FORMAT((5X,I3,5X,3(2X,F10.5),10X,3(2X,F10.5)))
204 FORMAT(1H0/20X,23HREACTANT BOND DISTANCES)
205 FORMAT(1H0/20X,22HPRODUCT BOND DISTANCES)
206 FORMAT(//20X,25HREACTANT COORDS AS BEFORE)
207 FORMAT(//5X,48H-----REACTANT-----)
208 FORMAT(//20X,24HPRODUCT COORDS AS BEFORE)
209 FORMAT(//5X,48H-----PRODUCT-----)
C
  GO TO 1000
END
```

```
      SUBROUTINE CONFOR (X,Y,Z,II,JJ,ANG,KKK,NANG,NROT)
      -----
      C THIS SUBROUTINE CALCULATES THE CARTESIAN COORDS OF A CONFORMER
      C USING THE SUBROUTINE ROTCOR AND DATA READ FROM THE MAIN PROGRAM.
      C -----
      DIMENSION X(50),Y(50),Z(50),II(6),JJ(6),ANG(6),KKK(6,10),NRCT(6)
      DIMENSION KK(6)
      C
      DO 11 I=1,NANG
      BETA=ANG(I)
      IR=II(I)
      JR=JJ(I)
      NR=NRCT(I)
      WRITE (6,20) BETA,IR,JR
      WRITE (6,21)
      DO 10 J=1,NR
10    KK(J)=KKK(I,J)
      CALL ROTCOR (X,Y,Z,IR,JR,BETA,KK,NR)
      DO 11 J=1,NR
      K=KK(J)
      WRITE (6,22) K,X(K),Y(K),Z(K)
11    CONTINUE
      C
20    FORMAT(1H0,5X,29HCOORDS CHANGED BY ROTATION CF,F8.2,1X,19HDEGREES
1    ABOUT BOND(,I2,1H,,I2,1H))
21    FORMAT(1H0,5X,4HATOM,9X,4HX(I),8X,4HY(I),8X,4HZ(I))
22    FORMAT(5X,I3,5X,3(2X,F10.6))
      C
      RETURN
      END
```

SUBROUTINE ROTCCR (X,Y,Z,I,J,THETA,KK,NN)

THIS SUBROUTINE ROTATES COORDS.

X,Y,Z ARE ARRAYS CONTAINING THE COORDS OF THE ATOMS (POINTS).
I,J IS THE BOND ABOUT WHICH THERE WILL BE AN ANTI-CLOCKWISE (AS
SEEN FROM J TO I) ROTATION OF THETA DEGREES OF THE NN ATOMS
(POINTS) INITIALED IN THE ARRAY KK.

DIMENSION X(50),Y(50),Z(50),KK(10),U(50),V(50)

XJ = X(J) - X(I)

YJ = Y(J) - Y(I)

ZJ = Z(J) - Z(I)

A = SGRT(XJ**2 + YJ**2)

COSDEL = YJ/A

SINDEL = XJ/A

B = SGRT(A**2 + ZJ**2)

COSGAM = ZJ/B

SINGAM = A/B

THETR = THETA*0.017453293

COSTH = COS(THETR)

SINTH = SIN(THETR)

DO 10 LL=1,NN

L = KK(LL)

X(L) = X(L) - X(I)

Y(L) = Y(L) - Y(I)

Z(L) = Z(L) - Z(I)

U(L) = X(L)

V(L) = Y(L)

X(L) = U(L)*COSDEL - V(L)*SINDEL

Y(L) = U(L)*SINDEL + V(L)*COSDEL

U(L) = Y(L)

V(L) = Z(L)

Y(L) = U(L)*COSGAM - V(L)*SINGAM

Z(L) = U(L)*SINGAM + V(L)*COSGAM

U(L) = X(L)

V(L) = Y(L)

X(L) = U(L)*COSTH - V(L)*SINTH

Y(L) = U(L)*SINTH + V(L)*COSTH

U(L) = Y(L)

V(L) = Z(L)

Y(L) = U(L)*COSGAM + V(L)*SINGAM

Z(L) = -U(L)*SINGAM + V(L)*COSGAM

U(L) = X(L)

V(L) = Y(L)

X(L) = U(L)*COSDEL + V(L)*SINDEL

```
Y(L) = -U(L)*SINDEL + V(L)*COSDEL
```

C

```
X(L) = X(L) + X(I)
```

```
Y(L) = Y(L) + Y(I)
```

```
Z(L) = Z(L) + Z(I)
```

```
10 CONTINUE
```

C

```
RETURN
```

```
END
```

LINE BCNLEN

CDC 6600 FTN V3.0-P296 OPT=1 72

```
SUBROUTINE BONLEN(X,Y,Z,N,BL)
```

```
DIMENSION X(50),Y(50),Z(50),BL(50,50)
```

```
DO 100 I=1,N
```

```
DO 100 J=1,N
```

```
BL(I,J)=SQRT((X(I)-X(J))**2+(Y(I)-Y(J))**2+(Z(I)-Z(J))**2)
```

```
100 BL(J,I)=BL(I,J)
```

```
RETURN
```

```
END
```

LINE MATCUT

CDC 6600 FTN V3.0-P296 OPT=1 72

```
SUBROUTINE MATOUT (A,N)
```

C
C
C
C
C
C

THIS SUBROUTINE PRINTS OUTS A(I,J) IN UP TO 12 COLUMNS ACROSS THE PAGE. IF N IS GREATER THAN 12, IT FIRST PRINTS A N X 12 ARRAY AND THEN A N X (N-12) ARRAY. IF N IS GREATER THAN 24 IT WILL PRINT TWO N X 12 ARRAYS FOLLOWED BY A N X (N-24) ARRAY, AND SO ON.

```
DIMENSION A(50,50)
```

```
K=0
```

```
1 L=K+1
```

```
K=K+12
```

```
K=MIN0(K,N)
```

```
WRITE (6,2) (I,I=L,K)
```

```
2 FORMAT (1H0,2X,12(7X,I2)//)
```

```
DO 3 I=1,N
```

```
3 WRITE (6,4) I,(A(I,J),J=L,K)
```

```
4 FORMAT (I4,2X,12F9.5)
```

```
IF (K .LT. N) GO TO 1
```

```
RETURN
```

```
END
```

CALL TMULT (THETAX,THETAY,THETCZ,THXYDZ)

C
C . EVALUATE PARTIAL DIFFERENTIALS
C

DO 118 I=1,NATS
DO 117 J=1,3
FX(I,J)=-THXYZ(1,J)
FY(I,J)=-THXYZ(2,J)
FZ(I,J)=-THXYZ(3,J)

117 CONTINUE

FX(I,4)=THDXYZ(1,1)*XO(I)+THDXYZ(1,2)*YO(I)+THDXYZ(1,3)*ZO(I)
FY(I,4)=THDXYZ(2,1)*XO(I)+THDXYZ(2,2)*YO(I)+THDXYZ(2,3)*ZO(I)
FZ(I,4)=THDXYZ(3,1)*XO(I)+THDXYZ(3,2)*YO(I)+THDXYZ(3,3)*ZO(I)
FX(I,5)=THXDYZ(1,1)*XO(I)+THXDYZ(1,2)*YO(I)+THXDYZ(1,3)*ZO(I)
FY(I,5)=THXDYZ(2,1)*XO(I)+THXDYZ(2,2)*YO(I)+THXDYZ(2,3)*ZO(I)
FZ(I,5)=THXDYZ(3,1)*XO(I)+THXDYZ(3,2)*YO(I)+THXDYZ(3,3)*ZO(I)
FX(I,6)=THXYDZ(1,1)*XO(I)+THXYDZ(1,2)*YO(I)+THXYDZ(1,3)*ZO(I)
FY(I,6)=THXYDZ(2,1)*XO(I)+THXYDZ(2,2)*YO(I)+THXYDZ(2,3)*ZO(I)
FZ(I,6)=THXYDZ(3,1)*XO(I)+THXYDZ(3,2)*YO(I)+THXYDZ(3,3)*ZO(I)

C
C EVALUATE S(J) AND A(J,K) AND THEN INVERT MATRIX A. HENCE CALCULATE
C DEL(J) AND REFINED VALUES OF THE PARAMETERS C(J).
C

DO 118 J=1,6
S(J)=S(J)+(XR(I)-X(I))*FX(I,J)+(YR(I)-Y(I))*FY(I,J)+(ZR(I)-Z(I))*
1FZ(I,J)

DO 118 K=1,6

A(J,K)=A(J,K)-FX(I,J)*FX(I,K)-FY(I,J)*FY(I,K)-FZ(I,J)*FZ(I,K)

118 CONTINUE

CALL MATINV (A,6,6,INDEX)

IF (INDEX.EQ.1) GO TO 124

DO 119 K=1,6

DEL(K)=0.0

DO 119 L=1,6

119 DEL(K)=DEL(K)+A(K,L)*S(L)

DO 120 J=1,3

K=J+3

C(J)=C(J)-DEL(J)

CR(K)=CR(K)-DEL(K)

C(K)=(180.0*CR(K))/3.141592654

N=C(K)/360.0

PN=N

C(K)=C(K)-PN*360.0

IF(ABS(C(J)).LT.1.0E-4) C(J)=0.0

IF(ABS(C(K)).LT.1.0E-2) C(K)=0.0

120 CONTINUE

ITER=ITER+1

EOLD=E

GO TO 109

124 WRITE (6,125)

125 FORMAT (//10X,21HMATRIX DID NOT INVERT)

GO TO 130

126 WRITE (6,127)

127 FORMAT(//40X,29HTHE CALCULATION HAS CONVERGED//)

GO TO 130

```

C
C      OBTAIN TRIPLE PRODUCT MATRIX THXYZ
C
C      CALL TMMULT (THETAX,THETAY,THETAZ,THXYZ)
C
C      E=0.0
C      DO 112 I=1,NATS
C
C      TRANSLATION OF THE ORIGIN
C
C      XO(I)=XP(I)-C(1)
C      YO(I)=YP(I)-C(2)
C      ZO(I)=ZP(I)-C(3)
C
C      EVALUATE NEW COORDS AND THE SUM OF THE DEVIATIONS
C
C      X(I)=THXYZ(1,1)*XO(I)+THXYZ(1,2)*YO(I)+THXYZ(1,3)*ZO(I)
C      Y(I)=THXYZ(2,1)*XO(I)+THXYZ(2,2)*YO(I)+THXYZ(2,3)*ZO(I)
C      Z(I)=THXYZ(3,1)*XO(I)+THXYZ(3,2)*YO(I)+THXYZ(3,3)*ZO(I)
C      D2(I)=(XR(I)-X(I))**2+(YR(I)-Y(I))**2+(ZR(I)-Z(I))**2
C      E=E+D2(I)
112 CONTINUE
C      IF(ITER.NE.0) GO TO 211
C      WRITE (6,210)
210 FORMAT (10H0ITERATION,35X,10HPARAMETERS/3H0MC,8X,1HX,14X,1HY,14X,1
1HZ,15X,7HTHETA-X,8X,7HTHETA-Y,8X,7HTHETA-Z,12X,12HSUM OF DISPS)
211 WRITE (6,212) ITER,(C(I),I=1,6),E
212 FORMAT (I3,3(F12.5,3X),6X,3(F10.3,5X),5X,F10.5)
C      IF(ABS(E-EOLD).LT.5.0E-6) GO TO 126
C      IF(ITER.EC.NITS) GO TO 128
C
C      SET UP MATRICES OF DIFFERENTIALS
C
C      DO 114 I=1,3
C      DO 114 J=1,3
C      THETDX(I,J)=0.0
C      THETDY(I,J)=0.0
114 THETDZ(I,J)=0.0
C      THETOX(2,2)=-SINC(4)
C      THETOX(2,3)=-COSC(4)
C      THETOX(3,2)= COSC(4)
C      THETOX(3,3)=-SINC(4)
C
C      THETDY(1,1)=-SINC(5)
C      THETDY(1,3)= COSC(5)
C      THETDY(3,1)=-COSC(5)
C      THETDY(3,3)=-SINC(5)
C
C      THETDZ(1,1)=-SINC(6)
C      THETDZ(1,2)=-COSC(6)
C      THETDZ(2,1)= COSC(6)
C      THETDZ(2,2)=-SINC(6)
C
C      CALL TMMULT (THETOX,THETAY,THETAZ,THDXYZ)
C      CALL TMMULT (THETAX,THETDY,THETAZ,THDCYZ)

```

CALL TPKULT (THETAX,THETAY,THETCZ,THXYDZ)

C
C . EVALUATE PARTIAL DIFFERENTIALS
C

DO 116 I=1,NATS
DO 117 J=1,3
FX(I,J)=-THXYZ(1,J)
FY(I,J)=-THXYZ(2,J)
FZ(I,J)=-THXYZ(3,J)

117 CONTINUE

FX(I,4)=THDXYZ(1,1)*XO(I)+THDXYZ(1,2)*YO(I)+THDXYZ(1,3)*ZO(I)
FY(I,4)=THDXYZ(2,1)*XO(I)+THDXYZ(2,2)*YO(I)+THDXYZ(2,3)*ZO(I)
FZ(I,4)=THDXYZ(3,1)*XO(I)+THDXYZ(3,2)*YO(I)+THDXYZ(3,3)*ZO(I)
FX(I,5)=THXDYZ(1,1)*XO(I)+THXDYZ(1,2)*YO(I)+THXDYZ(1,3)*ZO(I)
FY(I,5)=THXDYZ(2,1)*XO(I)+THXDYZ(2,2)*YO(I)+THXDYZ(2,3)*ZO(I)
FZ(I,5)=THXDYZ(3,1)*XO(I)+THXDYZ(3,2)*YO(I)+THXDYZ(3,3)*ZO(I)
FX(I,6)=THXYDZ(1,1)*XO(I)+THXYDZ(1,2)*YO(I)+THXYDZ(1,3)*ZO(I)
FY(I,6)=THXYDZ(2,1)*XO(I)+THXYDZ(2,2)*YO(I)+THXYDZ(2,3)*ZO(I)
FZ(I,6)=THXYDZ(3,1)*XO(I)+THXYDZ(3,2)*YO(I)+THXYDZ(3,3)*ZO(I)

C
C EVALUATE S(J) AND A(J,K) AND THEN INVERT MATRIX A. HENCE CALCULATE
C DEL(J) AND REFINED VALUES OF THE PARAMETERS C(J).
C

DO 118 J=1,6
S(J)=S(J)+(XR(I)-X(I))*FX(I,J)+(YR(I)-Y(I))*FY(I,J)+(ZR(I)-Z(I))*
1 FZ(I,J)

DO 118 K=1,6
A(J,K)=A(J,K)-FX(I,J)*FX(I,K)-FY(I,J)*FY(I,K)-FZ(I,J)*FZ(I,K)

118 CONTINUE

CALL MATINV (A,6,6,INDEX)

IF (INDEX.EQ.1) GO TO 124

DO 119 K=1,6

DEL(K)=0.0

DO 119 L=1,6

119 DEL(K)=DEL(K)+A(K,L)*S(L)

DO 120 J=1,3

K=J+3

C(J)=C(J)-DEL(J)

CR(K)=CR(K)-DEL(K)

C(K)=(180.0*CR(K))/3.141592654

N=C(K)/360.0

PN=N

C(K)=C(K)-PN*360.0

IF(ABS(C(J)).LT.1.0E-4) C(J)=0.0

IF(ABS(C(K)).LT.1.0E-2) C(K)=0.0

120 CONTINUE

ITER=ITER+1

EOLD=E

GO TO 109

124 WRITE (6,125)

125 FORMAT (//10X,21HMATRIX DID NOT INVERT)

GO TO 130

126 WRITE (6,127)

127 FORMAT (//40X,29HTHE CALCULATION HAS CONVERGED//)

GO TO 130


```

128 WRITE (6,129)
129 FORMAT(/40X,32HMAX NUMBER OF ITERATIONS REACHED/)
130 WRITE (6,131)(I,X(I),Y(I),Z(I),D2(I),I=1,NATS)
131 FORMAT(10X,21HNEW CCCPCS OF PROELOT/1H0,5X,4HATOM,8X,4HX(I),8X,4H
1Y(I),8X,4HZ(I),16X,5HD2(I)/(5X,13,5X,3(2X,F10.6),10X,F10.6))
RETURN
END

```

INE MATINV

CDC 6600 FTN V3.0-P296 OPT=1 72

```

SUBROUTINE MATINV (A,M,N,INDEX)

```

```

SUBROUTINE FOR INVERTING MATRIX WHOSE DIMENSICNS ARE M X N.
-----

```

```

TAKEN FROM WIBERG PAGE 45.

```

```

INDEX IS SET = 1 IF A DIVIDE CHECK ERROR OCCURS. INDEX IS 0
OTHERWISE.

```

```

DIMENSION A(6,6),B(6)

```

```

INDEX = 0

```

```

M1 = M - 1

```

```

N1 = N - 1

```

```

N2 = 0

```

```

DO 5 L=1,M

```

```

N2 = N2 + 1

```

```

IF (A(1,1) .EQ. 0.0) GO TO 6

```

```

B(N) = 1.0/A(1,1)

```

```

DO 3 K=1,N1

```

```

3 B(K) = A(1,K+1)*B(N)

```

```

DO 4 I=1,M1

```

```

A(I,N) = -B(N)*A(I+1,1)

```

```

DO 4 J=1,N1

```

```

4 A(I,J) = A(I+1,J+1) - B(J)*A(I+1,1)

```

```

DO 5 J=1,N

```

```

5 A(M,J) = B(J)

```

```

GO TO 8

```

```

6 WRITE (6,7) N2

```

```

7 FORMAT (2CHODIVIDE CHECK, RCH =,12)

```

```

INDEX = 1

```

```

8 RETURN

```

```

END

```

C
C
C

SUBROUTINE TMMULT (A,B,C,D)

MULTIPLYING MATRIX A BY B BY C TO GIVE D. DIMENSIONS 3 X 3.

DIMENSION A(3,3),B(3,3),C(3,3),D(3,3),P(3,3)

DO 10 I=1,3

DO 10 J=1,3

P(I,J)=0.0

DO 10 K=1,3

10 P(I,J)=P(I,J)+B(I,K)*C(K,J)

DO 20 I=1,3

DO 20 J=1,3

D(I,J)=0.0

DO 20 K=1,3

20 D(I,J)=D(I,J)+A(I,K)*P(K,J)

RETURN

END