mechanism, which would give 75 and 25% label retention, respectively.

A more detailed study of metastable ion characteristics than employed in the original tetralin study[17] was made to determine if the two proposals can be distinguished (Table VI). As can be seen, no significant difference can be found in either the relative metastable abundances or the kinetic energy releases of the various C_8H_8 ions. Thus, no information can be extracted on the mode of formation of $[C_8H_8]\cdot^+$ in tetralin, as these data suggest isomerization of all C_8H_8 ions to a common structure prior to fragmentation. The behavior of various C_8H_8 ions should be compared with the C_8H_8O ion metastables presented in Table II. For this latter ion, distinctive metastable characteristics are found depending on the source of $[C_8H_8O]\cdot^+$ and the differences, with the aid of isotopic labeling, can be interpreted unambiguously in terms of structure. Unfortunately, this is not the case for the cycloreversion reaction in tetralin, and the overall mechanism for this process still requires further study.

Conclusion

It has been clearly established that 1-tetralol undergoes two cycloreversion reactions to eliminate ethene and thereby produces a mixture of structural forms for the $M - C_2H_4$ daughter. Although the two pathways are competitive to produce the normal mass spectrum, one process dominates the metastable decompositions. The daughter ions show extremely large differences in metastable abundances which are readily interpreted in terms of structure. Competitive cycloreversion reactions seem to be the case for tetralin as well, but further studies are needed to substantiate this.

This study is a classic example of the dangers inherent in a literal interpretation of measurements of metastable abundances and kinetic energy release. In the unlabeled 1-tetralol, the metastable characteristics of $[C_8H_8O]\cdot^+$ are a composite of two isomeric structures undergoing decomposition, and these characteristics are fortuitously matched by a third structure from styrene oxide, which is not involved. The combination of deuterium labeling and metastable measurements allows the correct conclusions to be drawn.

Acknowledgment. The authors thank Dr. P.-H. Lin and Mr. David Russell for help in making some of the measurements, Dr. D. Pokorny and Mr. Eric Chiu for help with the synthesis, and Professor L. J. Parkhurst for translating ref 18. Support from the University of Nebraska Research Council is appreciated.

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Application of the Principle of Least Motion to Organic Reactions. 4.[1a] More Complex Molecular Rearrangements

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Abstract: The principle of least motion technique has been applied to a wide variety of unimolecular rearrangements involving large and relatively complex systems lacking symmetry. Results, with two exceptions, are in excellent agreement with the qualitative overlap considerations of the Woodward–Hoffmann approach where applicable and experimental observations when available.

The first application of the principle of least motion (PLM) technique to molecular rearrangements was reported[2a] a few years ago. It was recognized at that time that, despite the classical nature of the approach, the stereochemical predictions arising from the results parallel those based on the conservation of orbital symmetry (COS) method when applicable. Although this initial study utilized relatively few and rather simple model systems, it provided valuable information with regard to the wide scope of potential applicability of the PLM technique. For example, it was suggested that systems that lack suitable elements of symmetry, and thus cannot be rigorously treated by the COS approach, should be amenable to investigation by the present method, since the latter does not require the presence of any particular symmetry. Also, in those cases where

COS arguments are incapable of distinguishing between two or more allowed processes leading to stereochemically different products, the PLM technique may possibly assist in removing the ambiguity.

The purpose of the present investigation was to extend the least motion treatment to larger and more complex systems, with special emphasis placed on the suggestions outlined above.

The computational details have been outlined elsewhere[2b] and need no further description. It is noteworthy, however, that a fair number of the applications reported in the present paper have been recalculated[3] using mass weighted coordinates. The results revealed that the order of preference based on the $E_{\min}$ values obtained remained unchanged. Thus incorporation of mass, although more realistic, has no special advantage.

Molecular geometries were calculated from published structural data when available or otherwise from estimates based on suitable models.

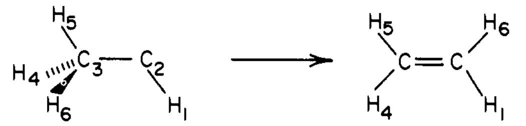
Results and Discussion

1,2-Hydrogen Migration in Carbenes. In an earlier paper[2a] we reported least motion calculations for rearrangement of methylcarbene to ethylene (**1** → **2**; R = H).

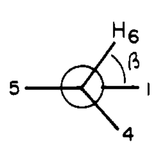
$$\underset{\mathbf{1}}{R{-}CH_2{-}\ddot{C}H} \rightarrow \underset{\mathbf{2}}{R{-}CH{=}CH_2}$$

It was recognized that various possibilities exist, depending upon the electronic states of the carbene and the olefin formed.[4-7] To assess the effect, if any, of a simple substituent (Me) on the PLM preferences exhibited in the earlier results, we have studied the conversion of ethylcarbene to propene (**1** → **2**; R = Me). Again four distinct possibilities were considered: singlet carbene to ground-state olefin, singlet carbene to excited singlet olefin, triplet carbene to ground-state olefin, and triplet carbene to excited triplet olefin. For comparative purposes the geometries of reactant and product were taken to be the same as used previously,[2a] but with one of the hydrogens replaced by a tetrahedral methyl group at an appropriate C-C distance.[8-10]

For the rearrangement of ethylcarbene to ground-state propene $E_{\min}$ was calculated for many rotamers of the reactant generated by rotation (β) about the C_2-C_3 bond (see structure **3**). The lowest value of $E_{\min}$ (5.26 Å^2) obtained was for β = 63°, whereas the corresponding value (3.73 Å^2) for the methylcarbene model was for β = 55°. These angles are remarkably close to those used in recent SCF calculations for[11,12] this interconversion.



3 **4**



For the investigation of the rearrangement in an excited state, both reactant and product were rotated simultaneously, as shown below, and $E_{\min}$ was calculated for a large number of rotational isomers.

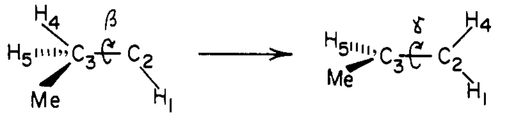


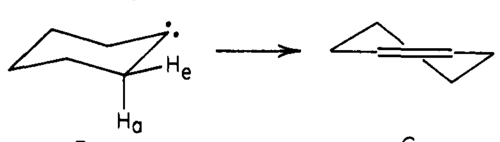
Table I. Lowest Values of $E_{\min}$ Corresponding to the Various Possibilities Considered for the Interconversion of Ethylcarbene to Propylene as Compared to Results Obtained for the Methylcarbene-Ethylene Rearrangement (in brackets)

States[a]		Angles, deg[b]		
Carbene	Olefin	β	γ	$E_{\min}$, Å^2
Singlet	Ground	63 (55)	0	5.26 (3.73)[c]
Singlet	Singlet exc.	180 (0)	70 (90)	5.53 (3.22)[d]
Triplet	Ground	69	0	5.49 (4.86)[c]
Triplet	Triplet	180 (0)	71 (90)	4.73 (2.77)[d]

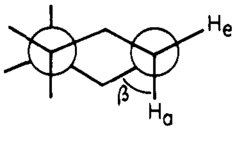
[a] Geometries associated with electronic states. [b] For definition of β and γ consult the text. [c] Minimum obtained from 18 calculated points. [d] Minimum obtained from 349 calculated points.

Results for the various modes investigated are summarized in Table I. As apparent, for the interconversion in both the excited singlet and triplet states, the lowest value of $E_{\min}$ was obtained for β = 180°, corresponding to the migration of a hydrogen anti-periplanar to the methine proton. This is to be contrasted with the result of the previous study involving methylcarbene, in which case the lowest $E_{\min}$ value obtained (β = 0°) corresponded to a syn-periplanar migration. This apparent reversal of stereochemistry upon substitution is not surprising. Examination of molecular models reveals that the syn-periplanar mode requires substantial reorganization of the methyl hydrogens, resulting in a significant enhancement of the total molecular motion. Consequently, substitution of a second methyl group at C_3 is expected to further increase the preference for the anti-periplanar mode. On the other hand, examination of the table reveals that methyl substitution has practically no effect on the preferred syn stereochemistry for the transformation into a ground-state olefin, indicating that steric factors do not influence this mode. Furthermore, both $E_{\min}$ values obtained for this process are considerably higher than those corresponding to the triplet-triplet interconversion. These observations suggest that the least motion approach favors the conversion of a carbene into an olefin with a "twisted" geometry. If, however, the formation of the twisted olefinic bond is not possible because of some geometrical constraint, then the rearrangement should take place via a syn-type of migration.

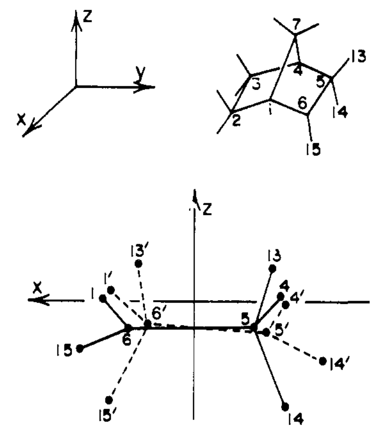
Formation of a twisted olefinic bond is indeed very unlikely in the case of small ring compounds such as the cyclohexyl system or the even more rigid brexane[13] system. Therefore, these are ideally suited for testing the prediction of the least motion approach. In addition, the geometry of these molecules is such that each potentially migrating hydrogen represents a particular stereochemical mode for the rearrangement. For example, in the conversion of cyclohexylidene (**5**) to cyclohexene (**6**), the migration of the axial hydrogen (H_a) corresponds to the syn mode (i.e., β = 60°), whereas migration of the equatorial hydrogen represents the anti-periplanar mode (i.e., β = 180°). Results of the least motion calculations



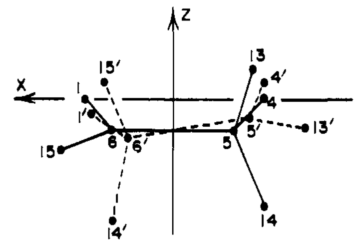
5 **6**



Migration of H_a $E_{\min}$ = 5.39 Å^2
Migration of H_e $E_{\min}$ = 9.18 Å^2



(a) exo-migration

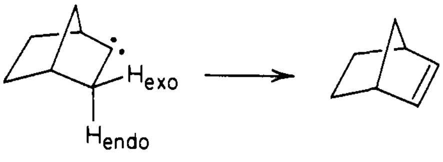


(b) endo-migration

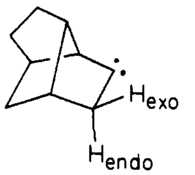
Figure 1. xz plane projections of reactant and product at $E_{\min}$ in the vicinity of the reaction centers for the 1,2-hydride shift in 2-norbornyl cation. Solid lines represent the reactant and dashed lines represent the product.

indicate an overwhelming preference for the syn mode. Similar conclusions were arrived at by Dewar et. al.[11] on the basis of a more sophisticated theoretical treatment.

The rearrangement of a bicyclo[2.2.1] system was also studied using norbornylidene (7) as a model. The choice of this molecule was based mainly on its experimental utility, since it is not ideally suited for testing the predicted syn preference. This is due to the fact that the two possible stereochemical modes (i.e., syn- and anti-periplanar) are not well defined by H_{exo} and H_{endo}, those being almost equidistant from the plane of the ring.[14] This near symmetry is clearly reflected by the results obtained: the $E_{\min}$ value for H_{exo} migration (9.31 Å^2) is only slightly lower than that for the H_{endo} shift (9.67 Å^2). Examination of the individual atomic displacements involved in each mode reveals that the least motion preference, albeit low, for the H_{exo} migration results from the dihedral angle θ (see below) value being somewhat less than 120°. In a distorted [2.2.1] system such as the brexanylidene (9), in which $\theta \approx 90°$, this preference would certainly be much more pronounced.



7 8



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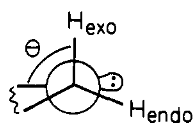
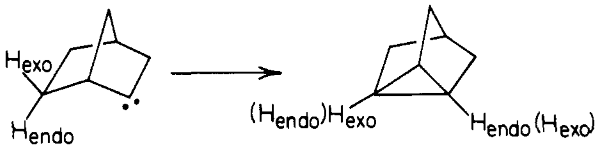


Recent experimental evidence supports these predictions: the migratory ratio H_{exo}/H_{endo} in an undistorted [2.2.1] system was found to be 13,[15] whereas in the case of the brexane system this ratio was reported to be 138.[13]

1,3-Hydrogen Migration in 2-Norbornylidene. According to reports in the literature[16] carbenes generated in norbornyl systems undergo very facile 1,3-insertion reactions. In fact, a 1,2-shift could only be observed when the formation of the three-membered ring was precluded by introducing special blocking groups.[15]

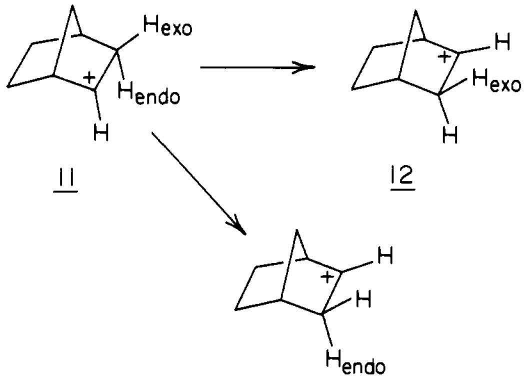
The stereochemistry of this process as considered by the PLM approach was via the examination of the conversion of **9a** to **10**. The preference of the least motion approach for the migration of the endo hydrogen (shown above) is in good agreement with the results of previous quantum mechanical model calculations for the stereochemistry of methylene insertion of Dewar[17] and Hoffmann.[18] Moreover, endo preference was also observed by labeling experiments.[16]



9a 10

H_{exo} migration: $E_{\min}$ = 16.78 Å^2
H_{endo} migration: $E_{\min}$ = 12.29 Å^2

1,2-Hydride Shift in 2-Norbornyl Cation. In a previous paper[2b] least motion considerations regarding the stereochemistry of 1,2-hydride shift in an open system (i.e., ethyl cation) were reported. The present study involved an extension of the previous work to cyclic molecules. The model used for the investigation was the 2-norbornyl cation (**11**), the rearrangement of which may possibly occur by means of either an exo (i.e., **12**) or an endo (i.e., **13**) hydride shift. The former mode is strongly favored by the least motion approach, since the $E_{\min}$ value obtained (5.69 Å^2) is considerably smaller than that computed for the latter mode (7.06 Å^2).



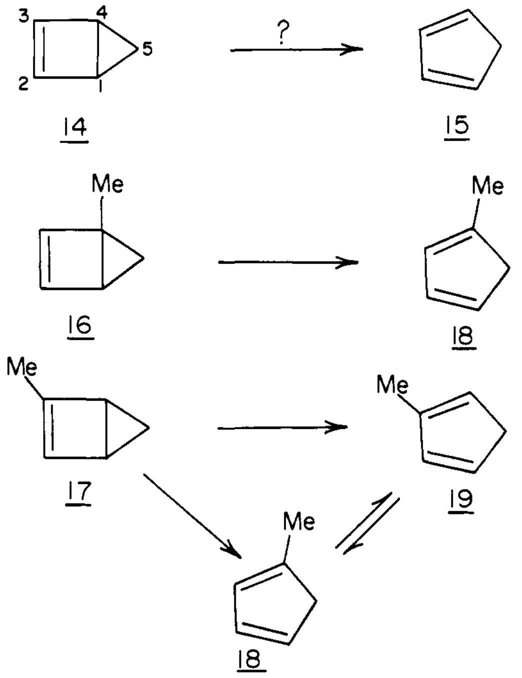
11 12 13

The high preference for the exo shift may be rationalized by considering the relative geometries of the reactant and product at $E_{\min}$. Figure 1 illustrates the xz plane projections of the above in the vicinity of the reaction centers. Examination of Figure 1a, corresponding to the exo shift, reveals that minimization of the migratory distance (13–13′) brought about a concomitant decrease in both the 14–14′ and 15–15′ distances without much molecular rotation. However, in the case of the endo shift (shown in Figure 1b), minimization of the migratory distance (14–14′) as well as both the 13–13′ and 15–15′ distances required substantial rotation of the product molecule and any further attempt to reduce these distances would have placed all the other atoms of the molecule away from their optimum position.

Additionally, a numerical comparison shows that the displacement of the migrating atom 13 for the exo shift (3.13 Å^2) is substantially smaller than that of atom 14 for the endo migration (4.06 Å^2), all others being of comparable magnitude.

Experiments performed on a series of bicyclo[2.2.1]heptyl cations also revealed[19] 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 (**14**) to cyclopentadiene (**15**) is still the subject of controversy.[20-22] Experiments utilizing the methyl derivatives **16** and **17**, carried out both in the gas phase and in solution, resulted in the conclusion that the rearrangement is concerted and regioselective. Two entirely different explanations were offered for the fact that compound **17** did not form exclusively **19**. The first of these involves a symmetry-allowed $[_{\sigma}2_s + {}_{\sigma}2_a]$ type of rearrangement.[21] More recently, however, another alternative was suggested:[22] initial cleavage of the 1,4-bond to form a vibrationally excited molecule **19**, which then rearranges to **18** by 1,5-hydride shift. This suggestion was supported by the fact that the conversion of **17** to **19** is strongly exothermic. It should be noted that the initial cleavage of the 1,4-bond in this case corresponds formally to the symmetry-disallowed disrotatory opening of the four-membered ring.



Considering these two mechanistic alternatives with the least motion in mind, calculations were carried out using the parent compound as a model (Scheme I). Surprisingly, the $E_{\min}$ value obtained for the disrotatory path (10.73 Å^2) was found to be much lower than that obtained for the $[_{\sigma}2_s + {}_{\sigma}2_a]$ process (17.69 Å^2). This finding is analogous to the recently reported results of Dewar and Kirschner,[23] who found a symmetrical transition state for the rearrangement.

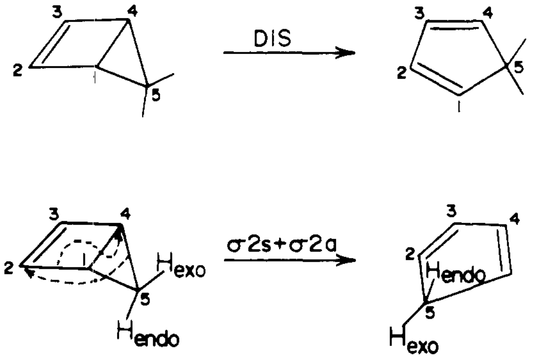
In view of the fact that stereochemical predictions arising from least motion considerations were almost always found to be in good agreement with those of the orbital symmetry approach, the present discrepancy was not easy to explain. Therefore other possible symmetry-allowed pathways were sought[24a] which may be operative in this rearrangement. These are shown in Scheme II.

Table II. Variation of $E_{\min}$ with the Mode of Rearrangement of Bicyclo[2.1.0]pent-2-ene

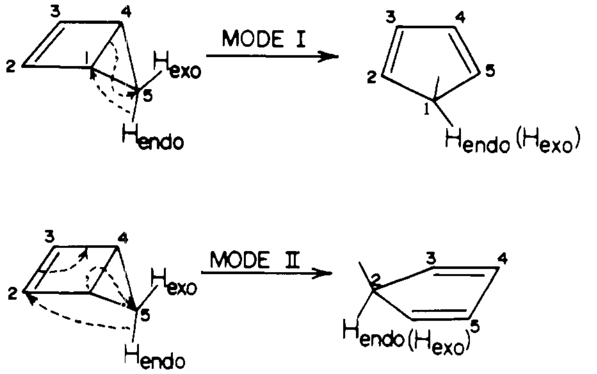
Mode	$E_{\min}$, Å^2
$[_{\sigma}2_s + {}_{\sigma}2_a]$ cycloaddition	17.69
Disrotatory ring opening	10.73
$[_{\sigma}2_s + {}_{\pi}2_s]$ process (II)	9.97,[a] 28.20[b]
Cyclopropane–propylene type (I)	6.71,[a] 22.09[b]

[a] Exocyclic hydrogen migrates. [b] Endocyclic hydrogen migrates.

Scheme I



Scheme II



Mode I is analogous to the cyclopropane–propylene rearrangement and mode II may be described as a $[_{\sigma}2_s + {}_{\pi}2_s + {}_{\sigma}2_s]$ process.

Calculations were carried out for both mode I and mode II. Since these modes involve migration of a hydrogen from C_5, each mode is associated with two distinct stereochemical possibilities (i.e., H_{exo} or H_{endo} migration).

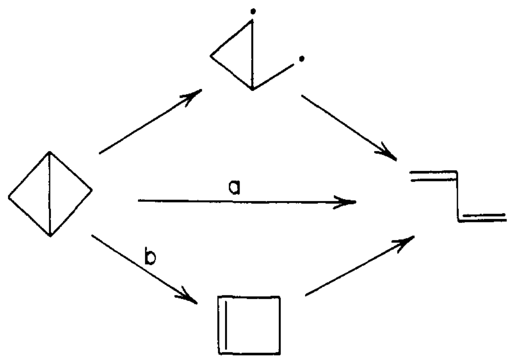
The summary of the results, including those obtained for the disrotatory ring opening and the $[_{\sigma}2_s + {}_{\sigma}2_a]$ pathway, is shown in Table II. An overall comparison of the $E_{\min}$ values listed in the table reveals that the least motion approach favors the symmetry-allowed cyclopropane–propylene route (mode Ia). On the other hand, the results of deuterium labeling studies[24b] are not in accord with a hydrogen transfer process.

Thus it seems that the rearrangement of the bicyclo[2.1.0]-pent-2-ene molecule is neither orbital symmetry nor least motion controlled. This conclusion, however, cannot be extended to substituted [2.1.0] systems until such calculations are carried out. This is because the present treatment is extremely sensitive to steric factors and substitution of a single methyl group can change the preferred stereochemical pathway, as was demonstrated previously.[25]

Rearrangement of Bicyclobutane. The thermal rearrangement of bicyclobutane to butadiene may conceivably occur in a concerted manner or by a biradical mechanism. In the former case two possibilities may be considered: a direct transformation to butadiene (path a) or a stepwise process involving

Table III. $E_{\min}$ Values Obtained for the Various Stereochemical Modes Investigated for the Rearrangement of Bicyclobutane and Its Methyl-Substituted Derivatives

Model	Mode	$E_{\min}$, Å^2
	I	14.60
	II	16.05
	III	13.83
	IV	15.45
	V	16.00
	I	21.42
	III	18.62
	I	32.58
	III	24.59



a cyclobutene intermediate (path b). For path a three stereochemically different modes can be envisioned, as shown in Scheme III.

Mode I corresponds to a quasi-disrotatory opening of both rings, while mode II requires a quasi-conrotatory motion. In mode III one ring is opened disrotatory and the other conrotatory. The first two modes are disallowed according to the Woodward–Hoffmann rules,[26] 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 orbital symmetry argument for mode III, qualitative overlap considerations[26] resulted in the conclusion that it should be an allowed $[_{\sigma}2_s + {}_{\sigma}2_a]$ process.

From the stereochemical point of view, the first step of path b may occur via a conrotatory or disrotatory motion as illustrated in Scheme IV, the former being favored by the orbital symmetry approach.

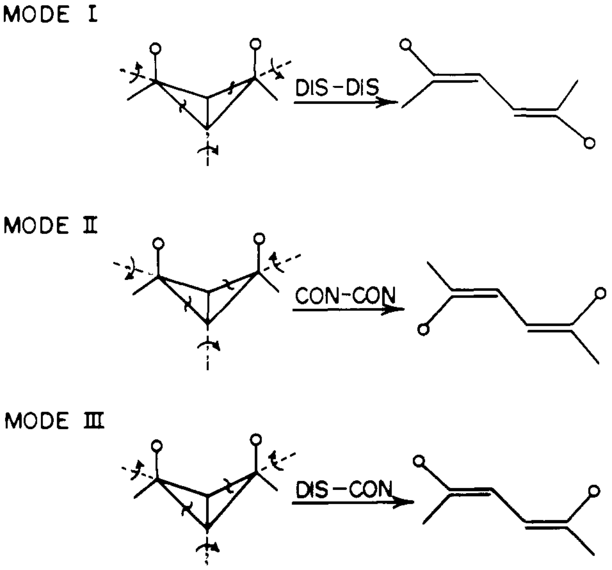
Least motion calculations were carried out for the various stereochemical possibilities discussed above using bicyclobutane as a model. In addition, the effect of molecular size on the stereochemistry of the direct transformation pathway was also studied by successive substitution of methyl groups for hydrogens. The results are shown in Table III.

The obtained $E_{\min}$ values indicate that the least motion approach favors the symmetry-allowed mode III for both the unsubstituted and substituted bicyclobutanes. It is noteworthy that the least motion preferred conrotatory motion for path b is itself also in accord with the predictions arising from the orbital symmetry approach.

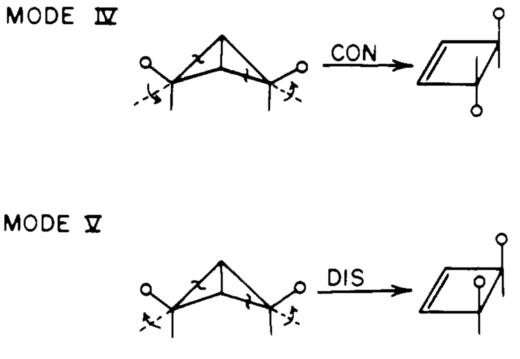
Experimental results from the thermal rearrangement of methyl substituted bicyclobutanes[27] confirm the predicted mode III. However, the results are also compatible with an alternative biradical type mechanism suggested recently by Dewar et al.[28] It seems, therefore, that further experiments, capable of distinguishing these alternative mechanistic possibilities, are needed.

Sigmatropic Rearrangements. The simplest case of a sigmatropic shift is the migration of a hydrogen. A suitable example of this process is the 1,5-shift in 1,3-pentadiene, which according to the Woodward–Hoffmann rules should be suprafacial.

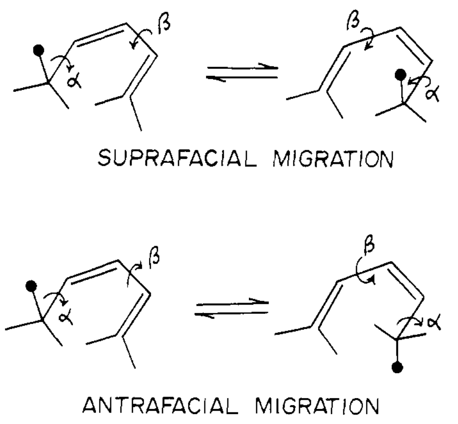
Scheme III



Scheme IV



Scheme V



Considering this problem with the least motion approach in mind, it is clear that the favored 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. In order to achieve this a three-dimensional conformational surface was generated for both the suprafacial and antarafacial modes by calculating $E_{\min}$ values as a function of the rotational angles α and β defined in Scheme V.

The surface obtained for the antarafacial migration is illustrated in Figure 2. The surface appears to be relatively shallow and symmetrical with a single minimum ($E_{\min}$ = 2.97

Table IV. Lowest Values of $E_{\min}$ Obtained for the Sigmatropic 1,3-, 1,5-, and 1,7-Hydrogen Shift

	$E_{\min}$, Å^2 for migration	
Mode	Suprafacial	Antarafacial
1,3	6.19	7.61
1,5	2.34	2.97
1,7	5.27	3.87

Å^2) at α = 38° and β = 50°, indicating that both the trigonal and the tetrahedral center have to bend substantially to accommodate the migration. In contrast, the surface obtained for the suprafacial migration (shown in Figure 3) is relatively steep and unsymmetrical. As before, a single minimum is obtained ($E_{\min}$ = 2.34 Å^2), but it is situated at α = 13° and β = 36°, suggesting that the tetrahedral center need not bend extensively in order to minimize the motion.

Comparing the lowest values for each mode of migration results in the conclusion that the least motion approach favors the suprafacial migration, in accord with both the predictions of the COS method and experiment.[29,30]

Similar investigation was carried out for both the 1,3-shift in propylene and the 1,7-shift in *cis*-1,3,5-heptatriene.

The former case is trivial in the least motion sense because the molecular framework is too small to be able to offset the excessive bending motion of the C–H$_{\text{mig}}$ bond required for the antarafacial migration. Therefore the 1,3-shift of any atom is predicted to take place supraficially by the present approach.

On the other hand, if the molecule is fairly large, such as the *cis*-1,3,5-heptatriene, one can envisage the molecular framework as undergoing a variety of vibrational motions, thus reducing the amount of bending required for an antarafacial migration. The results obtained (shown in Table IV) confirm the above; the $E_{\min}$ value obtained for the antarafacial shift is lower than that for the suprafacial mode. Table IV also shows the results obtained for both the 1,3- and 1,5-shifts. It is interesting to note that the absolute value of $E_{\min}$, which normally increases in proportion to the size of the molecule considered, is largest in the case of propene, the smallest system of the three.

1,3-Shift in Bicyclo[3.2.0]hept-2-ene. According to the Woodward–Hoffmann rules,[26] 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 with other than s-type orbitals, 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 atom.[26]

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 (**23**), the rearrangement of which to norbornene (**24**) may occur with retention or inversion of configuration at the migrating carbon, as illustrated in Scheme VI.

The PLM results obtained (shown on the scheme) clearly favor the inversion pathway, whereas intuitively the retention path was expected to be preferred.[31]

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.[32-35] It was reported that the reaction of **25** and **26** occurred[33,34] with inversion of configuration. Further work, however, furnished evidence[32,35] the rearrangement of **27** took place with retention of configuration. This led to the conclusion that the configuration inverting transition state from 27 is sterically too strained to permit the electronically "allowed" concerted process to occur, and thus a biradical mechanism was proposed for this system.

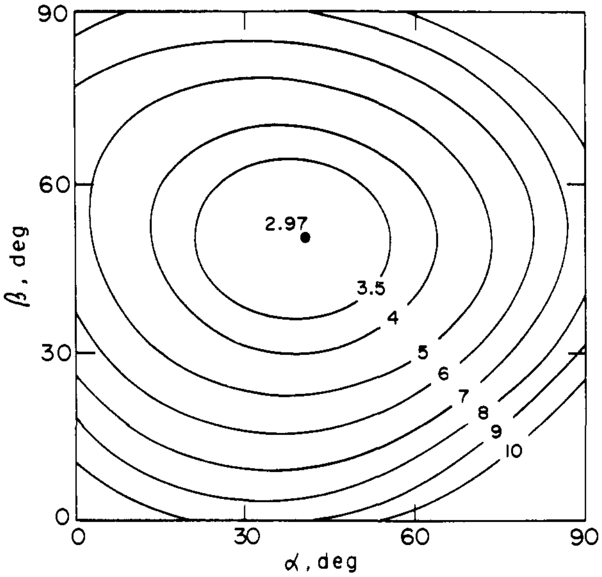


Figure 2. Variation of $E_{\min}$ with the dihedral angles α and β for the antarafacial 1,5-shift of a hydrogen in 1,3-pentadiene.

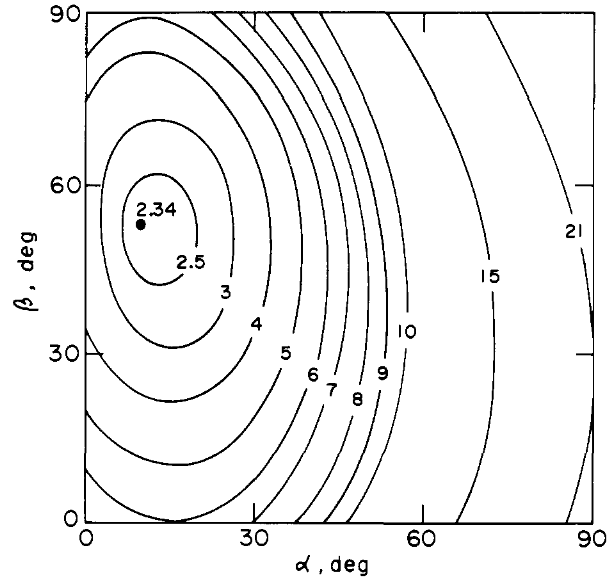
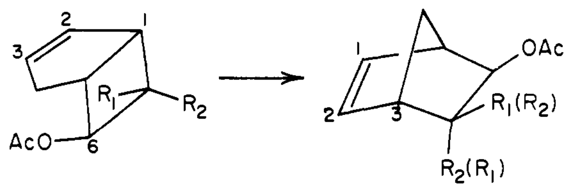


Figure 3. Variation of $E_{\min}$ with the dihedral angles α and β for the suprafacial 1,5-shift of a hydrogen in 1,3-pentadiene.

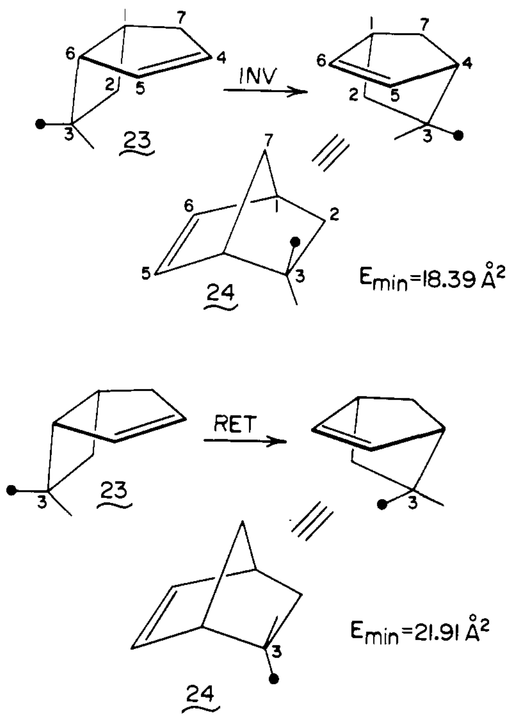


25, R$_1$ = H; R$_2$ = D
26, R$_1$ = H; R$_2$ = Me
27, R$_1$ = Me; R$_2$ = H

Conclusions

Within the framework of the present investigation the PLM technique has been applied to a wide variety of molecular rearrangements. Care has been taken to select models that are readily available for a laboratory experiment. As is apparent

Scheme VI



from the results, with only two exceptions, all the applications were successful in yielding stereochemical predictions which were in good agreement with either experimental observations or predictions arising from other theoretical approaches.

One situation where the least motion prediction was incompatible with a reported experimental study[24b] is the rearrangement of the bicyclo[2.1.0]pent-2-ene molecule. However, as mentioned previously, this rearrangement may proceed via chemically activated species,[22] in which case least motion considerations do not apply.

The other instance where the PLM approach resulted in an erroneous prediction was the rearrangement of methylcarbene and its methyl substituted homologue. On the basis of the geometries of reactant and product, this reaction was predicted to take place preferentially in the first triplet state. In contrast, both semiempirical[11] and ab initio[12] calculations favored the ground-state interconversion. This suggests that the reaction is non-least-motion controlled and its stereochemistry is dependent solely on stereoelectronic factors.[36]

It is noteworthy that the rearrangement of oxacarbenes to ketones is also non-least-motion controlled.[37] Interestingly, in this case the PLM approach favors the ground-state process, whereas ab initio calculations[38] predict low activation energy for the triplet–triplet interconversion.

These and other[39] known non-least-motion controlled reactions are of considerable importance regarding the critical evaluation of the reliability and limitations of the PLM technique. The criterion for least motion control in unimolecular rearrangements is presently under investigation and will be the subject of a forthcoming paper.

Acknowledgment. The authors are grateful for the continued support of the National Research Council of Canada.

References and Notes

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(4) At that time triplet carbene was taken to be linear.[5,6] However, a reinvestigation by Herzberg and Johns[7] then suggested that it may well be bent with a bond angle of 136° or even 132°. In the light of this, new PLM calculations were carried out (by J.A.A.) for triplet methylcarbene assuming a bond angle of 136° at the carbenic carbon. As was anticipated in footnote *j*, Table I of ref 2a, the new results were similar to those for the singlet case and so earlier conclusions were not materially affected.

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(8) In view of more recent studies[9,10] our earlier choice of C–C distances for singlet and triplet ethylenes[2a] seem too long. The use of shorter bond lengths would certainly result in smaller values of E_{min}, but it is doubtful that this would substantially alter the stereochemistry of the least motion pathways for the processes considered.

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(31) One of the referees has raised the point: why does the PLM procedure often differ from the intuitive result? It should be pointed out that the present PLM approach is a classical semiquantitative method which takes into account the displacement of every atom of the molecule. Intuition, on the other hand, tends to concentrate on the immediate reaction centers and often neglects consideration of the motion of the residual molecular fragment. When the molecule is small or fairly symmetrical, there is a good chance that intuitive result will agree with the calculated result. For example, the suprafacial mode for the 1,3-shift in propylene can be predicted intuitively to be the least motion path. However, in the case of a complex molecular framework, such as most of the systems considered in this report, one can hardly rely on intuition, because the motion of the residual molecular fragment is often an important contributor to the total molecular motion.

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