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ORBITAL SYMMETRY RULES AND STERIC HINDRANCE IN THE THERMAL 1-3 SIGMATROPIC REARRANGEMENT OF BICYCLO[3.2.0]HEPTENES TO NORBORNENES. EXTENDED HÜCKEL CALCULATIONS

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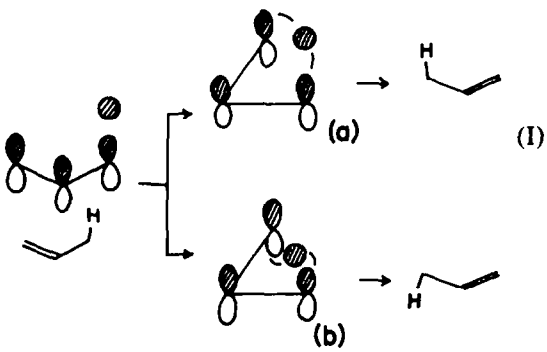
Abstract—An approximate reaction surface is calculated by Extended Hückel Theory for the title reaction. A discussion of the relative ease of various reaction paths is attempted and compared with previously known experimental results and with the predictions of orbital symmetry rules.

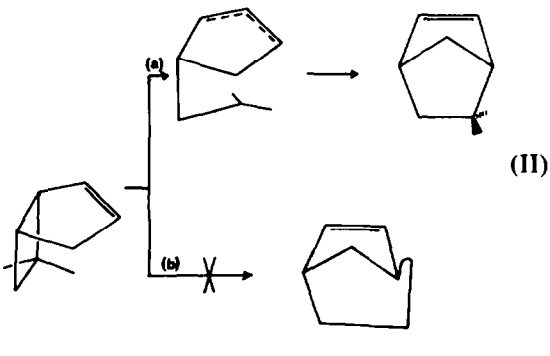
INTRODUCTION

An interesting case of the application of Woodward and Hoffman's orbital symmetry rules[1] is the class of reactions known as 1-3 sigmatropic shifts, as exemplified by the migration of a hydrogen atom in an allylic system.



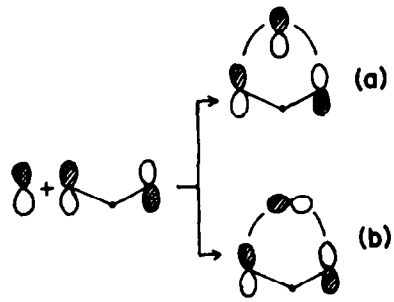
(I)

The so-called "suprafacial" path (a) is thermally disallowed, while the "antarafacial" path (b) is thermally allowed.[2] There are however cases in which the allowed antarafacial path is made impossible by stereochemical constraints, a classical example is the rearrangement of bicyclo[3.2.0]heptenes to norbornenes.[3]



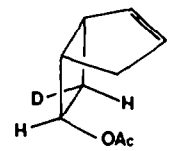
(II)

In such instances, the symmetry rules require that the reaction proceed with inversion of configuration at the migrating center, the p orbital of which can thus couple with the non-bonding molecular orbital of the allylic system.

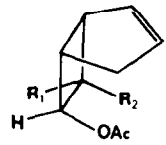


(III)

Path (a) is symmetry-forbidden and thermally disallowed, path (b) is symmetry-allowed and thermally allowed. This is substantiated by experimental findings[3] in the case of the thermal rearrangement of bicyclo[3.2.0]hept-2-ene to bicyclo[2.2.1]hept-5-ene (Fig. 1a).



$\frac{k_{inv}}{k_{ret}} = 19$ (a)



$\frac{k_{inv\ exo}}{k_{inv\ endo}} = 54$ (b)

$\frac{k_{ret\ endo}}{k_{inv\ endo}} = 7$ (c)

endo R_1=H, R_2=CH_3
exo R_1=CH_3, R_2=H

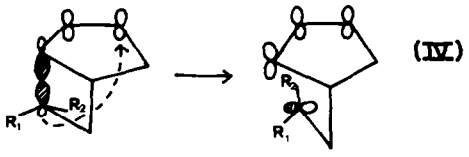
(a) For rearrangements with inversion and retention of configuration for the parent hydrocarbon.

(b) For rearrangements with inversion of configuration with bulky substituents.

(c) For rearrangements with inversion and retention of configuration in *endo*-MBCE.

Fig. 1. Ratios of the rate constants for the rearrangements of bicycloheptenes to norbornenes.[3]

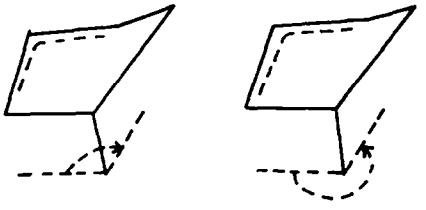
Besides predicting inversion of configuration, the symmetry rules require that the rotation take place in a specific sense, namely, the back lobe of the p-orbital of the migrating carbon atom should approach the migration terminus. It is easy to see that this means counterclockwise (CCW) rotation.



(IV)

If however the *endo* substituent R_2 is bulky (e.g. a methyl group) the CCW rotation produces high steric strain, therefore, the inversion of *exo*-7-methyl[3.2.0]hept-2-ene should be much faster than that of the *endo* derivative, if the predicted sense of rotation is operative. Again, experiment[3] confirms this (Fig. 1b). Moreover, the rate of rearrangement with retention of configuration in the case of the *endo* compound is about 7 times as great as the rate of rearrangement with inversion[3] (Fig. 1c). This last result is in contrast with the predictions of the Woodward-Hoffman rules and suggests that a different mechanism may be in operation. Another interesting experimental result is the fact that the *exo* compound does not epimerize to the *endo* isomer, while the *endo* isomer epimerizes with a rate comparable to the rate of rearrangement with retention and about 5 times as great as the rate of rearrangement with inversion.[4]

Furthermore, in principle the migrating group can follow what may be called an "inner" and an "outer" path.*



(V)

In the latter case, orbital symmetry rules should become much less important, and if they were to be followed, it can be seen that the senses of rotation for allowed and forbidden pathways should be reversed.

It seemed to us that the theoretical evaluation of the potential energy surfaces for the above described reactions might be a useful contribution towards a mechanistic interpretation of the experimental results.

Calculations

A semiempirical method that has proved successful in dealing with reaction surfaces[5] is the Extended Hückel Theory.[6] We report here the results of its application to the calculation of a model potential energy surface for the reaction of bicyclo[3.2.0]heptene (BCE) to norbornene (NBE) and of the corresponding 7-methyl substituted compound (MBCE) to 4-methylnorbornene (MNBE). This was done in a way that brings the effect of the inversion-producing rotation to the fore, thus allowing a detailed, though qualitative, discussion of both clockwise (CW) and CCW rotation. On the same surfaces information for the epimerization reactions are obtainable.

A number of approximations have to be made to reduce the complete multidimensional reaction surface to simple but still meaningful sections. An outline of our procedure is given as follows.

(i) A Cartesian coordinate system common to the two molecules was chosen, so that the atoms of the allylic system lie in the xy plane, atom 3 lies on the y axis, and atom 1 is at the origin. Cartesian coordinates were obtained for the carbon skeleton of BCE and NBE from literature molecular dimensions[7] (Fig. 2).

(ii) The reaction progress is materialized by a degree of advancement, λ, that goes from 0 (BCE) to 1 (NBE) by steps of 0·1.

(iii) The Cartesian coordinates of atoms 1 to 6, at a given value of λ, are calculated by the formula

$$Q_i = Q_i(\text{BCE}) + \lambda[Q_i(\text{NBE}) - Q_i(\text{BCE})]$$

(Q_i with $i = 1, 2, 3$ corresponds to x, y, z respectively); that is, they vary proportionally to the degree of advancement λ. This is a rough assumption, of course, and has almost no justification but its being simple and straightforward. However, the total displacements of atoms 1, 2, 3 and 5 are less than 0·25 Å, so that their freedom is very limited. Atom 4 has a z displacement of 0·86 Å, as it becomes the bridging atom in NBE, and atom 6 a y

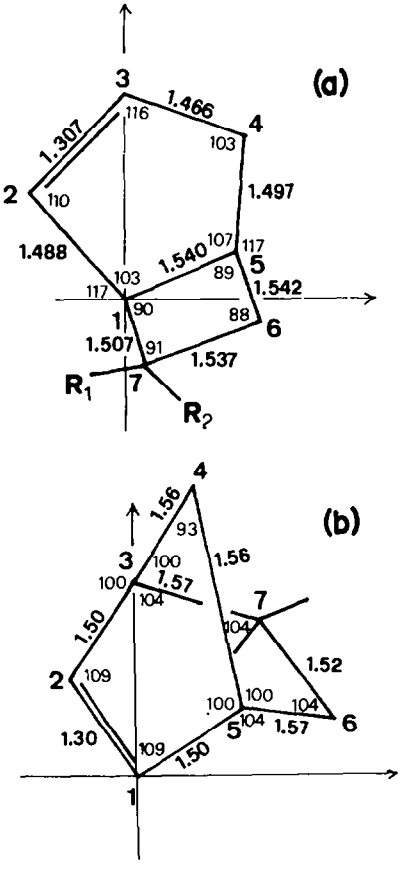


Fig. 2. Molecular dimensions of the carbon skeletons* of (a) bicyclo[3.2.0]heptene[7a] and (b) norbornene.[7b,c]

*We are grateful to Prof. W. von E. Doering for pointing out this possibility.

*Bond lengths in Angstroms. Numbering in (b) does not conform to IUPAC rules but is consistent with that in (a).

displacement of 1·18 Å, as it follows the motion of the migrating carbon atom. These two motions are so tightly connected with the reaction progress that we thought it justified to treat them in the same way as the parameters that describe the reaction-determining motion of atom 7. Moreover, we consider that any other reasonable assumption about the dependence of Q_i on λ would not significantly change the shape of the potential energy surfaces, nor the conclusions that have been drawn. This belief has been substantiated by the outcome of preliminary calculations.

(iv) The position of atom 7, at a given λ, is defined by three parameters, δ, χ and r, as displayed in Fig. 3. Of

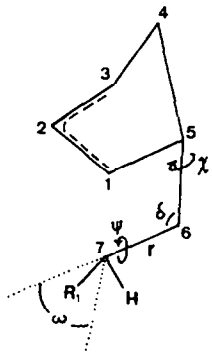


Fig. 3. Parameters to describe the motion of C-7.

these parameters, r and χ are calculated on the assumption that they vary proportionally to λ, in the same way as the Cartesian coordinates of atoms 1 to 6, from the value they have in BCE to the value they reach in NBE. The parameter δ was optimized in a way to be explained later.

(v) The coordinates of the hydrogen atoms (except those bound to C-7 and those of the methyl group) were calculated on the assumption that they are determined by the positions of the surrounding carbon atoms, the Appendix gives a sketch of the rules that predict the hydrogen atoms' positions, given those of the carbon atoms.

(vi) The positions of the atoms attached to C-7 have been determined as follows (Fig. 3). An angle, ψ, defines the rotation about the C-6–C-7 bond; $\psi = 0°$ corresponds to the situation in which the plane through atoms C-5, C-6 and C-7 bisects the R_1–C-7–H angle. ω is the angle between the bisector of the R_1–C-7–H angle and the direction of the C-6–C-7 bond. When R_1 = H, the HCH angle is 116°,† and the C–H distance 1·09 Å. When R_1 = CH_3, the H_3C–C-7–H angle is again 116°, the C–C distance is 1·52 Å, all angles in the methyl group are tetrahedral, and C–H distances are again 1·09 Å. The CH_3 group is kept in a staggered position with respect to the C-6–C-7 bond. Note that the relevant parameters ω and ψ account for the rehybridization and for the inversion of configuration respectively.

It is now possible to build the potential energy surface for the reaction. At any λ, ψ varies from 0 to 180° if R_1 = H, and from 0 to 360° if R_1 = CH_3 (Fig. 3), by steps of 30°. The λ and ψ pairs are the sampling points of the surfaces. The energy, at any of these points, is optimized with respect to δ and ω, the only parameters on which it now depends, all the others being in some way fixed. This picture displays the amount and the sense of rotation (and therefore of inversion of configuration) at the migrating group during the progress of the reaction.

Extended Hückel Theory was applied in its standard form,[6] using a program[8] that allows any manipulation of geometrical parameters for any kind of molecule and energy optimization.

Before discussing the results, a few considerations are needed. In a first approach, true minimization was carried out on both ω and δ, at any sampling point of the surface. The technique was a simple steepest-descent one, but it soon became evident that (a) the energy was about ten times more sensitive to variations in δ than to variations in ω, and (b) within a reasonable range of ω values, the energy was scarcely sensitive at all to variations in this parameter. Therefore, it was preferred to vary ω proportionally, both to the degree of advancement λ and to the extent of inversion ψ, so that at $\lambda = 0·5$ and/or $\psi = 90°$, $\omega = 0°$; and for $\psi > 90°$, $\omega(180° - \psi) = -\omega(\psi)$. This amounts to postulating a linear variation in the rehybridization at the migrating group. However, it is questionable whether this has any real significance in terms of energy, since differences in energy as little as 0·15 eV are calculated for angle differences as great as 30°.

Another problem arose when considering the energies of reactants and products. In fact, if angle δ is allowed to vary at $\lambda = 0$ and $\lambda = 1$, for $\psi = 0°$, the minimum is not in the experimentally known geometry. The values obtained for BCE and NBE are 96 and 110° respectively, as compared with experimental values of 90 and 104°. Energy differences are of the order of 0·5 eV. It was decided to use the minimized values, rather than the experimental ones, for uniformity of treatment. Forcing some points on the surface to have a preassigned geometry would introduce a different criterion and they would no longer be comparable with the rest of the surface.

RESULTS AND DISCUSSION

The calculated potential energy surfaces are shown in Figs. 4–6. Figs. 4 and 5 refer to the parent hydrocarbon in its ground and first excited configuration respectively. Fig. 6 refers to both the *exo*- and *endo*-methyl derivatives, only the inner path and ground configuration have been considered for these molecules. Fig. 7 displays the various reaction possibilities. Figs. 8 and 9 show the energy profiles corresponding to the dotted lines in Figs. 4 and 6, they correspond to reasonable paths on the surfaces. The abscissa coordinate for these energy profiles is the total displacement of the migrating carbon atom, as we thought it a more relevant coordinate than either λ or ψ in describing trajectories (except in the case of epimerization, where ψ has also been used as an alternative reaction coordinate).

(a) *Bicyclo*[3.2.0]*hept*-2-*ene to norbornene.* Looking at the surfaces in Figs. 4a and b an intermediate is revealed by a minimum near $\lambda = 0·5$ in the case of the outer path (Fig. 4b), while no definite minima occur in the case of the inner path. This is also evident on inspection of the shapes of the energy profiles in Fig. 8. This is a strong argument in favour of the inner path, since experimental facts do not suggest the presence of intermediates.[3] On the other hand, discrimination of the various stereochemically different inner path reactions is hazardous on activation energy grounds, since the essentially flat surface about 2·5 eV high above the zero should allow the system to evolve randomly in all directions. This is best realized by comparison of Figs. 8a–d, where it can be seen that only

†See Appendix.

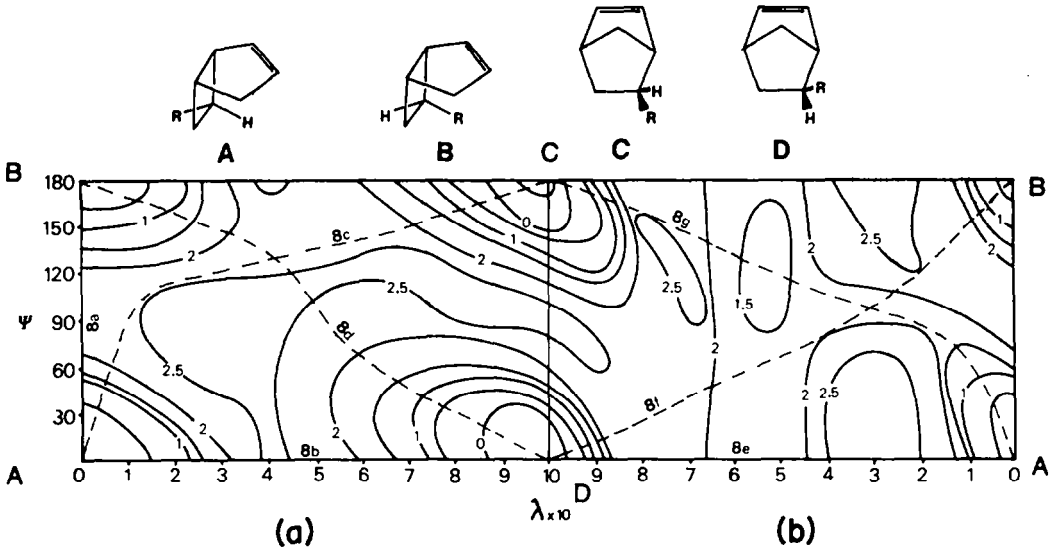


Fig. 4. Potential energy surface for the rearrangement of bicyclo[3.2.0]hept-2-ene to norbornene in the ground configuration; (a) inner path, (b) outer path.*

*Isoenergetic lines are shown at intervals of 0·5 eV. Zero energy set at $\lambda = 0$, $\psi = 0°$. Increasing ψ indicates clockwise rotation. Dotted lines show reasonable trajectories for the various rearrangements, numbers on these lines and on the edges give the Fig. in which the corresponding profile is shown.

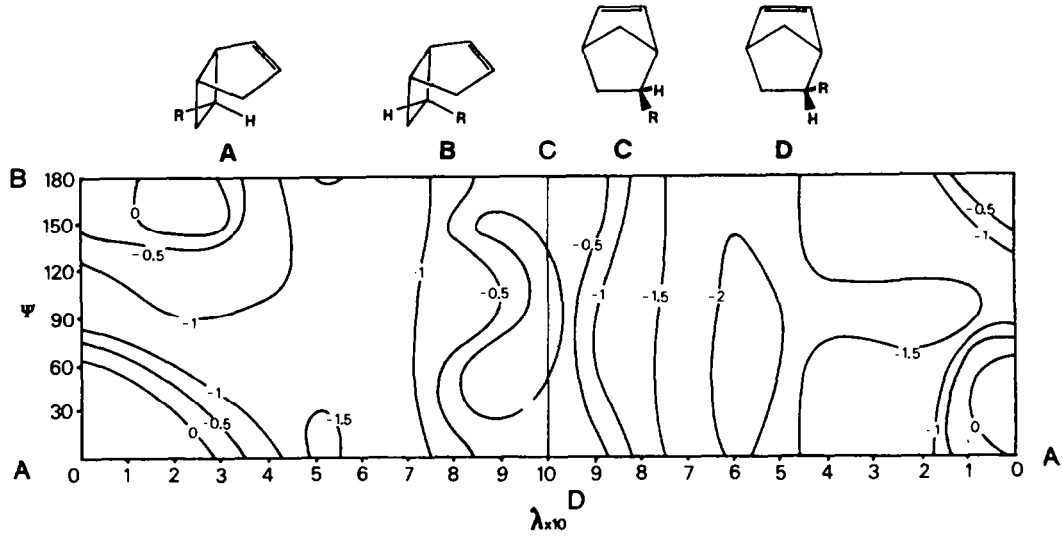


Fig. 5. First excited configuration potential energy surface for the rearrangement of bicyclo[3.2.0]hept-2-ene to norbornene.*

*The vertical separation between the zero-energy points ($\lambda = 0$, $\psi = 0°$) of the two surfaces is 4·34 eV.

the epimerization (Fig. 8a) has a significantly lower activation energy than the other reactions. Unfortunately, no experimental rate constants are available for epimerization.[3]

Given the above outlined results, any comparison of relative ease of forbidden and allowed paths should be very cautious. However, as can be seen from Figs. 8b–d, the CW rotation profile (Fig. 8c) is the only one that shows traces of an intermediate, thus suggesting that the reaction should be slowed down. Another hint in favour of CCW over CW rotation is the steepness of the left-side slope of the activation energy hill for CW rotation (Fig. 8c) as compared to the analogous one for CCW rotation (Fig. 8d). In conclusion, our order of reactivity would be epimerization > CCW inversion ≈ retention > CW inversion.

As to the comparison of these results with orbital symmetry rules, it is clear that no definite energy benefit is calculated along the allowed paths. Still, the effect of faster growth of orbital overlap along these paths is evident from the elongated shape of the energy hole of the product, and is visualized by comparing the right-side slopes of Fig. 8c and d (forbidden and allowed respectively). In the first, the energy starts decreasing only after

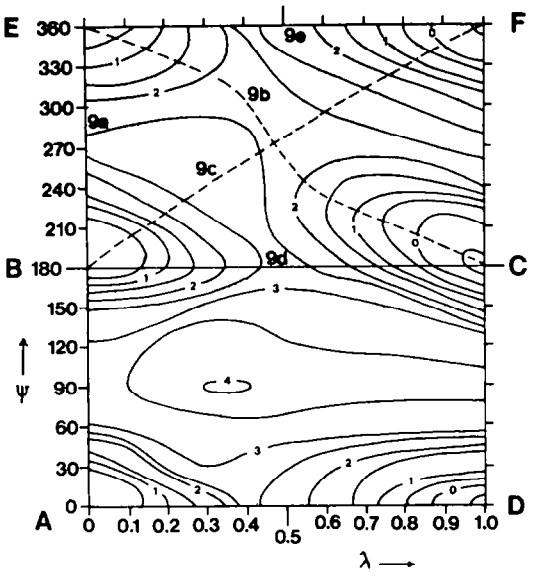


Fig. 6. Potential energy surface for the rearrangement of 7-methylbicyclo[3.2.0]hept-2-ene to 4-methylnorbornene.

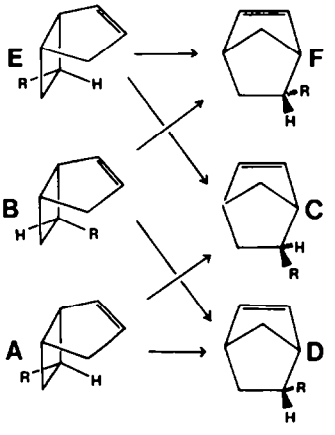
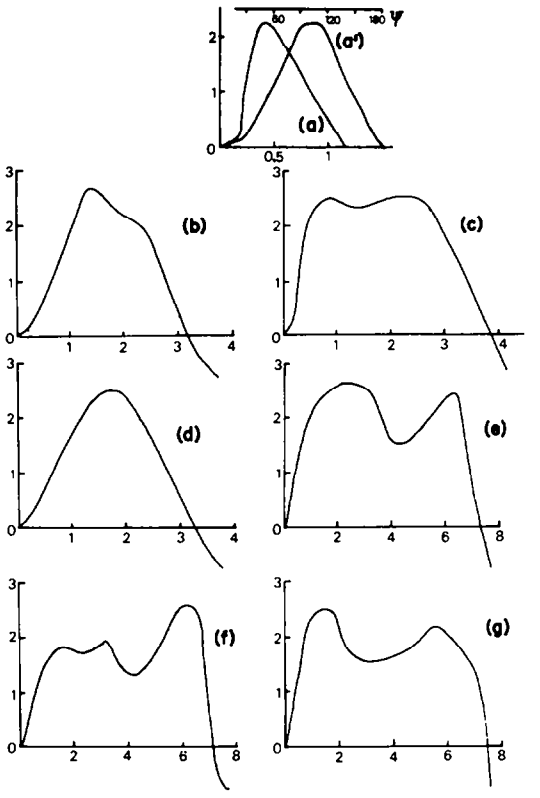


Fig. 7. Rearrangements of bicycloheptenes to norbornenes.



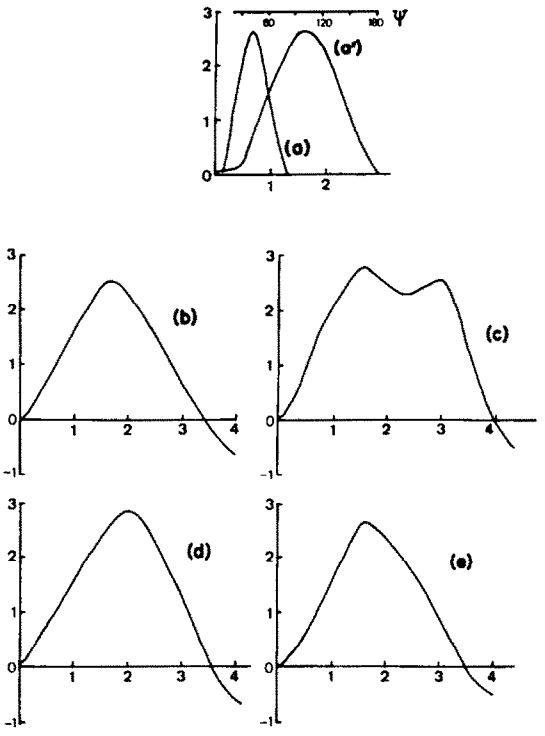
(a) epimerization; (a') epimerization with $\psi°$ as abscissa; (b) reaction with retention of configuration, inner path; (c) CW inversion, inner path; (d) CCW inversion, inner path; (e) retention, outer path; (f) CW inversion, outer path; (g) CCW inversion, outer path.

Fig. 8. Energy profiles for the trajectories of the rearrangements of bicyclo[3.2.0]hept-2-ene to norbornene.*

*Abscissa scale is the total displacement of the migrating centre (Å).

3 Å, while in the second after only 2 Å of total displacement. In both cases orbital overlap seems to come into play only when the height of the energy barrier has already been determined by other factors. The first excited configuration surfaces (Fig. 5) show, as expected, a reverse pattern of maxima and minima with respect to the ground configuration surface. In particular, at some points the vertical separation drops below 1 eV, suggesting that the ground state might be a triplet state.

(b) *7-Methyl bicyclo[3.2.0]hept-2-ene to 4-methylnorbornene.* Even a qualitative look at the surface in Fig. 6 shows that all paths that bring the methyl group towards the five-membered ring are clearly unfavourable (compare the lower and upper parts of Fig. 6), thus confirming that what Berson calls "steric blockade"[3] is operative. The discussion is therefore restricted to the upper part of Fig. 6, which shows the sterically allowed processes. The overall shape of this surface is analogous to the one for the parent hydrocarbon, and the same considerations apply. However, here a small but definite lowering of activation energy appears in the case of the allowed pathway (compare Figs. 9b and c). Moreover, the presence of an intermediate is revealed by a minimum in the curve in Fig. 9c even deeper than that for the analogous path in the case of the parent hydrocarbon. The path with inversion of configuration for the *exo*-isomer is slightly favoured over retention for the *endo*-isomer, by a small energy difference. These facts suggest the order of reactivity, epimerization *exo* ≈ epimerization *endo* ≈ inversion *exo* ≈ retention *exo* > retention *endo* > inversion *endo*. The difference in the ratios in Fig. 1 can be rationalized as follows. In the case of the largest ratio (Kinv *exo*/Kinv *endo* = 54) two factors, namely the difference in activation energy and the presence of an intermediate, contribute to make the favoured reaction faster, while in the case of the smaller ratio (Kret *endo*/Kinv *endo* = 7) only one of these effects, the small difference in activation energy, is operative. No rationalization of the fact, mentioned earlier, that the *endo*-isomer epimerizes while the *exo*- does not, can be found in our results. One possible explanation would be the failure of the Extended Hückel Theory to evaluate quantitatively the difference in energy between the two isomers. However, a non-bonded energy calculation[9] gave an energy difference of 2·2 kcal mole^{-1}. Also in the case of the methyl derivatives, the effect of faster orbital overlap growth along allowed paths has more effect on the slope of the right side of the energy hills (compare, e.g. Figs. 9d and e) than on the height of the hill itself.



(a) Left to right, epimerization of the *endo*-isomer; right to left, epimerization of the *exo*-isomer; (a') as for (a) but with $\psi°$ as abscissa. (b) *exo*, CCW inversion. (c) *endo*, CW inversion. (d) *endo*, retention of configuration. (e) *exo*, retention of configuration.

Fig. 9. Energy profiles for the trajectories of the rearrangements of 7-methylbicyclo[3.2.0]hept-2-ene to 4-methylnorbornene.*

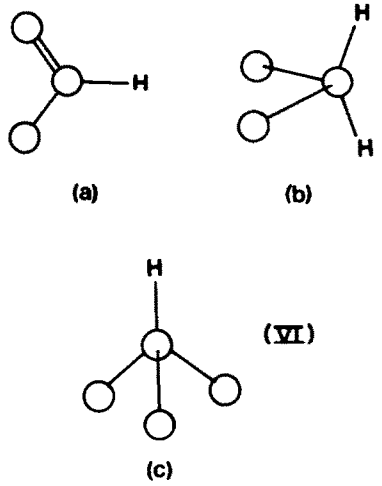
*Abscissa scale is the total displacement of the migrating centre (Å).

CONCLUSION

It may be rewarding to establish a formal analogy between the thermal rearrangement of BCE and the thermal enantiomerization and diastereoisomerization of 1,2 disubstituted cyclopropanes. The study of this second type of reaction has led to definitions and propositions[10] that can be applied to the present case. In 1,2 disubstituted cyclopropanes with different substituents the following reactions may occur, breaking of the bond opposite to the unsubstituted carbon followed by (a) rotation of group 1 and reclosure, (b) rotation of group 2 and reclosure, (c) rotation of both groups and reclosure. Reactions (a) and (b) produce geometrical isomerization (the two products being diastereoisomers) and reaction (c) produces optical isomerization. Clockwise and counterclockwise motions in cases (a) and (b), conrotations and disrotations in case (c) are observationally indistinguishable. In the present case, after rupture of the C-1–C-7 bond we may have rotation around the C-6–C-7 bond leading to epimerization, rotation around the C-5–C-6 bond leading to rearrangement with retention, rotation at both sites leading to rearrangement with inversion. This last rotation is not a full 180° rotation but is limited to about 76° when clockwise or to 360–76° when counterclockwise. In the methyl derivative clockwise and counterclockwise rotations involve significantly different energy variations. Another feature in BCE rearrangement, which is absent in cyclopropane, is the existence of the double bond. Both situations are amenable to the same description, the possible reactions are obtained by means of coupling internal rotations with the stretching vibration involved in the breaking of the carbon–carbon bond. In both cases knowledge of the shape of the potential surface is not enough to make a choice between different possibilities, a dynamical treatment would be necessary. In the case of cyclopropane a surface calculated by means of the Extended Hückel Theory[11] does not seem to be able to accommodate the experimental facts, which are instead in good agreement with the predictions obtained from the results of an accurate *ab initio* calculation.[12] In the case of the present study, Extended Hückel calculations produce potential surfaces which can accommodate, qualitatively, the known experimental facts and support a reaction mechanism based on the new concepts put forward for cyclopropane isomerizations. Theoretical calculations of quantitative significance could only be obtained by means of a dynamical approach.

APPENDIX: THE HYDROGEN ATOMS

The energy of the molecule was found to be scarcely sensitive to small displacements of the hydrogen atoms. For this reason, it was decided to adopt uniform geometrical criteria in placing the hydrogen atoms throughout the reaction progress. They are as follows. (a) The hydrogen atom is placed on the bisector of the C–C=C angle, at a given distance from the central C atom. (b) The hydrogen atoms are placed in a plane that bisects the C–C–C angle, perpendicular to the plane containing the carbon atoms, the distance from the central C atom is the same for both hydrogens, and the H–C–H angle obeys the requirements of orthogonality of sp^3 orbitals for C–C–C angles larger than 104°. Below this value, the H–C–H angle is given the fixed value of 116°, based on the experimental electron diffraction values of 115 and 114° for cyclopropane[13a] and cyclobutane[13b] respectively, and the X-ray value of 117° for the apical hydrogens in a norbornene frame.[7b] (c) The hydrogen atom is placed at a given distance from the C atom, while the C–H forms equal angles with the three C–C bonds. The value of the C–H distance was fixed at 1·09 Å throughout. Note that in BCE the hydrogen atom attached to C-1 is of type (c), while the one attached to C-3 is of type (a), in NBE they are vice-versa. The situation of BCE has been maintained up to $\lambda = 0{\cdot}4$, while that of NBE has been assumed for $\lambda \geq 0{\cdot}6$. For $\lambda = 0{\cdot}5$, the situation with lower energy (that of NBE) was assumed. The energy differences are however extremely small. All the involved calculations are incorporated in the already mentioned[8] molecular geometry and Extended Hückel energy program.



(VI)

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