served isotope effects are consistent with neither the diradical nor the diyl picture.

It is desirable to relate the α and γ effects to the degree of bonding between C_α and O and between C_γ and C_{ortho} in the transition state. If a linear[11] relationship between isotope effect and bond order is assumed, then these results imply a bond order of ~0.23-0.43 for the C_α-O bond and bond order of 0.22-0.62 for the C_γ-C_{ortho} bond. Using this approach a transition state structure in which bond making and bond breaking have proceeded to the same extent cannot be excluded, but a "looser" transition state structure,[12,13] one in which bond breaking has proceeded to a greater extent than bond making, seems more consistent with this work, as well as with the earlier kinetic and stereochemical results.[3,4] In this picture, the lag of bond making relative to bond breaking is responsible for a major portion of the activation energy. An alternative, significantly nonlinear relationship between isotope effect and bond order suggested by Humski, Malojčić, Borčić, and Sunko,[14] would suggest a tighter transition state, in which both the C_α-O and C_γ-C_{ortho} bond orders are greater. Quantitative information with which to refine and evaluate these approaches is not yet available, but we prefer the linear assumption for its simplicity and its qualitative consistency with the stereochemical evidence.

Further, the direct evidence that we have obtained for a concerted transition state structure is entirely consistent with the interpretation of solvent and substituent effects advanced by Rhoads.[15] Such a concerted transition state structure would be expected to change as substituent electronic demands are varied, leading to insensitivity to polar substituent effects and curvature in attempted linear free-energy correlations.[16]

Finally, it is instructive to compare these results with those of Gajewski and Conrad for the rearrangement of allyl vinyl ether.[10] Their results support an early transition state for that exothermic reaction. Our results support a later transition state for a rate-determining step which is endothermic by some 3-5 kcal/mol.[17] This pattern is consistent with Hammond postulate[19] (parallel effect)[20] predictions. Comparison with other hetero-Cope processes is deferred to the full paper.

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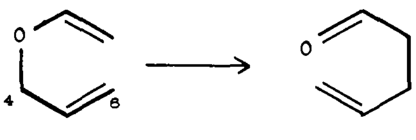
Aliphatic Claisen Rearrangement Transition State Structure from Secondary α-Deuterium Isotope Effects

Sir:

In a previous paper[1] it has been demonstrated that the secondary α-deuterium kinetic isotope effects on bond breaking and bond making in the all-carbon 3,3-sigmatropic (Cope) rearrangement vary relative to one another as a logical function of substitution.[2] Thus, the transition state structure for nearly degenerate 3,3 shifts resembles either two allyl radicals or cyclohexane-1,4-diyl depending on whether radical stabilizing substituents are on C_3 and C_4 or on C_2 and C_5, respectively.

The 3,3 rearrangement of allyl vinyl ether (AVE) presents a more difficult problem since the reaction is highly exothermic (17 kcal/mol),[3] a worthwhile characteristic of a useful reaction whose stereospecificity,[4] though not so high as the Cope rearrangement,[5] makes it a powerful synthetic tool.[6] The lower preference for chair over boat transition states in the aliphatic Claisen rearrangement relative to the Cope rearrangement has been attributed[4] to the exothermicity which requires that the transition state more resemble reactant than product (the parallel[2] or Hammond postulate effect[7]). Remaining questions about the rearrangement concern the effect of substituents at various positions which, in turn, require information about the transition state, specifically the extent of bond breaking and bond making. We here report that the KIE's at C_4 and C_6 in the 3,3 shift of 3-oxa-1,5-hexadiene (AVE) reveal that indeed the transition state "comes early" and that it involves much more bond breaking than making in contrast to the all-carbon 3,3 shift of relatively unperturbed 1,5-dienes.[1]



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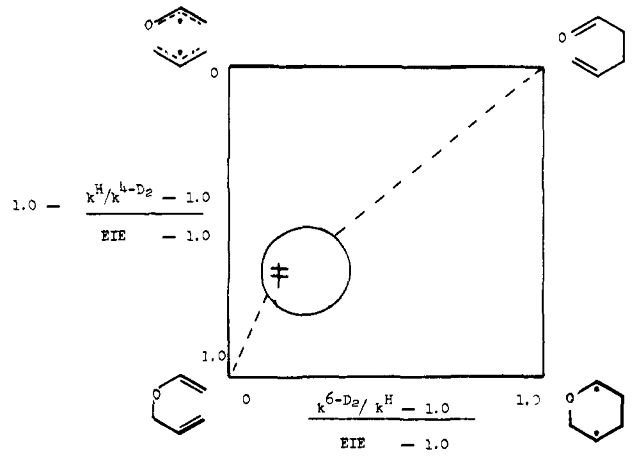
$$k^{H}/k^{4\text{-}D_2} = 1.092 \pm 0.005$$

$$k^{6\text{-}D_2}/k^{H} = 1.025 \pm 0.005$$

At 160.3 °C the normal KIE at C_4 is 1.092 ± 0.005 and the inverse KIE at C_6 is 1/1.025 ± 0.005.[8] It is meaningful to compare these KIE's with the maximum possible KIE's at each site which are the appropriate equilibrium IE's—provided that coordination number changes and electronegativities alone are responsible for the KIE's as they are in the EIE's.[12] Since the EIE's cannot be determined in the actual system, the C_6 KIE should be compared with the EIE for fractionation of deuterium between an *exo*-methylene and a saturated methylene flanked by two carbons; for two deuteriums this is 1.16 at 160 °C.[9,10] The EIE of deuterium between *exo*-methylene and a saturated carbon flanked by one carbon and one oxygen is 1.27 ± 0.03 determined from the equilibrium constant for allyl acetate-α,α-γ,γ-d_2 interconversion catalyzed by mercuric acetate at 160 °C.[10,11,17]

The ratio of the KIE to the EIE at the bond breaking site is (1.09–1.0)/(1.27–1.0) or ⅓, while that at the bond making site is only (1.025–1.0/1.16–1.0) or <⅙. A More O'Ferrall–Jencks diagram[13] for the AVE rearrangement using these IE ratios as coordinates[14] is shown in Scheme I where it is clear that the transition state is "early" presumably because of the exothermicity of the reaction.[7]

Scheme I



Since the AVE 3,3 shift involves more bond breaking than making, it appears that the bond-breaking alternative is more stable than the bond-making alternative. An estimate[15] of the relative free energies of the two nonconcerted extremes indicates that the former is more stable than the latter by ~7 kcal/mol primarily because of the greater entropy of the former.

Interestingly, the entropy of activation for the AVE rearrangement is less negative than for the Cope rearrangement,[16] suggesting more bond breaking than making in the former relative to the latter which is consistent with the isotope effects and the analysis of the relative energies of the nonconcerted alternatives.

Finally, the transition state structure suggests that radical stabilizing substituents on C_1, C_4, and C_6 will stabilize the transition state to a greater extent than placement of the same substituents on C_2 and C_5. The relative rates of reaction will, of course, depend on relative transition state and ground state stabilities.[17]

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Structure and Stereochemistry of Officinalic Acid, a Novel Triterpene from *Fomes officinalis*

Sir:

Fomes officinalis is a wood-rotting fungus which is found on the trunks of living or dead coniferous trees in the Pacific Northwest United States, Canada and in Europe.[1] A variety of triterpenes from this fungus[2] have been characterized since it was first studied in 1804.[3] Officinalic acid[4] ($C_{30}H_{44}O_6$, mp 272 °C, $[\alpha]_D$ −60° (c 0.5, dioxane)[5] is the trivial name assigned to a plentiful constituent (1.5% by weight) obtained from ether extracts of the ground mycelium.

In addition to bicarbonate solubility **1a** was characterized as a carboxylic acid by conversion (CH_2N_2) to a monomethyl ester, **1b** ($C_{31}H_{46}O_6$, HR, mp 236 °C, $[\alpha]_D$ −54 ° (c 0.15 dioxane)), and by its IR spectra (**1a**, 3210, 1730, 1709 cm^{-1}; **1b**, no OH, 1736 cm^{-1}). The presence of three carbonyls was established by the ^{13}C NMR spectrum of **1b** ($CDCl_3$) (δ 205.3, 172.6, 168.5). Compound **1b** was inert to monoperphthalic and m-chloroperbenzoic acids, gave negative unsaturation tests, and showed only a single ^{13}C NMR peak at δ 105.3 which is assigned to a ketal carbon with nothing further in the δ 100–150 region.

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