It is evident from Table XI that the fragmentation of lower A.P. gives the more abundant metastable. In the cases where the $M^+ - Br$ metastable is prominent, the A.P. of the other "characteristic fragment" (although unmeasurable in most cases) would be expected to be high (see Table I). In *p*-bromoethylbenzene (**20**), where the two fragmentations have similar appearance potentials, there is effective competition. It is noteworthy that the A.P. of $M^+ - Br$ in *p*-bromoethylbenzene (**20**) is considered less (10.80 eV) than that in bromobenzene itself (12.02 eV). This observation suggests that in the transition state for loss of a bromine radical from *p*-bromoethylbenzene, the benzene ring was partially or totally rearranged in such a manner that the structure of the $M^+ - Br$ species is probably a methyltropylium ion.[29]

Similarly, in *p*-bromophenol the two metastable ions are of comparable abundance and although the A.P. of the $M^+ - CO$ ion was not measurable because of interference of other peaks, it is quite feasible that this A.P. is close to that of the $M^+ - Br$ ion.[30]

Table XII further confirms our conclusions. Note that in *p*-chloroaniline (**31**) the two characteristic "metastable peaks" are of almost equal intensity and the two appearance potentials are only 0.13 eV apart.

In the spectra of all the *para*-substituted acetophenones measured, the $M^+ - CH_3$ metastables were the only ones observable from M^+ and in all cases the $M^+ - CH_3$ daughter ions had low appearance potentials (see Table VII). In all spectra measured, relative metastable abundances were independent of electron volts.

In conclusion, it may be stated that this treatment of the spectra of *para*-disubstituted benzenes may, in principle, be extended to those of *meta*-disubstituted benzenes, heteroaromatics, and polynuclear aromatics.

(29) See also P. N. Rylander, S. Meyerson, and H. M. Grubb, *J. Am. Chem. Soc.*, **79**, 842 (1957).

(30) The appearance potentials of $M^+ - Br$ in bromobenzene and $M^+ - CO$ in phenol are 12.02 and 11.67 eV, respectively.

Experimental Section

All relative ion abundances were determined using an AEI MS 9 mass spectrometer operating at a source temperature of 160–170° and with the slits set for a resolving power of approximately 2000 (10% valley definition). The source temperature, electron beam energy, accelerator protential (8 kV), and repeller potential remained constant within each run of a series of compounds. Samples were introduced through a heated inlet system.

Ionization and appearance potentials were determined by the semilogarithmic plot method.[31]

The relative (but not absolute) values of the I.P.'s and A.P.s. are estimated to be accurate within ±0.2 eV.

The solutions to the integrals for $[A^+]/[M^+]$ ratios were computed by the Titan (prototype Atlas 2) computer, University Mathematical Laboratory, Cambridge, using a six-point gauss quadrature, available as a Library routine for numerical integration. Dividing each of the integrals into three parts achieved an accuracy of 1%. Evaluation of the $[m^*]$ integrals required division of the integral into 0.1-eV segments. Peak areas were measured in the determination of observed $[m^*]/[M^+]$ ratios.

Acknowledgments. The award of a Junior Research Fellowship (to I. H.) at Churchill College, Cambridge, is gratefully acknowledged.

(31) F. P. Lossing, A. W. Tickner, and W. A. Bryce, *J. Chem. Phys.*, **19**, 1254 (1951).

Application of the Principle of Least Motion to Organic Reactions. A Generalized Approach

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Abstract: The application of the principle of least motion to organic reactions has been facilitated by a generalized method of calculation. The results of calculations for β eliminations, acetylene formation, enolization, 1,2-hydride shifts, pseudorotation, and the thermal cyclization of butadiene are in accord with experimental observation.

The *principle of least motion*, as put forward by Rice and Teller,[1] states that *those elementary reactions will be favored that involve the least change in atomic position and electronic configuration.* The applicability of this principle to the reactions of resonance-stabilized species,[2a] and to the stereochemistry of eliminations[2b] has been shown by Hine. Recently Miller[2c] critically reviewed the principle and suggested that it be renamed as a hypothesis. It can best be applied to systems where other factors remain essentially constant, and, because of its simplicity, can be used generally, provided the results are assessed critically.[2c]

The object of the present paper is to outline a more general method of calculation than that used previously,[2b] and to give examples of calculations that have been carried out for a variety of systems. Criticism can be leveled at the approach in that atoms which are not common to both reactant and product are ignored.[2b,3] Clearly this could lead to serious error where the atoms ignored constitute a complex grouping. For this reason the approach would seem to be best applied to molecular rearrangements where the constituent atoms remain constant. Calculations carried out for elimina-

(1) F. O. Rice and E. Teller, *J. Chem. Phys.*, **6**, 489 (1938); **7**, 199 (1939).

(2) (a) J. Hine, *J. Org. Chem.*, 31, 1236 (1966); (b) *J. Amer. Chem. Soc.*, **88**, 5525 (1966); (c) S. I. Miller, *Advan. Phys. Org. Chem.*, **6**, 185 (1968).

(3) This point was raised by one of the referees.

tions and enolization essentially only ignore a small number of atoms, and should not be in serious error if the energy of transference of these atoms is basically constant for the various conformations considered.

The approach to be outlined below is a generalization of that utilized by Hine in his treatment of eliminations.[2b] The underlying assumption is that a reaction occurs in such a way as to involve a minimum expenditure of energy in changing the positions of the atoms in the reactant to their corresponding positions in the product. If the stretching and bending of bonds essentially obey Hooke's law, the energy required to stretch or bend a bond is proportional to the square of the distance stretched or bent. Thus, following Hine,[2b] it will be assumed that reaction takes place such that the sum of the squares of the atomic displacements is a minimum.

Method of Calculation

Suppose that the coordinates of the n atoms of the reactant molecule are (x_i^R, y_i^R, z_i^R), and that the coordinates of the corresponding atoms in the product are (x_i^P, y_i^P, z_i^P), where only those atoms common to both reactant and product are considered. It is required to transform this latter set into some set (x_i, y_i, z_i)

$$E = \sum_{i=1}^{n} D_i^2 = \sum_{i=1}^{n} (x_i^R - x_i)^2 + (y_i^R - y_i)^2 + (z_i^R - z_i)^2 \quad (1)$$

such that eq 1 has a minimum value. The most general transformation of (x_i^P, y_i^P, z_i^P) to (x_i, y_i, z_i) which retains the same relative geometry within the molecule is firstly a translation of the origin of the first set (product coordinates) to a point $(-x, -y, -z)$, followed by rotation about the X, Y, and Z axes by angles θ_x, θ_y, and θ_z, respectively.

The condition that E now be a minimum is that $\partial E/\partial C_j = 0$ $(j = 1, \cdots 6)$, where $C_1 = x$, $C_2 = y$, $C_3 = z$, $C_4 = \theta_x$, $C_5 = \theta_y$, and $C_6 = \theta_z$. Differentiation of eq 1 with respect to C_j gives

$$\frac{\partial E}{\partial C_j} = -2\sum_{i=1} (x_i^R - x_i)\frac{\partial x_i}{\partial C_j} + (y_i^R - y_i)\frac{\partial y_i}{\partial C_j} + (z_i^R - z_i)\frac{\partial z_i}{\partial C_j} \quad (j = 1, \cdots 6) \quad (2)$$

Unless the set (x_i, y_i, z_i) represents the "best" values, that is it is calculated using the "best" values of the parameters C_j, then the summation will not be zero, but will have some value S_j. Hence

$$S_j = \sum_{i=1}^{n} (x_i^R - x_i)Fx_j^i + (y_i^R - y_i)Fy_j^i + (z_i^R - z_i)Fz_j^i \quad (j = 1, \cdots 6) \quad (3)$$

where $Fx_j^i = \partial x_i/\partial C_j$, $Fy_j^i = \partial y_i/\partial C_j$, and $Fz_j^i = \partial z_i/\partial C_j$.

Since S_j should be zero, the error in S_j is S_j itself, and it can be expressed in terms of the errors in the parameters C_j, *i.e.*, ΔC_l. Thus

$$S_j = \sum_{l=1}^{6} \frac{\partial S_j}{\partial C_l}\Delta C_j \qquad (j = 1, \cdots 6) \quad (4)$$

Differentiation of eq 3 with respect to C_l followed by substitution in eq 4 gives

$$S_j = \sum_{l=1}^{6}\left(\sum_{i=1}^{n} (x_i^R - x_i)\frac{\partial Fx_j^i}{\partial C_j} + (y_i^R - y_i)\frac{\partial Fy_j^i}{\partial C_l} + (z_i^R - z_i)\frac{\partial Fz_j^i}{\partial C_l} - Fx_l^iFx_j^i - Fy_l^iFy_j^i - Fz_l^iFz_j^i\right)\Delta C_l \quad (5)$$

$$(j = 1, \cdots 6)$$

If the first three terms of eq 5, which involve second-order differentials, are small when compared to the second three terms, and A_{lj} is the summation of these latter terms from $i = 1, \cdots n$, then eq 5 can be written

$$\mathbf{S} = \mathbf{A}\cdot\Delta\mathbf{C} \quad (6)$$

where $\mathbf{S}$ is the column vector (S_j), $\mathbf{A}$ is the 6×6 matrix (A_{lj}), and $\Delta\mathbf{C}$ is the column vector (ΔC_l). Multiplying both sides of eq 6 by the inverse matrix of $\mathbf{A}$ gives

$$\mathbf{A}^{-1}\cdot\mathbf{S} = \Delta\mathbf{C} \quad (7)$$

Thus if the inverse matrix $\mathbf{A}^{-1}$ can be computed, the estimated errors $\Delta\mathbf{C}$ can also be found and thus the values of C_l improved by a series of iterations.

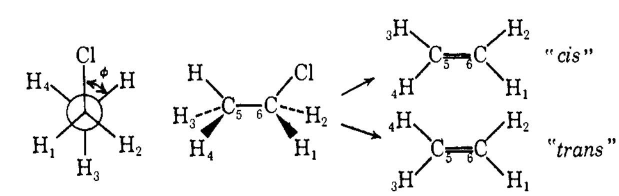
A computer program[4] was written on the basis of the above treatment. More of the mathematics used in the computation are given in the Appendix.

Results and Discussion

The program was first used to repeat and extend the previous calculations[2b] on the stereochemistry of eliminations. Subsequent calculations were carried out on simple systems which have some similarities to eliminations, and the most recent work involves a consideration of various molecular rearrangements.

Eliminations. Calculations were carried out on the synchronous elimination of hydrogen chloride from ethyl chloride for various dihedral angles between the two leaving groups. The geometries of the reactant and product molecules were calculated from the same molecular parameters as used earlier.[2b]

Strictly speaking it is possible to obtain two products from the elimination, one "*cis*," and the other "*trans*."[5] Both could conceivably result from a variety of rotational isomers of the ethyl chloride. Therefore the



minimum sum of the squares of the atomic displacements E_{min} leading from the reactant to both products was calculated for different values of the dihedral angle ϕ. The results are set out in Table I and plotted in Figure 1.

In his first article[2a] Hine showed that differences in E_{min} as small as 0.02 Å^2 could explain differences in ac-

(4) Details of the program LESMOT written in Fortran IV can be obtained from the author.

(5) This distinction can be made in the calculation since the hydrogens of the reactant and product molecules are specifically labeled. Hine's calculations[2b] for dihedral angles 0 and 60° gave a "*cis*" product, and those for 120 and 180° gave a "*trans*" product. In the present work the formation of both "isomers" for various dihedral angles was considered for the sake of completeness.

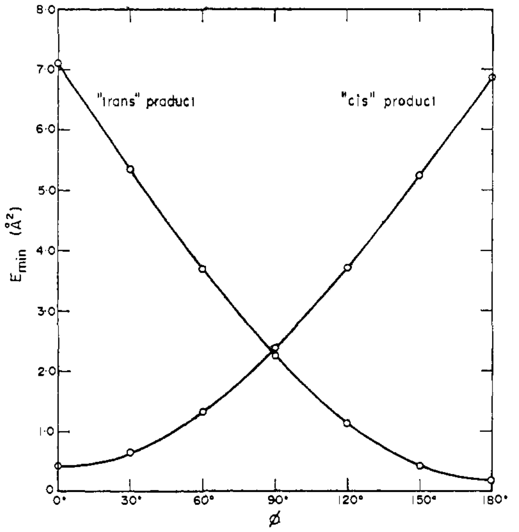


Figure 1. Variation of E_{min} with dihedral angle ϕ for the elimination of HCl from ethyl chloride.

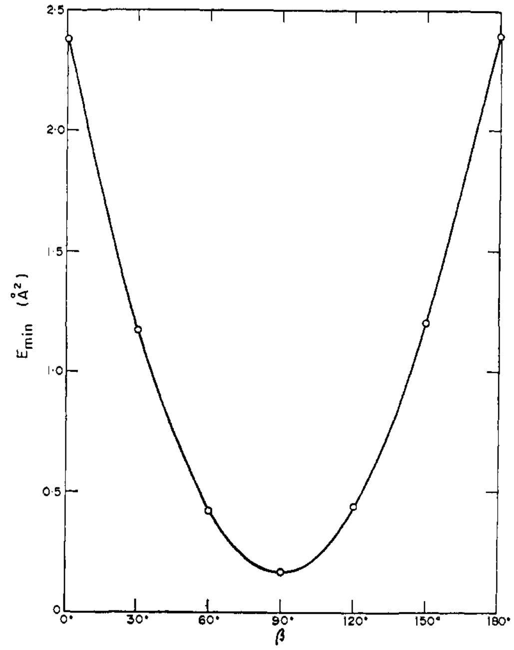


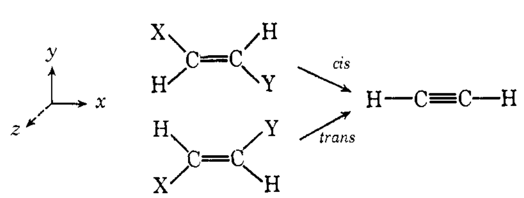
Figure 2. Variation of E_{min} with dihedral angle β for the enolization of acetaldehyde.

tivation energy of the order of 1 kcal/mol. The large differences in the data of Table I suggest, therefore, that formation of the "*cis*" product is only really feasible for small dihedral angles ϕ, and that formation of the "*trans*" product is favorable only for dihedral angles close to 180°. As from the previous work,[2b] it is predicted that a pure *trans* elimination (ϕ = 180°, E_{min} = 0.1851 Å^2) should be distinctly preferable to a pure *cis* elimination (ϕ = 0°, E_{min} = 0.4211 Å^2). In the case of elimination from molecules considerably more complex than ethyl chloride, and for which the conformational requirements are much more stringent, a reversed preference might well be observed. For $\phi \leqslant 150°$ a *trans* elimination becomes less favorable than a pure *cis* elimination.

Table I. Variation of E_{min} with Dihedral Angle for β Eliminations

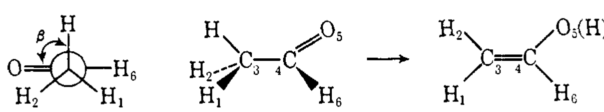
ϕ, deg	E_{min}, Å^2: "*cis*" Product	"*trans*" Product
0	0.4211	7.1124
30	0.6527	5.3628
60	1.3262	3.7013
90	2.3798	2.2546
120	3.7239	1.1344
150	5.2564	0.4268
180	6.8763	0.1851

Acetylene formation from simple olefins, which do not exhibit conformational isomerism, can occur by either a discrete *cis* elimination or a discrete *trans* elimination.



The geometries of the olefins were calculated assuming the same molecular parameters as for ethylene,[6] while that of acetylene was calculated using C≡C = 1.205 Å, and C—H = 1.059 Å.[7] For elimination from the *cis* olefin E_{min} = 1.2369 Å^2, and for that from the *trans* olefin E_{min} = 0.3200 Å^2. The considerably lower value of E_{min} for the *trans* elimination is in accord with known experimental facts for acetylene formation,[8] and with the previous prediction.[2b,9]

Enolization. The conformational preference of proton abstraction from the carbon α to a carbonyl group was studied using acetaldehyde as a model substrate. Its geometry was calculated from molecular parameters based on those of Wilson,[10] and that of its enol (enolate) was calculated using C—H = 1.09 Å, C=C = 1.34 Å, C=O = 1.35 Å,[7] assuming all bond angles to be 120°.



Values of E_{min} were obtained for various dihedral angles β between the leaving hydrogen and the carbonyl oxygen. The results, given in Table II and shown in Figure 2, clearly predict that enolization should be most facile for a rotamer having the hydrogen perpendicular to the trigonal plane (β = 90°).

Corey and Sneen[11] found that the 6-axial rather than the 6-equatorial hydrogen of 3β-acetoxycholestan-7-one was preferentially abstracted in enolization, and preferentially replaced in ketonization of the enol, even though steric factors would have been expected to dis-

(6) H. C. Allen, Jr., and E. K. Plyer, *J. Amer. Chem. Soc.*, **80**, 2673 (1958).
(7) "Tables of Interatomic Distances and Configuration in Molecules and Ions," Special Publications No. 11 and 18, The Chemical Society, London, 1958 and 1965.
(8) D. V. Banthorpe, "Elimination Reactions," Elsevier Publishing Co., New York, N. Y., 1963, pp 142–144.
(9) Hine[2b] argues that the values of E_{min} will be *cis* > *trans*, but does not quote any figures.
(10) R. W. Klib, C. C. Lin, and E. B. Wilson, Jr., *J. Chem. Phys.*, **26**, 1673 (1957).
(11) E. J. Corey and R. A. Sneen, *J. Amer. Chem. Soc.*, **78**, 6269 (1956).

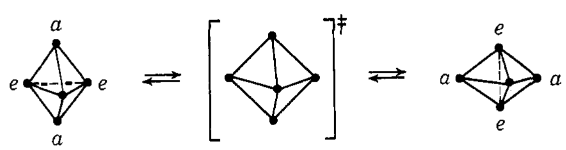
Table II. Variation of E_{min} with Dihedral Angle for Enolization

β, deg	E_{min}, Å^2
0	2.3824
30	1.1771
60	0.4202
90	0.1694
120	0.4399
150	1.2043
180	2.3948

courage axial attack. Their conclusion was that a major requirement of enolization (ketonization) is orbital overlap between the breaking (making) C_α–H bond and the C_α–C–O π system. Such overlap, of course, would be maximal if the α-hydrogen departed (approached) perpendicularly to the nodal plane of the π system. The present calculations point to a similar explanation and are consistent with the reported experimental results.

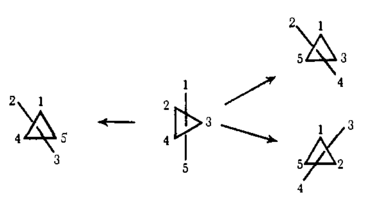
Molecular Rearrangements. An area in which the principle of least motion is possibly to be used most profitably is that of intramolecular rearrangements. In these reactions nothing is lost or gained by the system (other than energy), and so it is possible to take all atoms into account in the calculation. Moreover in such reactions the influence of external reagents or solvent molecules which may be present under the reaction conditions is expected to be much less important.

Pseudorotation. This is a very simple example of a molecular rearrangement and is defined for pentacovalent elements as the intramolecular process in which a trigonal bipyramid is transformed by deforming bond angles in such a way that it appears to have been rotated by 90° about one of the interatomic bonds.[12] Two atoms which were in equational positions become



axial, and conversely two atoms which were axial become equatorial.

For a compound of molecular formula AX_5 there are $5!/3!2! = 10$ pseudorotamers, each of which has an enantiomer, giving 20 species in all. Each of these species is directly related to three others by the process of pseudorotation, *e.g.*



A diagram for the complete pattern of interconversion of all 20 species can be drawn, and from this it can be seen that a minimum of five successive pseudorotations is necessary to interconvert enantiomers. Likewise, any two of the species can be interconverted by 5 or less pseudorotations.

Values of E_{min} were calculated for species which are interrelated by 1, 2, 3, 4, and 5 pseudorotations (ψ) as in Scheme I. Since in compounds of the type AX_5 it is often the case that the bonds to the axial atoms or groups are somewhat longer than those to the equatorial atoms or groups,[7] calculations were carried out for a hypothetical molecule having axial bonds of 1.10 Å, and equatorial bonds of 1.00 Å. The results are given in Table III, and clearly indicate that interconversion of I and II (Scheme I) should be more facile than the interconversion of I and any of the species III–IV. Thus the principle of least motion predicts that the easiest form of interconversion of species of the type AX_5 having a trigonal-bipyramidal structure is that which is known as pseudorotation.

Scheme I

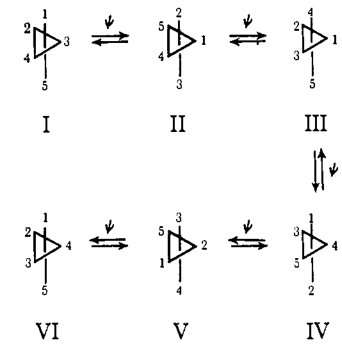
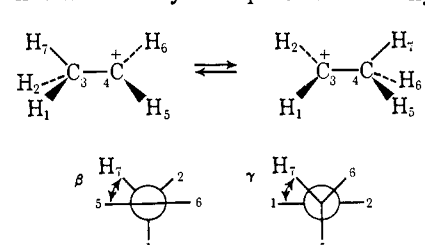


Table III. Values of E_{min} for Species AX_5 Interrelated by Successive Pseudorotations

Species–Species[a]	E_{min}, Å^2
I–II	1.2190
I–III	3.2165
I–IV	4.4200
I–V	5.2190
I–VI	5.9999

[a] Roman numerals refer to Scheme I.

1,2-Hydride Shift. The simplest example of this process is that which may take place in the ethyl cation.



For the sp^3 carbons tetrahedral symmetry was assumed with C–H bonds = 1.104 Å. The C–H bonds around the carbonium ion center were taken to be trigonally disposed with bond lengths = 1.086 Å. The C_{sp^3}–C_{sp^2} bond length was assumed to be 1.504 Å.[2a] Calculations were carried out for various dihedral angles β and γ between the migrating hydrogen (H_7) and the trigonal plane in the reactant and in the product, respectively. The results obtained *without including* the migrating H_7 in the calculation are shown in Table IV. For each value of β in the reactant E_{min} has its lowest value when

(12) (a) R. S. Berry, *J. Chem. Phys.*, **32**, 932 (1960); (b) F. H. Westheimer, *Accounts Chem. Res.*, **1**, 70 (1968); (c) E. L. Muetterties, *J. Amer. Chem. Soc.*, **91**, 4115 (1969).

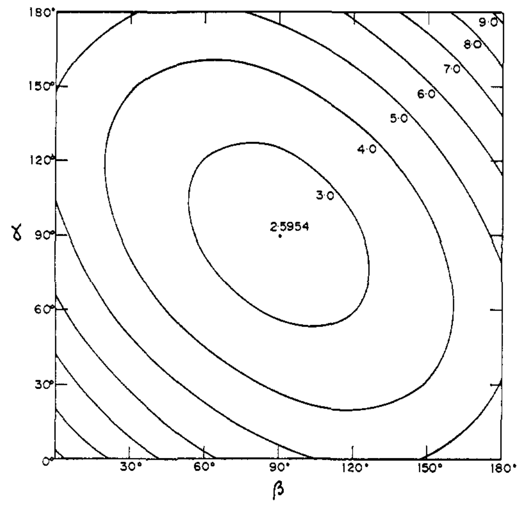


Figure 3. Variation of E_{min} with dihedral angles β (reactant) and γ (product) for a 1,2-hydride shift in the ethyl cation.

γ has the value $180° - \beta$. The over-all minimum of the results in Table IV occurs when both β and γ are 90°, that is, when the migrating hydride ion is perpendicular to the trigonal planes of both the reactant and the product.

Table IV. Values of E_{min} for the 1,2-Hydride Shift in Various Conformations of the Ethyl Cation, Migrating H^- Excluded[a]

	E_{min}, Å^2						
	γ, deg						
β, deg	0	30	60	90	120	150	180
0	6.9119	5.1757	3.5811	2.2321	1.2122	0.5836	0.3863
30	5.1757	3.5435	2.1619	1.1248	0.4970	0.3143	0.5863
60	3.5811	2.1619	1.0839	0.4244	0.2260	0.4970	1.2122
90	2.2321	1.1248	0.4244	0.1848	0.4244	1.1248	2.2321
120	1.2122	0.4970	0.2260	0.4244	0.0839	2.1619	3.5811
150	0.5836	0.3143	0.4970	1.1248	2.1619	3.5435	5.1757
180	0.3863	0.5836	1.2122	2.2321	3.5811	5.1757	6.9119

[a] Because of the symmetry of the reactant and the product it is not necessary to carry out all 49 calculations.

The results of calculations which *include* the migrating hydride ion are presented in Table V, and the surface

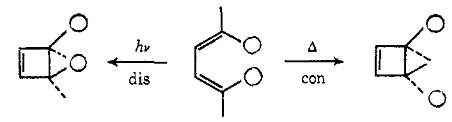
Table V. Values of E_{min} for the 1,2-Hydride Shift in Various Conformations of the Ethyl Cation, Migrating H^- Included[a]

	E_{min}, Å^2						
	γ, deg						
β, deg	0	30	60	90	120	150	180
0	9.2012	7.5311	6.1742	5.2668	4.8757	5.0185	5.6739
30	7.5311	5.8835	4.6050	3.8416	3.6604	4.0678	5.0185
60	6.1742	4.6050	3.4747	2.9156	2.9817	3.6604	3.8757
90	5.2668	3.8416	2.9156	2.5954	2.9156	3.8416	5.2668
120	4.8757	3.6604	2.9817	2.9156	3.4747	4.6050	6.1742
150	5.0185	4.0678	3.6604	3.8416	4.6050	5.8835	7.5311
180	5.6739	5.1085	4.8757	5.2668	6.1742	7.5311	9.2012

[a] See footnote *a*, Table IV.

that they describe is shown in Figure 3. The inclusion of the migrating moiety in the calculation considerably increases the values of E_{min}, but the increase is less for the cases where both β and γ approach 90°. The over-all effect is to favor even further that migration for the reactant having $\beta = 90°$ to give the product having $\gamma = 90°$. Thus the conclusion to be drawn from these calculations is the same as that which might be expected on electronic grounds, *i.e.*, that the hydride ion is most likely to migrate when it is perpendicular to the nodal plane of the vacant p_z orbital on the sp^2 carbon.[13]

Cyclization of Butadiene. The Woodward–Hoffmann rules[14] predict a conrotatory mode for the thermal cyclization of butadiene to cyclobutene, and a disrotatory mode for the photochemical process. Calculations using the known geometries[7] of butadiene and



cyclobutene gave the result that the conrotatory mode (E_{min} = 8.9308 Å^2) should be definitely favored over the disrotatory mode (E_{min} = 9.1911 Å^2). Since the calculation used ground-state geometries the result is pertinent to the thermal rather than the photochemical process. Consideration of the latter is hindered by the lack of knowledge of the geometries of the excited states of both the reactant and the product. The changes in geometry necessary to alter the preference to the disrotatory mode is currently under investigation, as also is the cyclization of butadiene to bicyclobutane.[15]

Conclusions

The application of the principle of least motion to the organic reactions considered in this paper leads to conclusions which are (a) in accord with experimental observation, and (b) similar to those arrived at on the basis of electronic arguments, *i.e.*, orbital overlap.

The agreement between the explanations based on the principle of least motion and those based on questions of orbital overlap might at first appear surprising and seem to be merely fortuitous. However, to argue that a particular reaction mode will be favored when the orbital overlap required to form the product is maximized along the reaction coordinate is to invoke implicitly the principle of least motion. Such arguments seek the easiest way to form the product in its most likely or familiar geometry from the known geometry of the reactant, and therefore as such are very close to the approach used above. However calculations of the type given here and by Hine[2] allow somewhat more quantitative judgements than can be made purely on *a priori* consideration of orbital overlap.

Any simple approach, such as that employed here, may be expected to break down when applied to more complex systems, *i.e.*, the predictions based on this approach are of a restrictive rather than a prohibitive nature. However a substantial part of the usefulness of this simple approach is that where it can be shown not to be applicable, other influences must be sought. These might be internal or external in origin, and might arise from steric effects, solvation requirements, reagent structure, and the like.

The calculations carried out so far have been based on simple unsubstituted systems, and conclusions drawn

(13) For an MO description of 1,2-hydride shifts see N. F. Phelan, H. H. Jaffé, and M. Orchin, *J. Chem. Educ.*, 44, 626 (1967).
(14) R. B. Woodward and R. Hoffmann, *J. Amer. Chem. Soc.*, 87, 395 (1965).
(15) (a) R. Srinivasan, *ibid.*, 85, 4045 (1963); (b) K. B. Wiberg and J. M. Lavanish, *ibid.*, 88, 5272 (1966); (c) K. B. Wiberg, *Tetrahedron*, 24, 1083 (1968).

from them may not be applicable to more highly substituted systems. However for substituents which do not exert large electronic or steric effects it is felt that the qualitative conclusions may be much the same. For example, the presence of methyl groups in molecules undergoing elimination probably would serve only to enhance the preference for the *trans* mode of elimination. Similarly it is not anticipated that the enolization of acetone would show a requirement much different from that found from the calculation on acetaldehyde. Such considerations are currently being tested by calculation on more highly substituted systems.

As emphasized above this type of calculation might most profitably be applied to molecular rearrangement and work in progress is concerned largely with such processes.

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Appendix

The transformation of the set $(x_i^{\mathrm{P}}, y_i^{\mathrm{P}}, z_i^{\mathrm{P}})$ into a new set (x_i, y_i, z_i) is carried out by means of four operations: translation of the origin to $(-x, -y, -z)$ and anticlockwise rotations about the X, Y, Z axes by angles θ_x, θ_y, θ_z. Combining the four operations

$$\begin{pmatrix} x_i \\ y_i \\ z_i \end{pmatrix} = \boldsymbol{\theta}_x\boldsymbol{\theta}_y\boldsymbol{\theta}_z\mathbf{Q}_i$$

where

$$\mathbf{Q}_i = \begin{pmatrix} x_i^{\mathrm{P}} - x \\ y_i^{\mathrm{P}} - y \\ z_i^{\mathrm{P}} - z \end{pmatrix}$$

and

$$\boldsymbol{\theta}_x = \begin{pmatrix} 1 & 0 & 0 \\ 0 & \cos\theta_x & -\sin\theta_x \\ 0 & \sin\theta_x & \cos\theta_x \end{pmatrix}$$

$$\boldsymbol{\theta}_y = \begin{pmatrix} \cos\theta_y & 0 & \sin\theta_y \\ 0 & 1 & 0 \\ -\sin\theta_y & 0 & \cos\theta_y \end{pmatrix}$$

$$\boldsymbol{\theta}_z = \begin{pmatrix} \cos\theta_z & -\sin\theta_z & 0 \\ \sin\theta_z & \cos\theta_z & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

The calculation also requires the differentials $\partial x_i/\partial C_j = Fx_j^i$, etc., where C_j are as defined in the text. It can be easily shown that

$$\mathbf{F}_1^i = \begin{pmatrix} Fx_i^i \\ Fy_i^i \\ Fz_i^i \end{pmatrix} = \boldsymbol{\theta}_x\boldsymbol{\theta}_y\boldsymbol{\theta}_z\begin{pmatrix} -1 \\ 0 \\ 0 \end{pmatrix}$$

$$\mathbf{F}_2^i = \boldsymbol{\theta}_x\boldsymbol{\theta}_y\boldsymbol{\theta}_z\begin{pmatrix} 0 \\ -1 \\ 0 \end{pmatrix}$$

$$\mathbf{F}_3^i = \boldsymbol{\theta}_x\boldsymbol{\theta}_y\boldsymbol{\theta}_z\begin{pmatrix} 0 \\ 0 \\ -1 \end{pmatrix}$$

$$\mathbf{F}_4^i = \boldsymbol{\theta}_x'\boldsymbol{\theta}_y\boldsymbol{\theta}_z\mathbf{Q}_i$$

$$\mathbf{F}_5^i = \boldsymbol{\theta}_x\boldsymbol{\theta}_y'\boldsymbol{\theta}_z\mathbf{Q}_i$$

$$\mathbf{F}_6^i = \boldsymbol{\theta}_x\boldsymbol{\theta}_y\boldsymbol{\theta}_z'\mathbf{Q}_i$$

where

$$\boldsymbol{\theta}_x' = \begin{pmatrix} 0 & 0 & 0 \\ 0 & -\sin\theta_x & -\cos\theta_x \\ 0 & \cos\theta_x & -\sin\theta_x \end{pmatrix}$$

$$\boldsymbol{\theta}_y' = \begin{pmatrix} -\sin\theta_y & 0 & \cos\theta_y \\ 0 & 0 & 0 \\ -\cos\theta_y & 0 & -\sin\theta_y \end{pmatrix}$$

and

$$\boldsymbol{\theta}_z' = \begin{pmatrix} -\sin\theta_z & -\cos\theta_z & 0 \\ \cos\theta_z & -\sin\theta_z & 0 \\ 0 & 0 & 0 \end{pmatrix}$$

On the basis of the treatment given in the text and using the mathematics above a computer program LESMOT was written.[4] Generally it converges quite rapidly, particularly for the displacements x, y, and z. It is less sensitive however to the angles of rotation particularly if they are converging on 90°, since in the latter case the differential rotational matrices ($\boldsymbol{\theta}_x'$, etc.) approach truncated identity matrices. Similarly if all the parameters are initially set at zero the program will register convergence since the translation vector is zero, and the rotation matrices are identity matrices.

The inclusion into the calculation of the terms involving second-order differentials (see eq 5) would require the evaluation of another 108 terms per atom, and would considerably complicate the computation. That these terms are not particularly important is evidenced by the ready convergence of calculations.