The Cope Rearrangement. MINDO/3 Studies of the Rearrangements of 1,5-Hexadiene and Bicyclo[2.2.0]hexane

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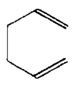
Abstract: MINDO/3 calculations are reported for the degenerate Cope rearrangement of 1,5-hexadiene and for the degenerate rearrangement of bicyclo[2.2.0]hexane and its conversion to 1,5-hexadiene. All these reactions are predicted to take place via a common stable intermediate, consisting of equilibriating biradicaloids related to the 1,5-cyclohexadiyl biradical. The reactions are not concerted pericyclic processes.

The preceding paper[2] summarized current ideas concerning the mechanism of the Cope rearrangement and reported new experimental evidence derived from kinetic studies of the rearrangements of phenyl derivatives of 1,5-hexadiene (**1**).[3] Our results seemed to support the suggestion by Doering et al.[4] that the Cope rearrangement is not a true pericyclic process but involves the formation of intermediates analogous to the 1,4-cyclohexylene biradical (**2**). In view of recent arguments by McIver,[5] it seemed moreover likely that if such a symmetrical species is involved in the reaction, it must be a stable intermediate.



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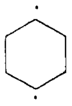


2.

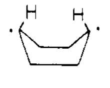
Theoretical considerations,[6] on the other hand, indicate that singlet biradicals cannot exist as such, undergoing Jahn-Teller-type distortions that remove the orbital degeneracy. The intermediate in the Cope rearrangement should then be a biradicaloid derived from the corresponding cyclohexylene biradical. It was shown[6] that one could on this basis account for the observations of Goldstein and Benzon[7] concerning the degenerate rearrangement of bicyclo[2.2.0]hexane, which appears to involve a species analogous to **2** but different from the intermediate in the "boat" Cope rearrangement. It was suggested that the two species correspond to Jahn-Teller isomers derived from the biradical **2**.

In view of the theoretical interest of these observations and deductions, we were anxious to obtain further information concerning the mechanism of the Cope rearrangement and the nature of the intermediates involved in it. Recent work in these laboratories[8] has shown the utility of MINDO/3[9] in this kind of connection; we have therefore carried out detailed MINDO/3 calculations for the Cope rearrangement of **1**.

Procedure

The calculations were carried out by the standard MINDO/3[9] closed shell program,[10] geometries being found by minimizing the energy with respect to all geometrical variables, making no assumptions and using the standard DFP[9] procedure. Transition states were located approximately by the reaction coordinate method,[11] taking the length of the breaking CC bond as reaction coordinate. They were then located exactly by the McIver-Komornicki procedure[12] (i.e., minimizing the scalar gradient of the energy) using a program developed here.[13] It was established that the points found in this way were true transition states by applying the McIver-Komornicki test,[12] i.e., calculating the force constant (Hessian) matrix and establishing that it had one, and only one, negative eigenvalue. Some of the intermediates in these reactions proved to be highly biradical-like in character. In such cases it is necessary[9,14] to include CI_0 (configuration interaction with the two lowest double excited configurations). The calculations were therefore repeated with inclusion of CI_0, the transition states again being located by the McIver-Komornicki[12,13] procedures.

MINDO/3 has been shown[15] to give good estimates of molecular vibration frequencies and hence of derived thermodynamic functions.[15] Vibration frequencies were calculated, without CI_0, for **1** and the transition states (Figure 2) leading to **3** and **4**, using the methods of ref 12, and entropies were then calculated using the calculated geometries to determine rotational contributions. In this way entropies of activation were estimated for the "boat" and "chair" Cope rearrangements of **1**.



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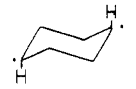

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Results and Discussion

Figure 1 shows the MERPs (minimum energy reaction paths) calculated, without CI_0, for the "chair" and "boat" Cope rearrangements of **1**. It will be seen that the symmetrical intermediates correspond to local minima on the potential surface as McIver[5] had predicted.[16] The corresponding potential wells are, however very shallow, 2.7 kcal/mol for the "chair" and 1.6 kcal/mol for the "boat".

The calculated heats of formation and overall enthalpies and entropies of activation are compared with experiment[4,7] in Table I. The agreement in the case of the "chair" rearrangement is very satisfactory. That for the "boat" seems at first sight less good. However, there seems no good reason for the large difference between the experimental values for the entropies of activation for the two reactions and our calculations make them almost identical. Since the accuracy claimed[7] for the experimental activation parameters for the "boat" rearrangement was low, it seems likely that the errors were in fact larger than anticipated. Our calculated value for the difference in activation enthalpy between the two reactions (6.3 kcal/mol) agrees well with the observed difference in free energy of activation at 523 °C (5.8 kcal/mol).

The structures calculated for the two transition states, and for the intermediates **3** and **4**, are shown in Figure 2. Note that the 3,4 and 1,6 bonds in the latter are little longer than normal paraffinic CC single bonds (boat, 1.63; chair, 1.61 Å). In the transition states of reactions leading to complete rupture of a CC bond, the length of the breaking bond is invariably ca. 2.0

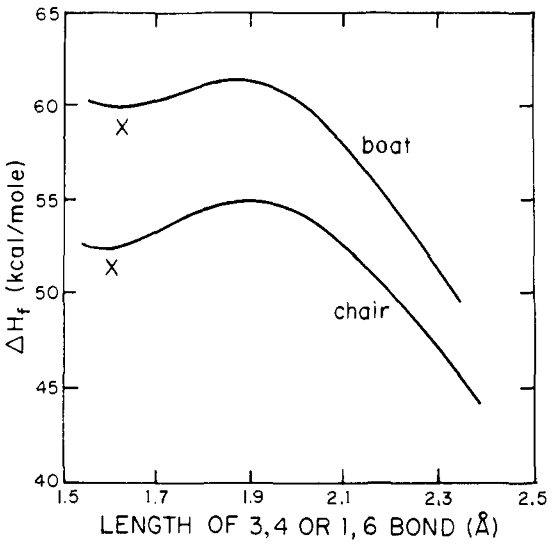


Figure 1. Plot of calculated heat of formation (ΔH_f) vs. the length of the 3,4 or 1,6 bond for points on the MERP for conversion of 1,5-hexadiene to the boat or chair 1,4-cyclohexylene biradicaloids (X).

Å.[19] The lengths of the other CC bonds in **3** and **4** (1.44 Å) are likewise greater than those in benzene (1.40 Å) or the allyl radical (1.42 Å according to MINDO/3), being indeed little less than the sp^2-sp^2 C-C bonds in typical polyenes (e.g., 1.46 Å in butadiene). Both intermediates thus have geometries quite close to that expected for the cyclohexylene biradical **2** and very different from those expected for other alternative structures.[2] Moreover, as expected[2] on this basis, the HOMOs of **3** and **4** have high orbital densities at the methine carbon atoms, being symmetric for reflection in the plane of symmetry bisecting the two allyl moieties.

The structures of the two transition states (Figure 2) differ greatly from those of the intermediates. In each case[20] one of the forming/breaking bonds is very little longer than a normal CC single bond ("chair", 1.559; "boat", 1.573 Å) while the other is greatly stretched ("chair", 1.899; "boat" 1.849 Å). The CC bonds in each allyl moiety are also very dissimilar in length ("chair", 1.382 and 1.474; "boat", 1.392 and 1.469 Å). The structure is thus displaced to a remarkable extent toward the corresponding 1,5-hexadiene (**1**), considering that the transition state is so very close to the intermediate in energy. Similar changes are also apparent in the geometries of the methylene groups, the group at one end of each allyl moiety now being almost planar while the other is more nearly tetrahedral.

On this basis one can make some predictions concerning the effects of substituents at the 3 or 4 positions of **1** on the rate of rearrangement. Such a substituent should lower the energy of the second transition state (i.e., that between the intermediate and the product) almost as much as it does that of the product (where it is now attached to a vinyl carbon) while its effect on the energy of the first transition state should be small (since this resembles the reactant in structure). The transition state for the reaction now corresponds to the first step, i.e., conversion of the reactant into the "biradical" intermediate.

Our experimental results[2] for the effects of ±E substituents in the 3 position fit nicely into this pattern. We would expect the effect of such a substituent to arise only from the change in hybridization of the adjacent carbon atom from sp^3 to something approaching sp^2. The effects of phenyl and α- and β-naphthyl were indeed very similar, implying that resonance interactions are not involved. The rate enhancement for the phenyl derivative corresponded to a change in activation energy of 2.1 kcal/mol. This is about one-third the amount that would be expected[21] for a full change in hybridization of the carbon atom in the 3 position from sp^3 to sp^2.

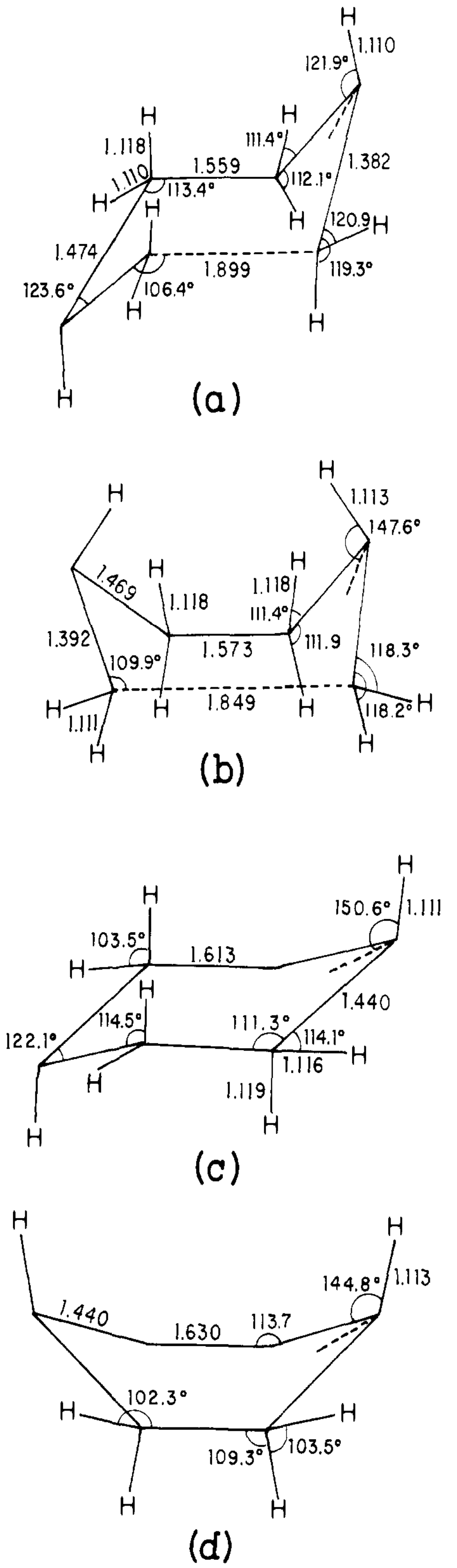


Figure 2. Calculated geometries (without CI_0, bond lengths in Å) for species involved in the Cope rearrangements: (a), (b), chair and boat transition states; (c), (d), chair and boat intermediates.

As noted above, the geometries of **3** and **4** correspond roughly to those expected for conformers of **2**. However, the 3,4 and 1,6 bonds are abnormally long for such a structure and the carbon atoms at the radical centers (C_2, C_5) are not planar. The latter result was quite unexpected and had indeed been overlooked in an earlier MINDO/2 calculation[17] because planarity of the methine carbons was assumed. At that time we were still using a very inefficient program for calculating

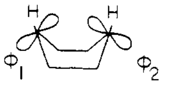
Table I. Calculated and Observed Heats of Formation, Heats of Activation, and Entropies of Activation of Species Involved in the Degenerate Cope Rearrangement of 1,5-Hexadiene

	ΔH_f[a]	$\Delta H^{\ddagger}$[b]	$\Delta S^{\ddagger}$[c]			
Species	Calcd	Obsd	Calcd	Obsd	Obsd	Calcd
1,5-Hexadiene (**1**)	19.0	20.2[d]				
Chair intermediate (**4**)	52.3					
Chair transition state	55.0	53.5	35.1[e]	33.5	−13.8	−17.0[f]
Boat intermediate (**3**)	59.7					
Boat transition state	61.3	64.9	41.4	44.7	−3.0	−14.7[f]

[a] Heat of formation, kcal/mol, at 25 °C. [b] Activation enthalpy, kcal/mol. [c] Activation entropy, cal/(deg mol) at 523 K. [d] S. W. Benson, "Thermochemical Kinetics", Wiley, New York, N.Y., 1968. [e] Calculated from the observed[d] heat of formation of **1** and the measured[f,g] activation enthalpies. [f] Reference 7. [g] Reference 4.

geometries and assumptions had to be made to enable the calculations to be carried out at reasonable cost. The resulting error indicates very forcefully the dangers inherent in any geometrical assumptions, however reasonable they may seem. Any such assumption is necessarily based on preconceived ideas concerning the mechanism of the reaction in question. Calculations based on such assumptions must then inevitably reproduce the mechanisms on which they were based. Calculations of reaction mechanisms in which *any* geometrical assumptions are made are therefore worthless and it is unfortunate that they still continue to appear in the chemical literature.

Since singlet biradicals cannot be stable entities,[6] it is not in fact surprising that the structures of **3** and **4** differ from that expected for **2**. Evidently **3** and **4** are biradicaloids[6,23] derived from **2** by some interaction between the radical centers. Consider first the "boat" intermediate **3**. Here the singly occupied AOs, ϕ_1 and ϕ_2, in the corresponding conformer of **2** (see **5**) can interact either directly across space or hyperconjugatively[24] via the intervening σ bonds (see **7**). In view of the symmetry (C_{2v}) of **3**, the AOs ϕ_1 and ϕ_2 must enter MOs of **3** in the form of combinations ($\phi_1 \pm \phi_2$). The direct interaction removes the degeneracy of ($\phi_1 + \phi_2$) and ($\phi_1 - \phi_2$) by lowering the energy of the symmetric combination and raising that of the antisymmetric one while the indirect interaction has the opposite effect,[24] lowering ($\phi_1 - \phi_2$) and raising ($\phi_1 + \phi_2$). It is evident that the distortion from planarity at the methine carbons indicated in **6** will increase the direct interaction; it will also decrease the indirect one since this depends on π interactions across the 2,3 and 4,5 bonds. Conversely the distortion indicated in **7** will decrease the direct interaction while increasing the indirect one. Thus the biradical **5** should undergo distortion to two Jahn-Teller isomers,[6] corresponding to **6** and **7**. The geometry calculated for the boat intermediate **3** indicates that it is a biradicaloid corresponding to the Jahn-Teller isomer **7**. This is confirmed by an examination of the HOMO eigenvector; this contains the combination ($\phi_1 - \phi_2$), the HOMO being antisymmetric for reflection in the plane of symmetry bisecting the 1,6 and 3,4 bonds. The geometry of **3** is entirely consistent with this picture. The indirect interaction (cf. **7**) will be increased by a change in hybridization of the 1,3,4,6 carbon atoms toward sp^2 with a concomitant increase in the p character of the AOs used in the 3,4 and 1,6 bonds. These bonds are consequently unusually long, owing partly to the high p content of the AOs used to form them and partly to the antibonding effect of the HOMO. Conversely the remaining CC bonds are shorter than "polyene" single bonds because of the π interactions across them.



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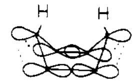

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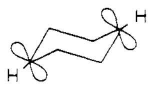
In the case of the "chair" biradical **8**, the direct interactions between the AOs ϕ_1 and ϕ_2 are negligible. The degeneracy of the biradical is removed only by indirect interactions which are increased by the distortion indicated in **9**. The structure of the chair intermediate does indeed correspond to such a biradicaloid, the HOMO again being antibonding across the 3,4 and 1,6 bonds. Both the Cope intermediates are thus biradicaloids derived from corresponding cyclohexylene biradicals by hyperconjugative interactions between the radical centers.



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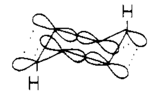

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An interesting confirmation of these conclusions seemed[6] to be provided by the rearrangements of bicyclo[2.2.0]hexane (**10**). Goldstein and Benzon[7] found that the tetradeuterio derivative **11** can undergo inversion to **12** without cleavage into **1**. This reaction must involve fission and re-formation of the transannular bond in **11**, and so must involve biradical-like intermediates such as **13** or **14**. These appear at first sight to be the same as the corresponding species involved in the boat Cope rearrangements of **15** or **16** so one would expect **15** and/or **16** to be formed in the rearrangement of **11** to **12**. This was not the case. On the other hand, an isomeric 1,5-hexadiene (**17**) was formed which must have arisen from the "chair" intermediate **18**. Thus **13** or **14** can give rise to diene via **18** but

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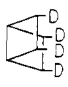

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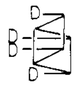

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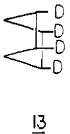

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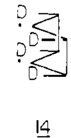

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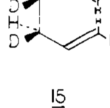

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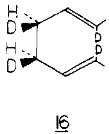

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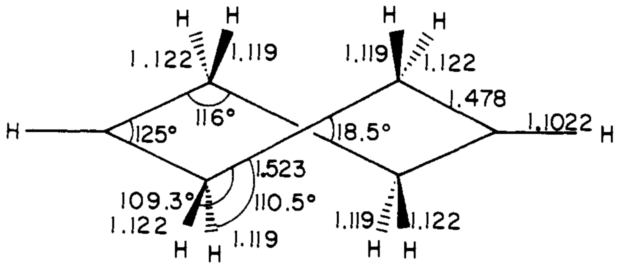
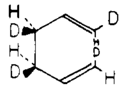


Figure 3. Calculated geometry (with CI_0) for the twist boat conformer **22** of the 1,4-cyclohexylene biradical.

not directly, a rather surprising result.

As we have seen, the interactions between the radical centers



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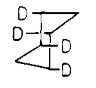

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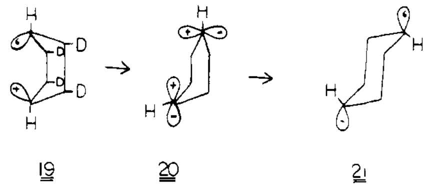
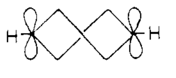
in **2** can be across space or through bonds. Predominance of one or the other leads to a removal of the degeneracy of the "singly occupied" orbitals and hence to a biradicaloid. In the boat Cope intermediate the indirect (through-bond) interaction predominates. On the other hand, **10** represents the extreme result of predominant across-space interaction. Weakening the central bond in **10** should lead to a biradicaloid in which the across-space interaction still predominates. Thus **13** and **14** are lumomers of the corresponding "boat" Cope intermediates and their conversion to **15** or **16** via the latter is accordingly "forbidden".[6,8] On the other hand, during conversion of **13** into **18** by the route indicated by **19** in **19–21**, the indirect inter-



19 20 21

action vanishes when the migrating methine is coplanar with the adjacent C_4 moiety (**20**) and then changes sign, being in phase with the direct interaction after this point. Evidently then **13** is a homomer of **18**; the conversion of **13** to **17** is therefore "allowed". This conclusion was confirmed by a MINDO/3 study of the conversion indicated by **19** → **20** → **21**. No HOMO/LUMO crossing took place. This is not the MERP for the reaction; however, any reaction path can be used in studies of this kind to establish whether a given pair of isomers are homomers or lumomers.

For completeness, it was, however, necessary to find the transition states both for this reaction and for the inversion of **10**, i.e., **11** → **12**. The transition states proved extremely difficult to locate by the reaction coordinate method; this indeed is why we originally studied the conversion of **11** to **17** by the symmetric path (**19** → **20** → **21**). A stationary point, with one negative eigenvalue in the force constant (Hessian) matrix, was finally located, corresponding to the twist boat **22**. This ap-



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peared to be the transition state for the inversion **11** → **12**. The energy calculated for this was, however, extremely high, corresponding to an activation energy for **11** → **12** of 61.1 kcal/mol (obsd,[7] 35.0 ± 0.3 kcal/mol). It seemed clear that **22** must be highly biradical-like in character, a conclusion confirmed by a very large decrease in energy on inclusion of CI_0 (47.9 kcal/mol). We therefore recalculated the entire potential surface for the various interconversion of **1**, **2**, and **10** with inclusion of CI_0 throughout.

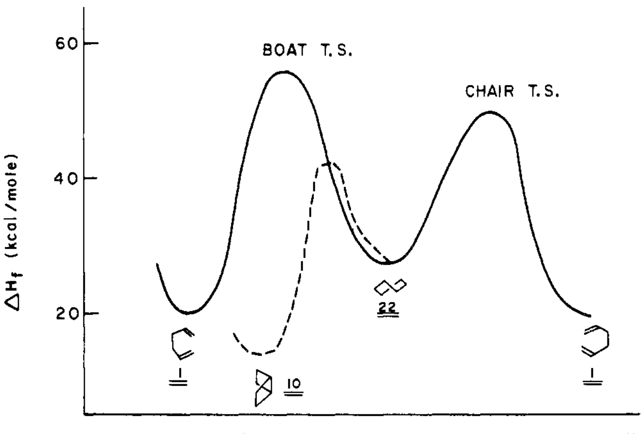

Figure 4. The potential surface for the 1,5-hexadiene rearrangement. All energies are calculated with inclusion of CI_0.

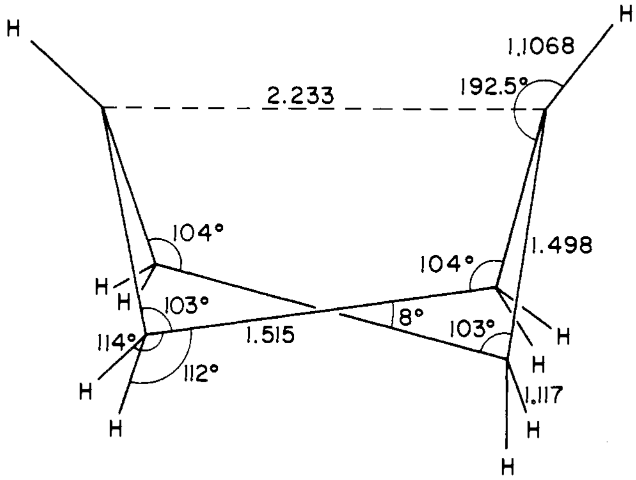

Figure 5. The calculated geometry (with CI_0, bond lengths in Å) of the transition state for conversion of **10** to **22**.

The energies of **1**, **10**, and of the "boat" and "chair" transition states (Figure 2) decreased by less than 6 kcal/mol while the geometries remained essentially unchanged. These are therefore normal closed shell species and the energies calculated without CI_0 are to be preferred.

The energies of the "boat" and "chair" intermediates **3** and **4** decreased by 23.9 and 20.0 kcal/mol, respectively. These species therefore fall in the awkward intermediate region between "normal" molecules and biradicaloids with high biradical character where the true energy probably lies somewhere between the values calculated with and without CI_0. When CI was included, **3** and **4** also ceased to be local minima on the potential surface, rearranging without activation to **22**, whose geometry is shown in Figure 3.

Thus with CI_0, all the rearrangements are predicted to occur via a common twist-boat biradicaloid intermediate **22**. Figure 4 indicates the form of the potential surface. This contains a large crater, corresponding to **22**, the transition states for the various reactions being the cols leading in and out of the crater. There are six of these in all, two corresponding to "chair" Cope transition states, two to "boat" Cope transition states, and the transition states leading to the degenerate isomers (cf. **11**, **12**) of **10**. The rates of the various reactions are determined solely by the energies of the various transition states. MINDO/3 predicts these to be in the order (**10** → **22**) < "chair" < "boat", in qualitative agreement with experiment.[7] Thus the interconversion of **11** and **12** takes place more rapidly than their conversion to **18**, and the Cope rearrangement of **1** takes place most easily by passage into, and out of, the **22** crater via the two "chair" transition states.

The energies of the "chair" and "boat" transition states (Figure 2) are correctly estimated, as is the activation energy for **10** → **22** (calcd, 28.1; obsd,[7] 35.0 ± 0.3 kcal/mol). The central C-C bond in the transition state for **10** → **22** (Figure 5) was calculated to be 2.23 Å, compared with a length of 2.87 Å in the twist boat **22**. The energy of **10** is certainly too low, owing probably to an underestimation of the strain energy in four-membered rings.[9]

It seems likely that the energy of the twist boat biradicaloid **22** (27.3 kcal/mol) is also too low. MINDO/3 allows for electron correlation via the parameterization of electron repulsion integrals, and it is therefore normally incorrect to include CI because this would lead to an overcompensation for correlation, and energies that are consequently too negative. It now seems that for "biradical" systems, the inclusion of CI_0 leads to energies that are too negative by ca. 15 kcal/mol.[25] We cannot therefore make any very definite predictions concerning the shape of the floor of the "biradicaloid crater". The distinction is fortunately of no chemical significance, since the overall reactions of **1** are independent of the floor of the crater. The errors in the calculated energies of **10** and the transition state for **10** → **22** appear to cancel to a large extent.

The Cope rearrangement of **1** therefore seems to differ significantly from any other pericyclic process we have so far studied. Some of these (e.g., the conversions of bicyclobutane to butadiene and of benzvalene to benzene) have indeed involved biradicaloids as stable intermediates, but these have had fixed geometries and electronic structures and have consequently been classifiable as homomers or lumomers of reactants and products. The stereochemical course of such reactions has therefore been controlled by the principles of orbital isomerism and the Woodward-Hoffmann rules, even though the reactions are not only not synchronous but not even concerted. In the Cope rearrangement of **1**, however, we have as a stable intermediate a complex of interconverting biradicaloids in which all memory of the orbital patterns in the reactant is lost. The stereochemistry of the reaction is controlled by the heights of the barriers separating the various reactants from this complex, and by the locking of stereochemistry of the 1 and 6 positions of **1** when it is converted into the intermediate biradicaloid, by formation of the new C_1C_6 bond. It is not in any way determined by the usual considerations of "allowedness" or "forbiddenness". Any such distinctions refer only to the interconversions of the various species inside the "biradical crater" and are therefore kinetically irrelevant. The Cope rearrangement of **1** indeed represents a new kind of isomerization which is subject neither to the principles of isomerism nor to the Woodward-Hoffmann rules. Here all HOMO/LUMO crossings, etc., occur inside a depression in the potential surface corresponding to a stable intermediate in the reaction, and the whole of this region is lower in energy than the barriers separating it from the various isomeric reactants. So far only one other reaction of this kind seems to have been recognized, i.e., the rearrangements of methylenecyclopropanes. Since these are unlikely to remain the only examples, it seems expedient to have some term for processes of this kind. The term "biradical reaction" would be inappropriate since, as we have seen, singlet biradicals cannot be stable species and the intermediates in these reactions are indeed biradicaloids, not biradicals. We therefore suggest that they be termed *biradicaloid reactions,* implying that they involve biradicaloid species as stable intermediates.

During the 20 months that have elapsed since this paper was submitted, McIver and Komornicki have published[26] full details of the calculations referred to in our ref 18. Since this work was carried out with an earlier version of MINDO and without CI their conclusions differ from ours.

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