aromatic. If, for example, the nmr spectrum then does not show low-field protons, this concerns the first question, not the second.

Fewer experimental heats of atomization of conjugated hydrocarbons are available than one would like, but for those available we have shown that the simple HMO method gives as accurate results, and therefore as accurate predictions of aromaticity, as

Dewar's Pariser–Parr–Pople method. Note again that in this work we have not modified the Hückel method itself. We have used it in the familiar simple version, and have changed only the reference structure to accord with Dewar's definition of aromaticity. It remains to be seen how far this success of the simple Hückel method can be extended. Preliminary work on heterocycles is encouraging.

Application of the Principle of Least Motion to Organic Reactions. II.[1] Molecular Rearrangements

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Abstract: Calculations using the principle of least motion have been extended to cover a variety of molecular rearrangements: cyclopropyl-allyl, butadiene-cyclobutene, hexatriene-cyclohexadiene, cyclohexane-cyclohexane, Cope, methylcarbene-ethylene. Despite the assumptions inherent in the approach, there is remarkable concordance with experimental observations and the predictions of more sophisticated theoretical models. The relation between the predictions of the present approach and those arising from consideration of orbital symmetry is discussed.

In the previous paper[1] a generalized method of calculation using the principle of least motion (PLM) was outlined. This approach, which is an extension of that used previously by Hine,[3] was applied to a variety of systems in order to gain insight into the types of reactions to which it might be usefully applicable. The present paper outlines calculations carried out on several molecular rearrangements. Since the PLM approach neglects those atoms not common to the reactant and the product,[1,3] such reactions should be particularly amenable to study.

Concern has been expressed[4] because the calculations consider only the motions of nuclei explicitly. However, the electronic structures of the reactant and the product are implicit in their geometries. For instance, the choice of a planar geometry for ethylene with equilibrium bond lengths and bond angles implies that the electronic structure corresponds to that of the ground state. To require that the geometry of the reactant change smoothly to that of the product implies that their electronic structures interchange smoothly also. The conservation of orbital symmetry[5] also requires that electronic structure and molecular geometry change smoothly from reactant to product.

The understanding of the stereochemical courses of many rearrangements has been greatly enhanced by the invocation of orbital symmetry and, in particular, by the work of Woodward and Hoffmann.[5] However, not

all systems of interest can be treated by such an approach. In some instances there may not be suitable elements of symmetry present to enable the correlation of energy levels. In other cases, symmetry arguments may not be able to distinguish between two allowed processes having different stereochemical consequences. It is hoped that PLM calculations may prove to be of value in such cases.

Method of Calculation

The minimum sum of the squares of the atomic displacements (E_{min})[1] between reactant and product was calculated using the program LESMOT, the basis of which was described earlier.[1,6] For systems where many different conformers of the reactant and/or product were considered, a program LESMOT/2 was utilized which incorporates LESMOT as a subroutine and which evaluates the desired conformations from given initial geometries of the reactant and the product.

The geometries of the molecules studied were calculated[7] either from their published molecular parameters, or from estimates based upon suitable models.[8] The parameters used are listed in Table I.

(1) Part I: O. S. Tee, J. Amer. Chem. Soc., 91, 7144 (1969).
(2) (a) Author to whom correspondence should be addressed at Sir George Williams University; (b) University of Toronto.
(3) J. Hine, J. Amer. Chem. Soc., 88, 5525 (1966).
(4) In particular by one of the referees.
(5) R. B. Woodward and R. Hoffmann, "The Conversation of Orbital Symmetry," Academic Press, New York, N. Y., 1970, and references therein.
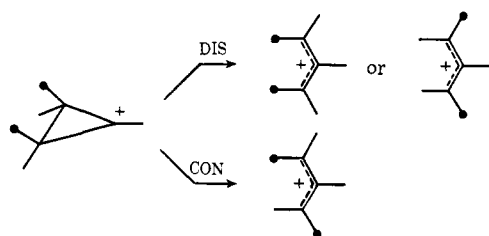
(6) The mathematical approach described earlier[1] is very similar to that used for least-squares fitting to nonlinear functions. See, for example: (a) J. B. Scarborough, "Numerical Analysis," John Hopkins Press, Baltimore, Md., 1958; (b) H. Kim, J. Chem. Educ., 47, 120 (1970); (c) N. R. Draper and H. Smith, "Applied Regression Analysis," Wiley, New York, N. Y., 1968, Chapter 10.
(7) Calculation was either by hand or using the program CORCAL (Quantum Chemistry Program Exchange, Indiana University, Bloomington, Ind., 1970, program no. 130).
(8) "Tables of Interatomic Distances and Configuration in Molecules and Ions," Chem. Soc., Spec. Publ., No. 11 (1958); No. 18 (1965).

Table I. Molecular Parameters Used for Calculation of Geometries

Molecule	Bond	Length, Å	Bond angles,[a] deg	Ref
Cyclohexane	C—C	1.54	te	e
	C—H	1.10		
1,5-Hexadiene	C—C	1.54	te, tr	e
	C=C	1.34		
	=C—C	1.50		
	=C—H	1.09		
	—C—H	1.10		
Cyclopropyl cation	As cyclopropane, except cationic site planar			f–h
Allyl cation	As in literature			g, h
Cyclopropyl X	As cyclopropane			f–h
Methylcarbene				
singlet	C—C	1.504[b]	te, 103	i, j
	C—H	1.12		
	(Me)C—H	1.104[b]		
triplet	C—C	1.46	te, 180	i, j, l
	C—H	1.06		
	(Me)C—H	1.104		
Ethylene				
ground state		As in literature		n
excited singlet	C—C	1.69[c]	tr, or te	i
	C—H	1.086	(see text)	m
excited triplet	C—C	1.58[c]	tr, or te	i
	C—H	1.086	(see text)	m
Butadiene		As in literature		n
Cyclobutene		As in literature		o
1,3,5-Hexatriene		As in literature		n
1,3-Cyclohexadiene		As in literature		p
twist–chair				
"boat" [d]	As in literature except angles 123 = 115°, 234 = 120°, 216 = 114° 50′			p

[a] te = tetrahedral; tr = trigonal. [b] Used previously[1,3] for the ethyl cation. [c] Suggested by calculation (see footnote i). [d] Assumed to have a plane of symmetry as shown in text illustration. Angles numbered as text illustration. [e] Reference 8. [f] O. Bastiansen, F. N. Fritsch, and K. Hedberg, *Acta Crystallogr.*, **17**, 538 (1964). [g] D. T. Clark and G. Smale, *Tetrahedron*, **25**, 13 (1969). [h] D. T. Clark and D. R. Armstrong, *Theor. Chim. Acta*, **13**, 365 (1969). [i] J. C. D. Brand and D. G. Williamson, *Advan. Phys. Org. Chem.*, **1**, 365 (1963). [j] A referee has drawn our attention to a recent paper by G. Herzberg and J. W. C. Johns [*J. Chem. Phys.*, **54**, 2276 (1971)] who, on the basis of new experimental data, suggest that triplet carbene may be nonlinear with a bond angle as low as 123°. We feel that PLM calculations for triplet methylcarbene taking this into account would give results very similar to those obtained for the singlet case.[k] [k] Originally the calculations involving singlet methylcarbene used a bond angle of 120° at the divalent carbon. At the request of a referee they were repeated using the experimental figure of 103°. This change, however, did not affect the conclusions in any way. [l] Cf. methylacetylene: C. C. Costain, *J. Chem. Phys.*, **29**, 864 (1958). [m] H. C. Allen, Jr., and E. L. Plyler, *J. Amer. Chem. Soc.*, **80**, 2673 (1958). [n] W. Haugen and M. Traetteberg, *Acta Chem. Scand.*, **20**, 1726 (1966). [o] B. Bak, J. J. Led, L. Nygaard, J. Rastrup-Andersen, and G. O. Sorensen, *J. Mol. Struct.*, **3**, 369 (1969). [p] C. DiLauro, N. Neto, and S. Califano, *ibid.*, **3**, 219 (1969).

Results and Discussion

Cyclopropyl–Allyl Transformations. Formally the opening of a cyclopropyl cation to produce an allyl cation can occur in either a disrotatory (DIS) or a conrotatory (CON) manner[5,9] and on the basis of sym-

metry arguments Woodward and Hoffmann predicted that the disrotatory process would be preferred.[5,9] This prediction is supported by both semiempirical[9–11] and *ab initio* calculations,[12] although the latter do not support the contention that the mode of ring opening is determined by the symmetry of the highest occupied orbital.[12]

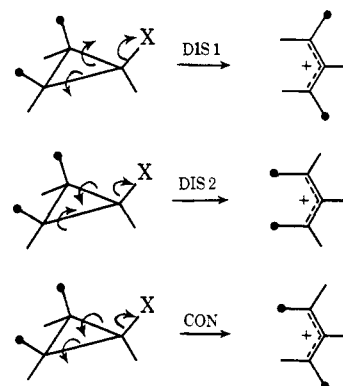(9) R. B. Woodward and R. Hoffmann, *J. Amer. Chem. Soc.*, **87**, 395 (1965).
(10) See Table I, footnote g.
(11) W. Kutzelnigg, *Tetrahedron Lett.*, 4965 (1967).
(12) See Table I, footnote h.

PLM calculations carried out on this system also favor the disrotatory mode (E_{min} = 7.05 Å²) over the conrotatory mode (E_{min} = 8.38 Å²).

If ring opening of the cyclopropyl system is concerted with loss of leaving group (*e.g.*, X), then two distinguish-

able disrotatory processes and one conrotatory process are possible. Semiempirical[9–11] and *ab initio*[12] calculations predict that the DIS2 process should be by far the most facile. The results of PLM calculations were

Mode	E_{min}, Å²
DIS2	5.35
DIS1	8.64
CON	8.38

Thus, PLM also predicts that the DIS2 process should be greatly favored. Moreover, it also predicts, as do more sophisticated calculations,[9-12] that the DIS1 and CON processes would proceed with similar difficulty.

From the recent experimental work of Schleyer and Saunders and others,[13] it is clear the opening of the cyclopropyl ring is concerted with loss of leaving group and is through the DIS2 mode. Moreover, the kinetics of the solvolyses of 1-chloroaziridines is consistent with a similar mode of ring cleavage.[14]

Butadiene–Cyclobutene Transformation. In the first paper of this series[1] results were presented of PLM calculations which favored a conrotatory over a disrotatory mode for the thermal cyclization of butadiene to cyclobutene, this being in agreement with the Woodward–Hoffmann rules and with experiment.[5] These calculations have now been repeated and extended using more recent literature geometries.[15,16] Values of E_{min} were calculated for various angles α corresponding to rotation about the central bond of butadiene. The results, in Table II, confirm the pref-

Table II. Variation of E_{min} with α for the Thermal Conversion of Butadiene to Cyclobutene
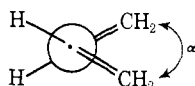
| α, deg | E_{min}, Å² | |
	DIS	CON
0	9.07	8.83
5	9.09	8.58
10	9.17	8.38
15	9.29	8.23
20	9.45	8.136
25	9.67	8.089
30	9.93	8.093
35		8.148
40		8.25
45		8.41
50		8.62
55		8.88
60		9.18

erence for the conrotatory process, and also suggest that reaction occurs most easily when the butadiene is twisted about the central bond by 25–30°. The disrotatory process, on the other hand, would prefer reaction from a completely planar precursor. These preferences are not surprising in view of the symmetry requirements of the two processes.

Recent theoretical[17] and experimental[18] studies favor nonplanar transition states for the conrotatory process. Semiempirical valence bond calculations by van der Lugt and Oosterhoff[17] suggest a value of 40° for α in the transition state, whereas experiments with phenyl-substituted dienes[18] having nonplanar ground states suggest a value of 45°.

(13) P. von R. Schleyer, T. M. Su, M. Saunders, and J. C. Rosenfeld, *J. Amer. Chem. Soc.*, **91**, 5174 (1969), and references therein.
(14) P. G. Gassman, D. K. Dygos, and J. E. Trent, *ibid.*, **92**, 2084 (1970).
(15) See Table I, footnote n.
(16) See Table I, footnote o.
(17) W. Th. A. M. van der Lugt and L. J. Oosterhoff, *J. Amer. Chem. Soc.*, **91**, 6042 (1969).
(18) G. A. Dooriakian, H. H. Freedman, R. F. Bryan, and H. P. Weber, *ibid.*, **92**, 399 (1970).

It should be noted that even though the present PLM results were obtained from geometries slightly different from those used earlier,[1,8] the value of E_{min} (for $\alpha = 0°$) are little changed: DIS, $-9.1911, 9.0693$ (difference $= 0.1218$); CON, $-8.9307, 8.8337$ (difference $= 0.0971$). Both changes are small and in the same direction, and thus do not alter the interpretation of the results.

1,3,5-Hexatriene–1,3-Cyclohexadiene Transformation. This transformation is the next higher homolog to that just discussed, and is predicted by orbital symmetry conservation to occur in a disrotatory manner in the

"twist-chair"
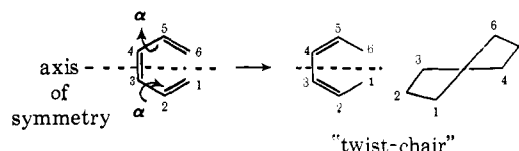
thermal process.[5] Initially PLM calculations were carried out using the known geometries of the reactant[15] and product[19] for various rotations about the 2,3 and 4,5 bonds of the triene, $\alpha = 0$ corresponding to an all-planar configuration of the triene. The results shown in columns 2 and 3 of Table III clearly favor a conrotatory

Table III. Variation of E_{min} with α for the Hexatriene–Cyclohexadiene Transformation

| α,[a] deg | E_{min}, Å² | | |
	CON[b]	DIS[b]	DIS[c]
0	5.90	9.24	9.02
5	4.84	8.50	8.05
10	4.01	7.97	7.15
15	3.40	7.65	6.31
20	3.013	7.54	5.63
25	2.859	7.64	4.90
30	2.934	7.95	4.35
35	3.23		3.91
40	3.76		3.60
45	4.49		3.421
50			3.395
55			3.53
60			3.83

[a] See illustrations for definition of α. [b] Product with axis of symmetry, *i.e.*, "twist-chair." [c] Product with plane of symmetry, *i.e.*, "boat."

process. However, 1,3-cyclohexadiene has a nonplanar "twist-chair" structure,[19] and since this has an axis of symmetry as shown, it is not surprising that PLM favors the conrotatory mode.

The disrotatory mode requires a plane of symmetry to be conserved during the reaction and so transformations leading to a "boat" form of the product were also con-

"boat"
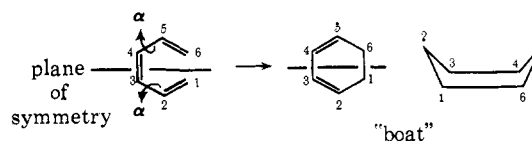
sidered for this mode. The variation of E_{min} with rotations are listed in column 4 of Table III, and it is seen that there is a significant improvement in the minimum value of E_{min} for the DIS process. However, comparing the minimum values for both processes, PLM still favors the conrotatory ($E_{min} = 2.859$; $\alpha =$

(19) See Table I, footnote p.

25°) over the disrotatory process (E_{min} = 3.395; α = 50°). This is the first example where the present type of PLM calculation has given an incorrect prediction.

Despite this failure the PLM results are informative and illustrate the power of orbital symmetry requirements. From the present results the disrotatory process involves more atomic motion and requires greater nonplanarity of the reactant triene which must lead to diminution of π overlap. Yet it is known experimentally that the thermal cyclization of hexatrienes is in accord with the Woodward–Hoffmann rules.[5] Thus, the requirements of orbital symmetry conservation are much more important than the disadvantages inherent in the disrotatory process.[20] It is also noteworthy that PLM and conservation of symmetry along the reaction coordinate both require that, in the DIS process, the cyclohexadiene be formed in an unfavorable "boat" form which, presumably, subsequently relaxes to the more stable "twist-chair" form.

Cyclohexane Interconversions. It is currently felt that the chair forms of cyclohexane do not interconvert directly but *via* the intermediacy of a twist form, and that the boat form represents the transition state between two twist forms.[21]

The results of PLM calculations carried out for the interconversions of various forms of cyclohexane are set out in Table IV. Initially the geometries were

Table IV. Values of E_{min} for Interconversions of Cyclohexane Conformers[a]

| Interconversion | E_{min}, Å² | | |
	A	B	C
Chair–chair	33.1	1.58	1.24
Chair–twist[b]	19.6	1.16	0.916
Chair–boat	19.5	1.16	0.914
Twist[b]–boat	3.56	0.242	0.185
Twist[b]–twist[c]		0.862	0.665

[a] Columns A, B, and C are as follows. A, calculations with all atoms considered: C–C bond, 1.54 Å; CH bond, 1.10 Å; all bond angles tetrahedral. B, as A but neglecting hydrogen atoms. C, neglecting H atoms and using C–C bond, 1.533 Å, C–C–C bond angle, 111.6° (*cf.* ref 21a). [b] The so-called "symmetrical twist" form (ref 21c). [c] Two twist forms related to a common boat form.

calculated using the molecular parameters in Table I, and including all carbon and hydrogen atoms. These geometries gave the results in column A of Table IV. Since the barriers separating the various conformers will largely result from distortion of carbon–carbon bond lengths and carbon–carbon–carbon bond angles, the motions of carbon atoms alone might predict the difficulty of the various interconversions. The results of calculations using only carbon atoms are shown in column B of Table IV and it can be seen that they completely parallel those in column A. Thus, exactly the same predictions could be made without including the hydrogen atoms. Column C of Table IV contains the results of calculations also using only the carbon atoms but which were obtained from geometries calculated

using more accurate molecular parameters:[21a] C–C bond length, 1.533 Å; C–C–C bond angle, 111.6°. Again completely parallel results were obtained emphasizing that the choice of molecular parameters is not critical.[22]

The results of Table IV predict that a direct chair–chair interconversion would be most difficult and that it is more likely that chairs interconvert *via* the intermediacy of a twist or boat conformer.[23] Similarly the twist–twist interconversion is predicted to be more difficult than the twist–boat interconversion suggesting that twist forms interconvert *via* a boat form. These predictions are in accord with currently held views.[21] Moreover, the numerical results are qualitatively in accord with current estimates[21a,b] of the energy differences between the various species, *i.e.*, the twist and boat differ little in energy, but both differ considerably in energy from the chair.

The Cope Rearrangement. This thermally allowed [3,3] sigmatropic shift[5] can conceivably take place through either a "chair" or "book" transition state.[24] PLM calculations were carried out for the degenerate rearrangement of 1,5-hexadiene proceeding through both types of transition states.

For reaction proceeding through a book-like transition state, rotamers of the reactant and product were generated from initially planar geometries by varying the dihedral angles γ illustrated below. The results of

book-like
transition state
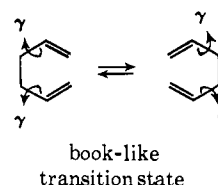
calculations carried out on the rotamers thus obtained are shown in Table V. The minimum value of E_{min} (1.989 Å²) occurs when $\gamma = 73°$.

Table V. Variation of E_{min} with Dihedral Angle γ for "Book"-Like Transition States in the Degenerate Cope Rearrangement of 1,5-Hexadiene

γ, deg	E_{min}, Å²	γ, deg	E_{min}, Å²
0	24.5	60	3.16
5	23.0	65	2.43
10	21.2	70	2.046
15	19.3	71	2.012
20	17.2	72	1.993
25	15.1	73	1.989
30	13.0	74	2.000
35	11.0	75	2.027
40	8.94	80	2.39
45	7.14	85	3.15
50	5.55	90	4.31
55	4.21		

(20) Hoffmann, *et al.*, have recently considered some systems where orbital symmetry requirements preclude the approach of reactants along the path of least motion: see R. Hoffmann, R. Gleiter, and F. B. Mallory, *J. Amer. Chem. Soc.*, **92**, 1460 (1970).

(21) (a) J. B. Hendrickson, *ibid.*, **89**, 7036, 7043, 7047 (1967); (b) H. M. Pickett and H. L. Strauss, *ibid.*, **92**, 7281 (1970); (c) J. D. Dunitz, *J. Chem. Educ.*, **47**, 488 (1970); (d) references cited in these papers.

(22) This we have found to be true in other systems, *e.g.*, butadiene-cyclobutene, and methylcarbene–ethylene (*vide infra*). It seems likely the preferences exhibited by PLM calculations are dependent more on molecular symmetry than on the particular numerical choice of bond lengths and bond angles.

(23) The results of Table IV do not exhibit a marked preference between the chair–twist and chair–boat conversions. J. B. Hendrickson [*J. Amer. Chem. Soc.*, **89**, 7047 (1967)] has calculated 11.0 kcal/mol for the chair–twist barrier and 11.3 kcal/mol for the chair–boat barrier.

(24) S. J. Rhoads in "Molecular Rearrangements," P. de Mayo, Ed., Vol. 1, Interscience, New York, N. Y., Chapter 11.

Table VI. Variation of E_{min} with Dihedral Angles and for Chair-Like Transition States in the Cope Rearrangement of 1,5-Hexadiene

| α, deg	E_{min}, Å²								
	β, deg								
	0	40	50	52.5	55	57.5	60	65	70
0	25.2								
40		8.96	9.78				12.8		
50		6.06	5.69				7.66		
55		5.15	4.23				5.69		
60		4.62	3.17				4.16		
65		4.46	2.53				3.06		
70		4.67	2.31		2.048		2.41	3.39	4.99
71				2.085	2.012	2.095			
72				2.086	1.994	2.057			
73				2.105	1.993	2.036			
74				2.141	2.010	2.034			
75		5.27	2.50		2.044		2.21	3.00	4.41
80		6.23	3.11		2.48		2.47	3.08	4.31
85			4.12		3.34		3.17	3.62	4.70

For chair-like transition states rotamers were generated by varying the dihedral angles α and β as illustrated below. The PLM results obtained for various

chair-like
transition state
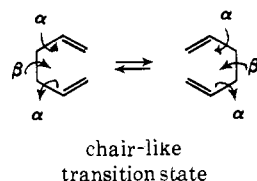
values of α and β are shown in Table VI, from which it is seen that the minimum value of E_{min} (1.993 Å²) occurs when $\alpha = 73°$, $\beta = 55°$.

The minimum values for each type of transition state are thus: book-like, $E_{min} = 1.989$ Å²; chair-like, $E_{min} = 1.993$ Å². The difference between these two values (0.004 Å²) is far too small for a preference to be indicated.

For both the Cope rearrangement and the Claisen rearrangement a chair-like transition state appears to be favored.[25] It has been argued that conformational factors and negative orbital overlap at the "spine" of the book tend to disfavor book-like transition states.[5,26] However, these are small secondary effects and may easily be overridden in molecules having special structural features.[24,26] For example, the nondegenerate conversions **1** → **2** and **3** → **4** are constrained to proceed
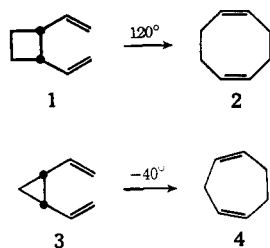
through book-like transition states by the cis relationship of the vinyl groups in **1** and **3**. However, **1** is converted to **2** easily, and **3** is so labile that it cannot be isolated.[24,27a] Many other examples involving cyclic structures are known.[24,27]

(25) See ref 205 on p 148 of Woodward and Hoffmann.[5]
(26) S. I. Miller, *Advan. Phys. Org. Chem.*, **6**, 185 (1968), and references therein.
(27) The facile degenerate isomerizations of bullvalene and related compounds must also have book-like transition states. See, for

Methylcarbene–Ethylene.[28] This system is one of which very little is known, and it is hoped that the following PLM results will be of predictive value.

The migration of a hydrogen of methylcarbene **5** to

5
singlet or
triplet?

ground state, excited
singlet or triplet?
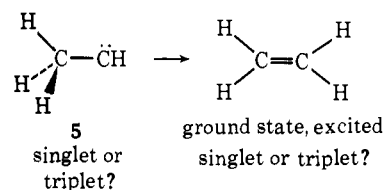
produce ethylene could conceivably occur in a variety of ways depending upon the electronic state of the reactant and the state in which the ethylene is produced. PLM calculations were carried out for various possible conversions and the results are summarized[29] in Table VII.

Table VII. Minimum Values of E_{min} for Conversions of Methylcarbene to Ethylene

States		Ethylene	Angles,[a]		E_{min},	Ref
Carbene	Ethylene	geometry[a]	β	γ	Å²	
Singlet	Ground	Regular	55		3.73	b
Singlet	Singlet	Type 6	0	90	3.22	c
Singlet	Singlet	Type 7	0	109	3.48	d
Triplet	Ground	Regular			4.86	e
Triplet	Triplet	Type 6		90	3.02	f
Triplet	Triplet	Type 7		92	3.44	g

[a] For illustrations of the geometry types **6** and **7** and for definition of the angles β and γ see text and illustrations. [b] Minimum from 27 calculations located by 1-deg increments. In all cases 4 decimal places are needed to distinguish the minima located by 1-deg increments. [c] Minimum from 49 calculations. Values of E_{min} for $\beta = 0°$ are symmetrically disposed about $\gamma = 90°$. [d] Minimum from 59 calculations located by 1-deg increments in γ. [e] Single calculation, since there are no conformation angles in product or reactant. [f] Minimum from seven calculations. Values of E_{min} are symmetrically disposed about $\gamma = 90°$. [g] Minimum from 22 calculations located by 1-deg increments.

example: (a) W. v. E. Doering and W. R. Roth, *Tetrahedron*, **19**, 715 (1963); (b) W. v. E. Doering and W. R. Roth, *Angew. Chem., Int. Ed. Engl.*, **2**, 115 (1963); (c) G. Schroder and J. F. M. Oth, *ibid.*, **6**, 414 (1967).
(28) The authors are grateful to Professor A. Nickon for suggesting this system to them. Experimental work in progress in his laboratory is aimed at the elucidation of the stereochemistry of carbene rearrangements.
(29) See Table I, footnote *k*.

Singlet carbene is nonlinear with a HCH bond angle of 103°,[30] although it has been considered as sp^2 hybridized with an electron pair in an sp^2 lobe, and a vacant p_z orbital.[31,32] Triplet carbene is probably linear[30] and can be thought of as sp hybridized with the unpaired electrons singly occupying the p_y and p_z orbitals.[31,32]

For the conversion of singlet methylcarbene to ground-state ethylene, values of E_{min} were calculated for various values of β, the dihedral angle between the migrating hydrogen (H_6) and the carbenic hydrogen (H_1). The minimum value of E_{min} was obtained with
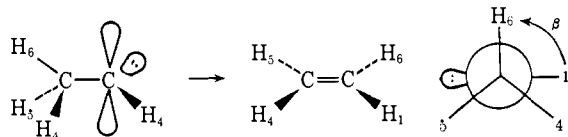
$\beta = 55°$. From an electronic viewpoint it might be anticipated that migration toward the vacant p_z orbital ($\beta = 90°$) or toward the sp^2 lone pair ($\beta = 180°$) would be preferable. However, from a PLM point of view it appears that the constraints arising from prescription of an all-planar product disfavor such migrations.

The structures of the excited singlet ($^1B_{1u}$) and triplet ($^3B_{1u}$) states of ethylene are not known since its electronic spectrum is too diffuse to be amenable to rigorous analysis.[30] Various theoretical calculations[30,33,34] favor nonplanar structures for these excited states and two basic possibilities have been considered: structure 6 in which trigonal CH_2 planes intersect at right angles

6   **7**
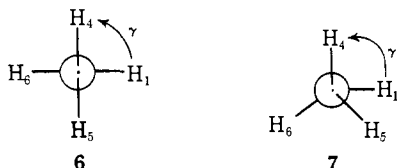
($\gamma = 90°$),[33] and structure 7 in which the configuration at each carbon is pyramidal and there is a twist ($\gamma = 90°$) about the C–C axis.[34] This latter structure qualitatively resembles the ground state of hydrazine.[30] Both types of structure, 6 and 7, were considered as potential products in the system under discussion, and in each case calculations were carried out for a variety of values of γ.

For the conversion of singlet methylcarbene to excited singlet ethylene of structure type **6** the minimum value of E_{min} results when $\beta = 0°$ and $\gamma = 90°$. That is, PLM predicts the preferential migration of a hydrogen (H_6) from a position *antiperiplanar* to the carbene lone pair as shown below.[35] Intuitively a syn-periplanar migration might have been predicted.[36] The

corresponding PLM calculations for conversion leading to excited singlet ethylene of structure type **7** also favor a basically antiperiplanar migration.

The conversion of triplet methylcarbene to ground-state ethylene is most unlikely since it requires a spin inversion, but its calculation was included for comparative purposes. For the conversion of triplet methylcarbene to triplet-state ethylene of structure types **6** and **7** the calculations favor formation of products with dihedral angles of $\gamma = 90$ and 92°, respectively.

Comparing the results of Table VII, the favored conversion of singlet (or triplet) methylcarbene is that leading to an excited state singlet (or triplet) of structure type **6** in which the trigonal CH_2 planes intersect at 90°.

The construction of correlation diagrams[5] using the symmetries of the reacting orbitals of the carbenes (singlet or triplet) and the ethylenes (ground state, singlet, or triplet) was considered as a means of predicting which conversions would be favored. Symmetry correlation is not possible for either carbene rearranging to ground-state ethylene since there are not equal numbers of orbitals of the same symmetry in the reactant and product. However, it does appear possible to construct diagrams for the conversions leading to the corresponding excited states (singlet or triplet) of ethylene. Thus, both PLM calculations and orbital symmetry requirements favor formation of the product ethylene in an excited state.

Experimentally, hydrogen migration is facile, in that it is competitive with insertion into double bonds, and it appears to occur from the singlet state.[37] However, at this time it is not known what the stereochemistry of the migration is, or in what state the olefin is initially produced.[28]

Conclusions

This paper has presented the results of PLM calculations for various systems capable of undergoing molecular rearrangement. Including two systems discussed earlier,[1] eight such reactions have been considered in all. Despite the theoretical naiveté of the PLM approach,[38] the results, with one exception, are in agree-

However, from consideration of the relation of the reactant to product in the configurations generating E_{min} for both modes the predicted preference appears quite reasonable. Similarly analysis of the values of E_{min} in terms of the individual atomic displacements[1] D_i assists rationalization of the indicated preference.

(30) See Table I, footnote *i*.
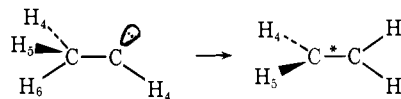(31) R. Hoffmann, G. D. Zeiss, and G. W. Van Dine, *J. Amer. Chem. Soc.*, **90**, 1485 (1968).
(32) R. Gleiter and R. Hoffmann, *ibid.*, **90**, 5457 (1968).
(33) R. S. Mulliken and C. C. J. Roothaan, *Chem. Rev.*, **41**, 219 (1947). For more recent work see: (a) U. Kaldor and I. Shavitt, *J. Chem. Phys.*, **48**, 191 (1968); (b) R. J. Buenker, *ibid.*, **48**, 1368 (1968).
(34) A. D. Walsh, *J. Chem. Soc.*, 2325 (1953). For more recent work see: (a) L. Burnell, *J. Chem. Phys.*, **43**, 529 (1965); (b) L. Burnell and C. Litt, *Mol. Phys.*, **9**, 433 (1965); (c) M. Barfield, *J. Chem. Phys.*, **47**, 3831 (1967).
(35) The asterisk in the illustration denotes an excited state of ethylene.
(36) At first glance it is not easy to see why migration anti-periplanar to the carbene lone pair is preferred over syn-periplanar migration.
(37) I. Moritani, Y. Yamamoto, and S.-I. Murahashi, *Tetrahedron Lett.*, 5697, 5755 (1968).
(38) Comments by referees prompt a restatement of the position underlying this and previous papers. As Hine has pointed out,[39] the principle of least motion is implicit in Eyring's approach to reaction rate theory[40] and explicit in ideas put forward by Dewar.[41] The so-called Hammond's postulate,[42] which is very similar to earlier remarks by Dewar,[43] also contains least-motion arguments in a fairly explicit form. It is anticipated, therefore, that the PLM approach currently being applied may prove to be at least of heuristic value even though it may break down from time to time.
Deviations from classical (Newtonian) mechanics become apparent at the atomic and molecular level requiring the invocation of quantum mechanics. The PLM approach used in this and previous papers[1,3] is essentially a classical argument and will, therefore, only operate in molecular systems when it is not in conflict with quantum mechanical requirements. Comparison of two potential reaction pathways using least-motion arguments may only be fruitful when the two pathways are subject to the same quantum mechanical restraints. Similar restrictions apply also to Hammond's postulate and to linear free-energy relationships, yet these approaches have proved very useful in the past.

ment with either experimental results or the predictions of more sophisticated models where available. The one system where the PLM prediction is incorrect is the electrocyclic interconversion of 1,3,5-hexatriene and 1,3-cyclohexadiene, where the least-motion pathway is proscribed by orbital symmetry requirements.[20]

In considering the relationship of the PLM approach to that based on the conservation of orbital symmetry[5] (COS) four particular types of situation can be visualized. In the first where, because of the lack of suitable elements of symmetry, the COS approach cannot be used the PLM approach seems to offer a useful alternative. The second situation is where both approaches are applicable and are in agreement. The third type of situation is where COS does not distinguish between two symmetry-allowed processes, but the PLM approach does, e.g., cyclopropyl X solvolyses. In the fourth type of situation there is disagreement between the predictions of the two approaches, but the requirements of COS outweigh those of PLM.[20]

A useful and interesting side product of PLM calculations is the insight they give into the atomic motions that are occurring during a reaction. From a consideration of the relative geometries of the reactant and product in the configuration where the value E_{min} is

generated,[1] it is apparent that many atoms probably undergo motion during reaction. In a migration, for instance, suitable motions by the rest of the molecular framework may help reduce the amount of motion undergone by the migrating moiety. For the case of an anti elimination from an olefin to produce an acetylene,[1] reactant and product geometries are related in such a way as to suggest that the acetylene will be produced with some rotational energy. For the corresponding syn elimination it appears that the acetylene produced will have some translational energy.

The results presented here also emphasize the degree of nonplanarity of the transition states involved in the electrocyclic transformations of butadiene and hexatriene, and in the Cope rearrangement.[44]

(39) J. Hine, *J. Org. Chem.*, 31, 1236 (1966).
(40) (a) A. Sherman and H. Eyring, *J. Amer. Chem. Soc.*, 54, 2661 (1932); (b) G. E. Kimball and H. Eyring, *ibid.*, 54, 3876 (1932).
(41) M. J. S. Dewar, "The Electronic Theory of Organic Chemistry," Oxford University Press, London, 1949, pp 104, 144.
(42) G. S. Hammond, *J. Amer. Chem. Soc.*, 77, 334 (1955).
(43) M. J. S. Dewar, *Discuss. Faraday Soc.*, 2, 261 (1947).

(44) Some of the systems considered in this and previous papers[1,3] involve reaction proceeding from different starting conformers but no account has been taken of differences in conformer energies.[45] As long as these differences are smaller than the difference in energy of the associated transition states the predictions of the PLM approach may still be valid. If, however, they are larger the predictions would not be invalid. It is not readily apparent how the approach might be modified to take account of these differences.
(45) This point was raised by a referee.

Dissociation Constants of 8-Substituted 9,10-Ethanoanthracene-1-carboxylic Acids and Related Compounds. Evidence for the Field Model for the Polar Effect[1]

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Abstract: Several 8-substituted 9,10-ethanoanthracene-1-, 8-substituted 9,10-dihydroanthracene-1-, and 8-substituted anthracene-1-carboxylic acids have been prepared. The dissociation constants for the acids have been measured in 50% aqueous ethanol. Many traditionally acid-strengthening dipolar substituents, for example, the fluoro, chloro, and cyano groups, exhibit the opposite influence in the bridged anthracenes. Empirical tests of the results reveal that steric and hydrogen bonding interactions play no important role in the determination of acid strength. The reversed substituent effects therefore indicate that dipolar substituent effects have an angular dependence in accord with an electrostatic field model for the polar effect.

Investigations designed to assess the relative merits of the through-bond induction model and the electrostatic field model for the polar effect[3] suggest that the field model offers a better physical description of the observed influence of monopolar and dipolar substituents.[4] This conclusion is based, for the most part, upon differences in the magnitude of the substituent effects predicted by the two limiting models. For example, the reaction constant for the dissociation of 4-substituted bicyclo[2.2.1]heptane-1-carboxylic acids is 1.18-fold greater than the reaction constant for the 4-substituted bicyclo[2.2.2]octane-1-carboxylic acids.[5]

(1) Chemistry of the Bicyclo[2.2.2]octanes. XIII. This research was supported by a grant from the National Science Foundation.
(2) National Science Foundation Fellow at the University of Chicago, 1964–1968.
(3) The term polar effect is used to characterize the observed influence of unconjugated, sterically remote substituents on reaction processes. This designation permits the use of the terms inductive effect and field effect for the description of the transmission mechanism.

(4) L. M. Stock, *J. Chem. Educ.*, in press.
(5) C. F. Wilcox and C. Leung, *J. Amer. Chem. Soc.*, 90, 336 (1968).