

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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- (16) With good radical stabilizing substituents at C₂ and C₅ of 1,5-hexadiene, thermochemical estimates similar to those above suggest that a cyclohexane-1,4-diyl might be accessible in the 3,3 shift.

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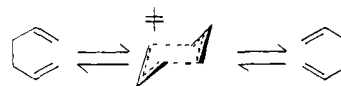
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Variable Transition-State Structure in the Cope Rearrangement as Deduced from Secondary Deuterium Kinetic Isotope Effects

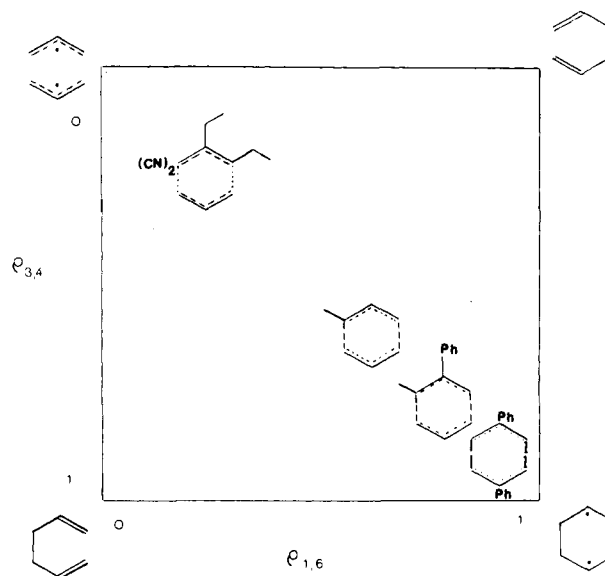
Sir:

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



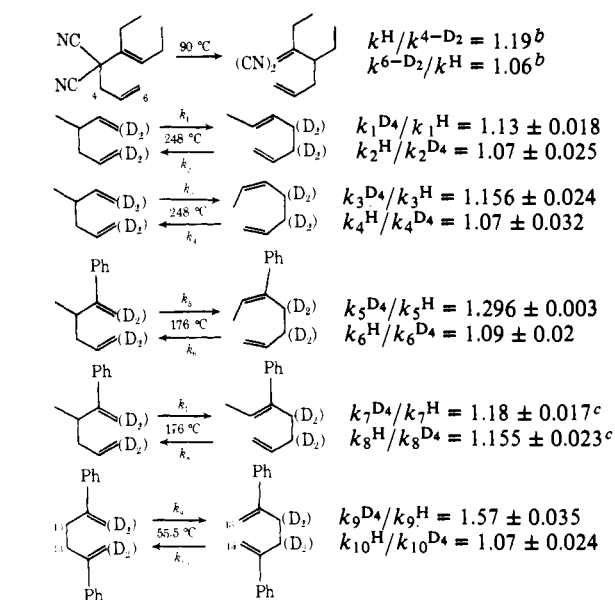
the partial bonds between the allylic moieties still must be resolved. While we cannot answer this question in an absolute sense, previous work with substituted materials, herein further elaborated with secondary deuterium kinetic isotope effects (KIE's), suggests a dramatic change in the magnitudes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

Table I. Secondary Deuterium KIE's in Various 3,3 Shifts^a

state structures, as deduced by changes in the relative KIE's, vary as predicted above.¹⁰

The KIE's are shown in Table I; the rate constants for the three-component reversible reactions were determined by a SIMPLEX^{11a,b} fit to the data using the integrated rate expressions of Frey and Solly.^{11c} Each reaction was sampled roughly 12 times and each sample was analyzed at least 4 times using GC and an electronic integrator giving reproducibility of $\pm 1\%$. The diphenyl-1,5-hexadiene reaction was monitored by HR-220 ¹H NMR spectroscopy which gave reproducibility in integrations of $\pm 1\%$.

Since no functional relationship between secondary KIE's and bond-order changes is available, the absolute location of the various transition states on the diagram are unknown. However, if the relationship is nearly linear,¹³ then the behavior of most degenerate 3,3 shifts can be reasonably rationalized,¹⁴ recognizing that the transition states should resemble the nonconcerted alternative, i.e., two allyl radicals or cyclohexane-1,4-diyl, that is more stable.

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- Clearly other bond orders are changing beside those of the diagram, although the total bonding at C₂ and C₅ as measured by secondary deuterium KIE's at these sites does not appear to change; i.e., *meso*-3,4-dimethyl-1,5-hexadiene-2,5-d₂ reacts only $1.5 \pm 0.5\%$ slower than the protio material.
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$$-\ln(A - A_e)/(A_0 - A_e) = (k_f + k_b)t$$

- While we realize that a complete force-field analysis is useful in more carefully assigning the origin and magnitudes of these KIE's and that KIE's are not necessarily simply related to the bond orders in question, most literature suggests that our assumption is a reasonable starting point for more detailed analysis.
- For instance, the entropy of activation of acyclic boat 3,3 shifts is much less negative than chair 3,3 shifts,¹⁵ indicating that the transition state is looser and more two-allyl radical-like; this is because the boat-like diyl should be 5–10 kcal/mol less stable than the chair-like diyl, while the relative stabilities of the two allyl radicals in boat and chair geometries should be much less affected. The full paper will consider the myriad of other observations which are rationalizable in this framework.
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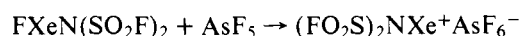
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An Unusual Xenon Cation Containing Xenon–Nitrogen Bonds

Sir:

The earlier synthesis of $\text{FXeN}(\text{SO}_2\text{F})_2^1$ from XeF_2 and $\text{HN}(\text{SO}_2\text{F})_2$ demonstrated that xenon was capable of forming bonds to elements other than oxygen and fluorine under ordinary laboratory conditions. Since this report there have been no further examples of new compounds of this type. We have been working to provide additional examples of xenon–nitrogen bonds and to prepare the first xenon–carbon bond. Recently, we have been successful in the preparation of several new xenon–nitrogen species, thus eliminating the possibility that $\text{FXeN}(\text{SO}_2\text{F})_2$ is unique. This work describes one of these new compounds, an unusual complex salt containing a dinuclear xenon cation with xenon–nitrogen bonds.

After the synthesis of $\text{FXeN}(\text{SO}_2\text{F})_2$, we looked for ways to further identify the xenon–nitrogen bond. Because the xenon–fluorine bond in $\text{FXeN}(\text{SO}_2\text{F})_2$ appears to be very similar to that in XeF_2 , the canonical form $\text{FXe}^+\text{N}(\text{SO}_2\text{F})_2^-$ does not appear to dominate the bonding. It therefore seemed reasonable that $\text{FXeN}(\text{SO}_2\text{F})_2$ might react with a strong Lewis acid, such as AsF_5 , in the following way:



A 1:1 adduct is indeed formed, but it is unstable and we have been unable to determine its structure. We have found that the