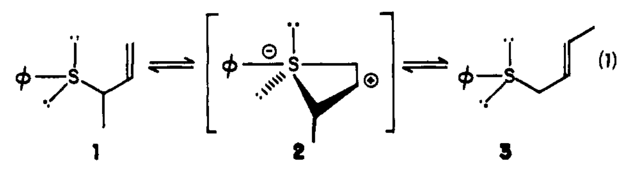
Secondary Deuterium Isotope Effects in the Thia-allylic Rearrangement

Sir:

An associative transition state has been deduced[1] from measurements of the sulfur (heavy atom) isotope effect in the thia-allylic rearrangement.[2] In this reaction mechanism an intermediate (possibly represented by **2**) is formed in which the central sulfur assumes a hypervalent state through electron donation from the allylic double bond, thus creating a TBP (or equivalent)[3] structure.

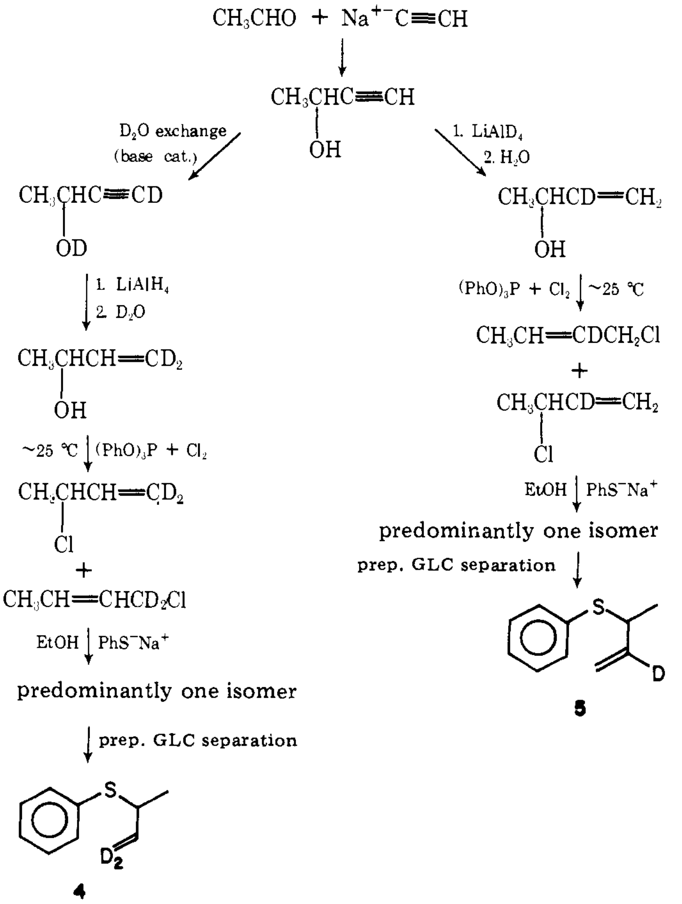


A second criterion of transition-state structure, the secondary deuterium isotope effect,[4] has now been applied in the effort to realize further clarification of the structural features of intermediate **2**. For this purpose the γ and β deuterated analogues of α-methylallylphenyl sulfide, **4** and **5**, respectively, were synthesized by the methods outlined in Scheme I.

Thermolysis of an ~50-50 mixture of **4** and the undeuterated substrate **1** for varying extents of reaction in a degassed decalin solution and analysis of the deuterium content of the isolated product by means of the recently developed high-precision mass spectrometric method[1] afforded the data plotted in Figure 1. Since this is an equilibrium reaction, an extrapolation to zero time was carried out in accordance with common practice[1,5] to arrive at the experimental value $(k_H/k_D)_\gamma = 0.936 \pm 0.004$ per deuterium.

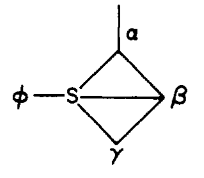
An inverse secondary deuterium isotope effect of this magnitude[6] clearly signifies that the terminal carbon has achieved a large measure of sp^3 character in the C-S bond-forming transition state leading to the intermediate **2**. This, moreover, is in full agreement with the conclusion reached previously through measurement of the heavy atom isotope effect.[1] It compares well with $k_H/k_D = 0.908$ (65 °C) reported by Baldwin[7] for C-C bond formation in the transition state of a cyclobutane ring closure in the addition of styrene to diphenylketene.

Scheme I



To estimate the corresponding degree of bonding at the β carbon of the allyl side chain, a degassed mixture of **5** and **1** (~50:50) was analogously thermolyzed. Applying the same graphical method of analysis[1,5] to the data calculated from determinations of the deuterium content of product samples isolated after each of three different intervals of reaction at 198 °C, the value of $(k_H/k_D)_\beta = 0.918 \pm 0.015$ was obtained. This result suggests that the TBP-structured intermediate must be amended to allow for considerable increase in covalency at the β-allylic carbon from what is represented by **2**.

Since the isotope effects at the β and γ positions are so similar, it can be inferred that in the transition state there is little difference in the strengths of the bond between the central sulfur atom and the β- and γ-allylic carbons. However, though this provides support for representing the hypervalent intermediate in the thia-allylic rearrangement as **6**, it must not be assumed that the C$_\beta$-S bond is a normal covalency. Kinetic studies[8a] have shown a significant degree of charge development and polarizability in this bond; this is consistent with solvent-rate and activation effects that are correlated with variations of the substituent on the phenyl ring and at the β carbon.[8]



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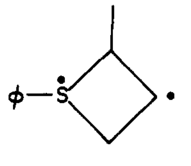

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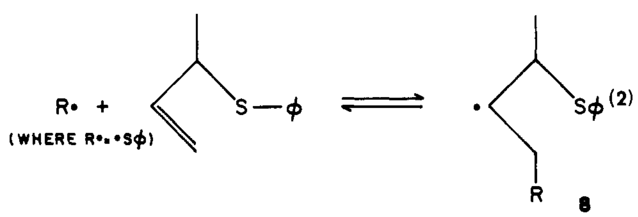
Another point of interest arises in connection with the magnitude of $(k_H/k_D)_\beta$. In radical additions at olefinic centers the carbon developing the new radical function shows no secondary deuterium isotope effect ($k_H/k_D \approx 1.0$)[9] and appears to retain the same degree of bonding in the activated complex. Thus, the large inverse value of $(k_H/k_D)_\beta$ would tend to exclude any radical structure resembling **7** as an intermediate in the thia-allylic rearrangement.[10] Radical chain mechanisms, such as that expressed by eq 2, in which the intermediate **8** is formed in the rate-determining step, are also eliminated by this criterion. Though an intermediate like **8** has been previously proposed[11-14] for thiyl radical catalyzed alkylallyl sulfide rearrangements, other evidence[15] in addition to the inverse value of $(k_H/k_D)_\beta$ makes **8** highly unlikely in the thermal rearrangement of arylallyl sulfides.[2,10] Furthermore, the rearrangement (neat) at room temperature in the presence of light[2,10] is also characterized by an inverse $(k_H/k_D)_\gamma$,[16] suggesting that the photocatalyzed isomerization travels a path which is parallel to that of the thermal reaction. This behavior has the appearance of a crossing from a low-lying electronic to a vibrationally excited ground state of the reactant, which



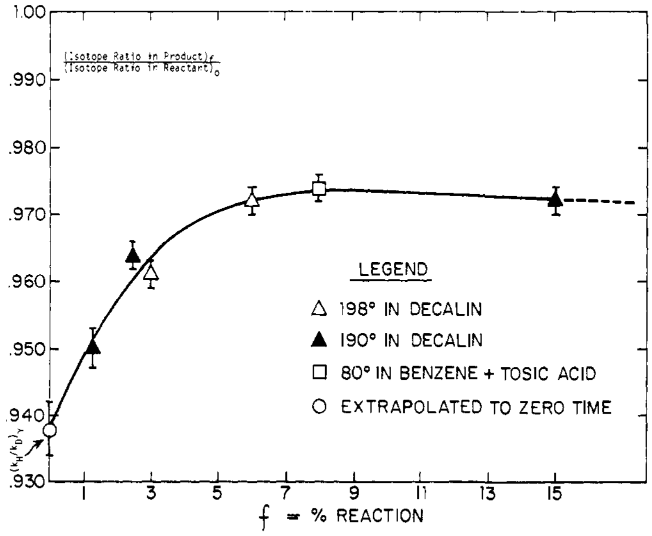
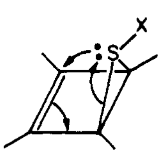


Figure 1.

then undergoes the same associative rearrangement mechanism as the purely thermal process.[17]

Acid catalysis of the thia-allylic rearrangement has also been observed by others.[10,18] The mechanism advanced,[10] namely, dissociation to an allyl cation following protonation of the central sulfur, is susceptible to the secondary deuterium isotope test. When an ~50:50 mix of **4** and **1** was rearranged in a degassed benzene solution containing tosic (*p*-toluenesulfonic) acid at 80 °C, the $(k_H/k_D)_\gamma$ value was virtually identical with that obtained for the uncatalyzed reaction (see Figure 1). This result renders an allylic cation intermediate[10] untenable. Furthermore, it reinforces the concept[1,8,15,19] that all thia-allylic rearrangements proceed through octet expansion of sulfur in various states of hypervalency, some created through the agency of catalysis[15,19] involving some form of coordination of sulfur by the catalytic species.

A pertinent case in point is concerned with the proposal[20] of a concerted, pseudopericyclic process of thia-allylic rearrangement of the allylic sulfide, represented by **9**. Thus, the



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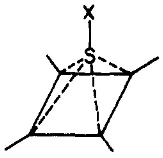

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rapid isomerization reaction, which is detected by fluctional behavior in the NMR has been justified by quantum mechanical considerations.[21] This picture was preferred to an associative intermediate **10** with permutational isomerism, arising out of the octet-expanding abilities of the central sulfur. At first glance **10** might appear to involve an intolerable degree of strain. We submit, however, that this square pyramid (sp) structure, though bound at each of its basal vertices, is made more credible as an isomerization intermediate by the evidence presented here in support of the thiacyclobutane structure **6** in the usual thia-allylic process. Moreover, the ~12-kcal lowering of the activation energy for automerization[20,21] in **9** occasioned by the change from sulfide to sulfoxide (X = lone pair to X = oxygen) is made more understandable as a consequence of the lowering of the barrier to pseudorotation associated with increased hypervalency of the sulfur.[22] If the unshared pairs on sulfur played a decisive role in the automerization process, as postulated[20,21] in the pseudopericyclic rearrangement mechanism, this large activation energy difference is not easily explained.

References and Notes

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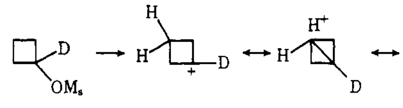

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(22) Unpublished results of D. Benko from these laboratories indicate that aryl allyl sulfoxides undergo thia-allylic rearrangement by a process analogous to that experienced by aryl allyl sulfides.

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Anomalously Intense Raman Spectra of Pyridine at a Silver Electrode

Sir:

Raman spectra of pyridine adsorbed at a silver electrode which had previously been roughened by repeated electrochemical cycling have already been reported by Hendra and coworkers.[1,2] The purpose of this communication is to report that the Raman spectra of pyridine at a silver electrode, after a single oxidation-reduction cycle and particularly when recorded during and immediately after the cycle, are remarkably and anomalously intense. As an indication of the extent of this intensity enhancement the Raman signals that we observed from the ring-stretching modes of surface pyridine were roughly five times the corresponding signals from pure liquid pyridine in a conventional multipass optical cell, and they saturated the detection system of our spectrometer for an incident laser power of only 15 mW (514.5 nm) and 4-cm^{-1} slits! The resulting high signal/noise ratio enables the intensities of bands due to pyridine at different types of surface site to be readily measured. This letter thus also presents preliminary results on the variation in intensity of the 1025-cm^{-1} band of