

Table II. Dimer Orientations and Heats of Formation of Water-Acetaldehyde Dimers^{a,b}

R_{OO} , Å	θ_1 , deg	χ_1 , deg	χ_2 , deg	ΔH_F° kcal/mol
2.85	119	0	0	-88.3
2.65	119	0	0	-83.8
2.45	119	0	0	-76.6
2.86	123	0	180	-87.8
∞				-97.2

^a Heat of formation of water is -53.6 kcal/mol and heat of formation of acetaldehyde is -43.6 kcal/mol. R_{OO} is the distance between the oxygen atom of water and the carbonyl oxygen. θ is the angle between the internuclear line (x axis) and the principal axis of acetaldehyde. χ_1 and χ_2 measure the rotation of the molecules about their principal axes (see Figure 2).

author, we obtained a repulsion of 8.9 kcal which could not be reduced by varying the geometry (Table II). These results lead us to conclude that the MINDO/3 method is not suitable for the evaluation of hydrogen bonding and casts a serious doubt on the credibility of the numerous calculations that have been made with this method on intermolecular complexes.

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References and Notes

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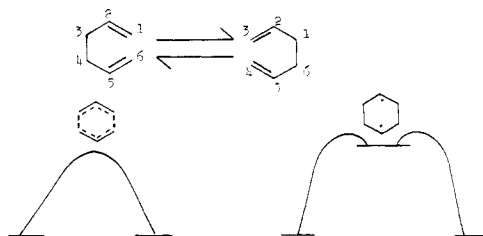
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On the Mechanism of the Cope Rearrangement

Sir:

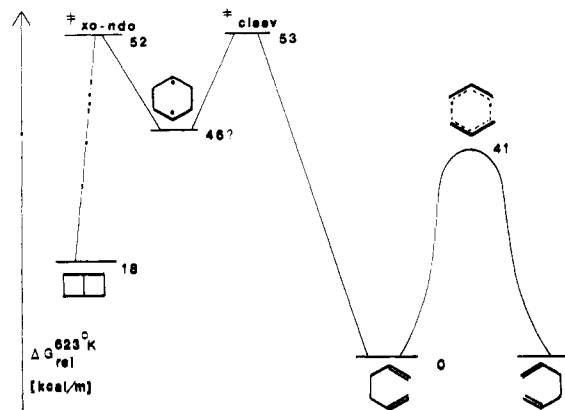
Despite intensive work,¹ the mechanism of the [3,3]-sigmatropic shift of 1,5-hexadienes remains unclear. At issue is whether it is a concerted process via a single transition state with partial bonding between C_1 and C_6 and between C_3 and C_4 or whether cyclohexane-1,4-diyl (a biradicaloid) is an intermediate.

The latter alternative, suggested by Grob^{2a} and by Doering,^{2b} is supported both theoretically by MINDO calculations³ and McIver's rules⁴ and experimentally by a constant multiplicative rate increase upon 2-phenyl and 2,5-diphenyl substitution.⁵ However, the experimental observations could equally well be due to a change in a single transition state toward a diyl-like species.



Unfortunately, the elegant stereochemical studies of Doering and Roth⁶ and of Hill⁷ are consistent with both alternatives; these results require a chair-like arrangement of six carbons in the lowest energy pathway. The single-stage concerted path should proceed suprafacially (or antarafacially) on both allylic moieties according to the orbital symmetry conservation principle,⁸ and secondary considerations favor the chair over the boat.⁸ On the other hand, the diyl is apparently generated in the thermal isomerization of bicyclo[2.2.0]hexanes (BCH) to 1,5-hexadienes, and the stereochemistry observed is consistent with least-motion cleavage of a chair-like cyclohexanediyl.^{9,10}

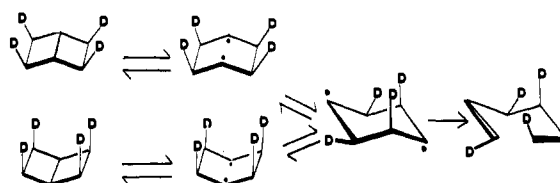
We wish to point out that, if the cyclohexanediyl is involved in the cleavage of BCH, as experiment and MINDO calculations suggest, then it is not accessible in the 3,3 shift of 1,5-hexadiene by 12 kcal/mol. Using Goldstein's values for the heats of formation and entropies of the relevant species at 250 °C,^{9c} BCH is 18 kcal/mol less stable (in free energy) than 1,5-hexadiene. The transition state for BCH cleavage, which is that for cleavage of the diyl, is 53 kcal/mol above 1,5-hexadiene. The low-energy 3,3-shift transition state is only 41 kcal/mol above 1,5-hexadiene.



The thermochemistry therefore indicates that the diyl, regardless of its stability, is insulated from the low-energy 3,3-shift energy surface by a kinetic barrier 12 kcal/mol above the actual transition state, which, by elimination, is that for the single-stage concerted route.

Evidence that the diyl is involved in the BCH cleavage comes from the work of Goldstein who demonstrated that exo-endo isomerization of 2,3,5,6-tetradeuterio-BCH occurs at the same rate as cleavage to 1,5-hexadiene.¹⁰ This geometric isomerization would appear to involve central bond rupture to a boat diyl which flips through the chair diyl to the boat again. The cleavage presumably proceeds from the chair diyl as even the MINDO calculations suggest.^{3a}

Just why the MINDO calculations lead to a prediction of inordinate stability for the diyl or why McIver's rules based



on transition state theory lead to the postulate of the diyl as an intermediate must be addressed by their proponents. It may be conceivable that a symmetrical, delocalized species is an intermediate in the 3,3 shift, but this would represent a unique situation not previously considered in hydrocarbon thermal isomerizations.

It should also be noted that MINDO calculations¹¹ and McIver's rules¹² predict an unsymmetrical transition state in the Diels-Alder reaction, but Thornton's multiplicative deuterium kinetic isotope effects in a retro-Diels-Alder reaction suggest a symmetrical transition state.^{13,14}

Finally, the notion that substitution at various positions can alter the geometry of the transition state in any 3,3 shift is an important one which rationalizes not only the increase in rate of 2- and 2,5-phenyl materials but the rate increases owing to substitution at C₃ and C₄. These transition-state changes are also reflected by secondary deuterium kinetic isotope effects.^{15,16}

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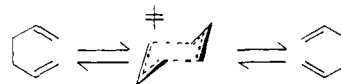
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Variable Transition-State Structure in the Cope Rearrangement as Deduced from Secondary Deuterium Kinetic Isotope Effects

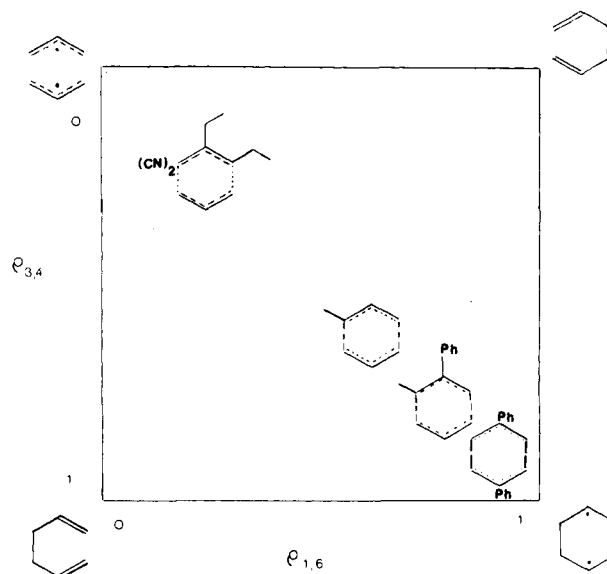
Sir:

An accompanying communication demonstrates that the 3,3 shift in 1,5-hexadiene (the Cope rearrangement) does not proceed via cyclohexane-1,4-diyl, but by the only alternative yet proposed, namely, a concerted reaction via a single transition state in which there is partial bonding between C₁ and C₆ and between C₃ and C₄.¹ While the gross geometry of this transition state has been demonstrated by Doering and Roth and by Hill to be a "chair",² the question of the magnitude of



the partial bonds between the allylic moieties still must be resolved. While we cannot answer this question in an absolute sense, previous work with substituted materials, herein further elaborated with secondary deuterium kinetic isotope effects (KIE's), suggests a dramatic change in the magnitudes of these partial bonds as a function of substituents.

It is well known that good radical-stabilizing substituents not only on C₃ and C₄ but on C₂ and C₅ of 1,5-hexadiene accelerate the rate of the 3,3 shift.⁴ In the former case the rate response suggests that the transition state more resembles two allyl radicals, while in the latter case it more resembles cyclohexane-1,4-diyl. Indeed, these two extremes represent, to a first approximation, the range of transition-state structures available to the 3,3 shift.^{4b} These two extremes represent a range of weak to large coupling of two allyl radicals. A convenient representational device to depict this range of transition-state structures is a More O'Ferrall-Jencks diagram⁵ whose structural axes are the C₁-C₆ and the C₃-C₄ bond orders.^{4b,6} The free-energy coordinate might be represented by contours which are best not included for sake of clarity. However, the relative free energies of the extremes with respect to 1,5-hexadiene, at 200 °C, can be guessed to a crude approximation from group additivities.⁷ It is also true that the transition-state free-energy for diyl cleavage is 53 kcal/mol above 1,5-hexadiene,¹ so a high-energy ridge surrounds the diyl but the exact location of the ridge is unknown.



Within the context of this diagram and discussions surrounding it, stabilization of either of the radical extremes should draw the transition-state structure toward the more stable alternative,⁵ and so secondary deuterium KIE's, which respond primarily to changes in force constants which to first approximation reflect bonding changes, ought to reveal these changes.⁸

The KIE's at C₄ and C₆ in the irreversible rearrangement of a 1,2-dialkyl-3,3-dicyano-1,5-hexadiene have been determined, and the normal KIE at C₄ is three times the inverse KIE at C₆.⁹ In work described below the normal KIE at C₃ and C₄ in nearly unperturbed acyclic systems is roughly one half to two thirds that of the inverse KIE at C₁ and C₆, while in 2-phenyl-1,5-hexadiene the normal KIE at C₃ and C₄ is roughly one third of the inverse KIE at C₁ and C₆. Finally, the normal KIE at C₃ and C₄ of 2,5-diphenyl-1,5-hexadiene is roughly one eighth of the inverse KIE at C₁ and C₆. Thus the transition-