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MINDO/3 Study of the Thermal Isomerizations of Methylbicyclo[2,1,0]pent-2-ene and its 1- and 2-Methyl Derivatives

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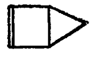
Summary MINDO/3 calculations are reported for the thermal rearrangements of bicyclo[2,1,0]pent-2-ene, and of its 1- and 2-methyl derivatives, to cyclopentadienes, and for the interconversion of 1- and 2-methylcyclopentadiene; the results suggest that only normal electrocyclic and sigmatropic rearrangements are involved.

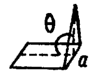
BICYCLO[2,1,0]PENT-2-ENE (**1**) rearranges on heating to cyclopentadiene (**2**).[1,2] Several mechanisms have been considered[3] for this electrocyclic process but the choice between them is still in doubt.

In view of our recent success [4–7] in interpreting the course of the electrocyclic reactions of cyclobutene and cyclopropyl, using the MINDO/2 semiempirical SCF procedure,[8] we decided to study the conversion of (**1**) into (**2**) in a similar manner, using a modification (MINDO/2′ [9]) of the original MINDO/2 method. Complications arose (*cf.* refs. 5—7) when the reaction was followed using as the reaction co-ordinate either the length (r) of the breaking bond (a in **3**) or the angle (θ in **3**) between the C(3) and C(4) planes. In each case the reaction showed 'chemical hysteresis,'[6] since the conversion of (**1**) into (**2**) is a 'forbidden'[10] antiaromatic[11] electrocyclic reaction. The transition state was finally located by a two-dimensional grid search,[6] using r and θ as reaction co-ordinates. The transition state had C_v symmetry (see below) and the calculated activation energy (111·7 kJ mol⁻l) agreed very well with experiment[2] (112·5 kJ mol^{-1}).

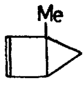
These calculations were subject to some uncertainty in view of the tendency[9] of MINDO/2′ to underestimate strain energies. Recently a new version of MINDO (MINDO/3 [11]) has been developed here, in which most of the failings of MINDO/2′ seem to have been overcome.† A greatly improved geometry program,[12] based on the Davidon–Fletcher–Powell algorithm,[13] has also been developed, and also a procedure[14] for locating transition states directly by minimising the scalar gradient of the energy (*cf.* ref. 15).


(1)


(2)



(3)



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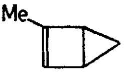

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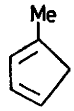
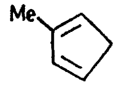


(6)



(7)

We have used these techniques to reinvestigate the conversion of (**1**) into (**2**). Preliminary studies indicated that the r,θ potential surface was very similar to that given by MINDO/2′ and the corresponding transition states also had similar structures (Figure). The calculated activation energy (113·3 kJ mol^{-1}) also agreed well with the MINDO/2′ value and experiment.

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† In the case of hydrocarbons, MINDO/3 differs from MINDO/2′ only in the use of different orbital exponents (ζ) for 2s and sp AOs and different values for the U, α, and B parameters. The relevant values are: U_H, −12·505; $U_C(2s)$, −51·79; $U_C(2p)$, −39·18; ζ_H, 1·3; ζ_C (2s), 1·739; ζ_C (2p), 1·710; B_{HH}, 0·2448; B_{CH}, 0·3150; B_{CC} 0·4199; α_{HH}, 1·489; α_{CH} 1·476; α_{CC}, 1·371. Other parameters have the values listed in ref. 9. Our MINDO/3 and geometry programs have been deposited with Q.C.P.E.

It will be seen that the transition state is predicted to have a symmetrical structure (Figure). The conversion of (**1**) into (**2**) is therefore a normal concerted electrocyclic process in spite of the fact that it violates the Woodward–Hoffmann rules.[7] This is an important conclusion since it has been implied[10] that 'forbidden' pericyclic reactions cannot take place in a concerted manner. It should be added that the calculations reported here carry considerable weight since MINDO/3 has been tested by calculations for various properties of hundreds of molecules, ions, and radicals, and for over fifty reactions.[16]

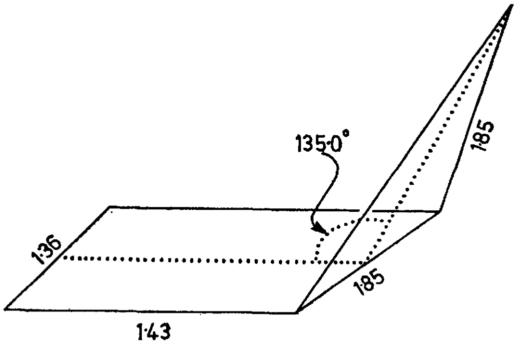

FIGURE. Calculated geometry for conversion of bicyclo[2,1,0]-pentene into cyclopentadiene. Distances in Å.

The symmetry of the transition state is clearly due to geometric constraints since 'forbidden' electrocyclic reactions normally take place in an unsymmetrical manner.[17,18] As a result, the characteristic[17] HOMO/LUMO crossing coincides here with the transition state.

While these results seemed unambiguous, we felt that further work was needed in view of doubts[19–21] concerning the mechanisms of the analogous rearrangements of the 1-methyl-(**4**) and 2-methyl-(**5**) derivatives of (**1**) to corresponding derivatives (**6**,**7**) of (**2**). In particular, two different explanations have been suggested for the fact that (**5**) rearranges to a mixture of (**6**) and (**7**), not to (**7**) alone. One[20] of these regards the rearrangement as an internal (${}_{\sigma}2_s + {}_{\sigma}2_a$) cycloaddition involving either the 1–2 and 4–5 or the 1–5 and 2–4 bonds of (**1**). The other[21] attributes the formation of (**6**) from (**5**) to a secondary rearrangement of (**7**), possibly by a 'hot molecule' process since the conversion of (**5**) into (**7**) is strongly exothermic.

We studied the rearrangements of (**4**) and (**5**) using MINDO/3 and the techniques indicated above. The transition states were very similar to that for (**1**) → (**2**) (Figure) while the calculated activation energies for (**4**) → (**6**) and (**5**) → (**7**) were 109·2 and 123·0 kJ mol^{-1} respectively. Thus (**4**) should rearrange more rapidly than (**1**) or (**5**), as indeed appears to be the case. We also studied the rearrangements of (**4**) to (**6**) or (**5**) to (**7**) by the suggested[20] (${}_{\sigma}2_a + {}_{\sigma}2_a$) mechanism but could find no such path that did not have a very high activation energy ($\gg$250 kJ mol^{-1}).

We therefore conclude that the rearrangements of (**4**) and (**5**) are normal 'forbidden' electrocyclic reactions, like that of (**1**), and that the formation of (**6**) from (**5**) must take place *via* (**7**). This conclusion is supported by recent MINDO/3 calculations[22] for the rearrangements of cyclopentadienes by 1,5 hydrogen shifts.

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