

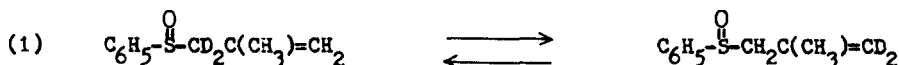
THERMAL (1,3)-ALLYLIC REARRANGEMENTS IN SULFOXIDES AND SULFONES

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Abstract Rates and activation parameters for thermal (1,3)-allylic rearrangement have been determined for the systems β -methylallyl phenyl sulfoxide (2) and the corresponding sulfone (3), with evidence presented for a dissociative reaction mechanism.

Considerable effort has been directed recently toward exploring the synthetic applications of (1,3)-allylic rearrangements in sulfur systems.¹ The nature of the rearrangement reaction in simple allyl aryl sulfides has been extensively investigated with evidence presented in support of either a dissociative, radical chain mechanism² or an associative rearrangement mechanism involving ligand stereomutation in a cyclic, trigonal-bipyramidal intermediate.³ No comparable mechanistic studies of the (1,3)-allylic rearrangement in simple acyclic sulfoxides or sulfones have been described, although there have been several recent observations of thermal (1,3)-rearrangements in cyclic unsaturated sulfoxides. These include the perfluorotetramethyl Dewar thiophene-S-oxide system, for which a concerted "pseudopericyclic" mechanism has been proposed,⁴ and the 9-thiabicyclo[4.2.1]nona-2,4,7-triene-9-oxide system, for which a radical dissociation process has been suggested.⁵

As a result of the present investigation, we are able to report the first direct comparison of the relative rates and activation parameters for thermal (1,3)-allylic rearrangement in a structurally related set of compounds consisting of a sulfide, a sulfoxide and a sulfone. The β -methylallyl phenyl system was selected for this comparative study. Kwart has reported^{3a} that β -methylallyl phenyl sulfide (1) undergoes thermal (1,3)-allylic rearrangement by a unimolecular process in nitrobenzene. We have found that the corresponding β -methylallyl phenyl sulfoxide (2) and sulfone (3) systems also undergo the thermal (1,3)-rearrangement by first-order processes in nitrobenzene solutions. To facilitate kinetic analysis, samples of 2 and 3 were selectively deuterated at the α -allylic position via base catalyzed hydrogen/deuterium exchange using potassium *tert*-butoxide in *tert*-butanol-0-d and tetrahydrofuran at -40°. The rate studies were performed using degassed solutions in sealed sample tubes, and the reactions, depicted in equation 1 for the sulfoxide, were readily monitored by ¹H-nmr analysis of the signal intensities in the α (δ 3.4 in 2, δ 3.8 in 3) and γ (δ 4.9 in 2 and 3) spectral regions. The results established that the reactions are cleanly first-order, allowing rate constants to be determined⁷ for the sulfoxide at temperatures of 110, 120 and 130° and for the sulfone at temperatures of 150, 160 and 170°. The comparative data are summarized in Table I.



The relative reaction rates at 150° reveal that for this particular system, susceptibility toward (1,3)-allylic rearrangement increases progressively from the sulfone (3) through the sulfoxide (2). However, the rather narrow span in rates is noteworthy in view of the following evidence which suggests that the sulfide (1), which is intermediate in reactivity, undergoes rearrangement by an entirely different mechanism than that which appears to be involved in the

Table I. Rate Constants and Activation Parameters for (1,3)-Allylic Rearrangement in β -Methylallyl Phenyl Sulfide (1), Sulfoxide (2) and Sulfone (3).

Compound ^a	Rate Constants $\times 10^5, \text{sec}^{-1}$ at 150°C	Relative Rates at 150°C	ΔG^\ddagger kcal/mol at 150°C	ΔH^\ddagger kcal/mol	ΔS^\ddagger cal/mol·K
1 $\text{C}_6\text{H}_5\text{SCH}_2\text{C}(\text{CH}_3)=\text{CD}_2$	6.7 ^b	1.7×10	33.3 ^b	27.7 ± 0.9^c	-13.3 ± 2.2^c
2 $\text{C}_6\text{H}_5\text{S}(\text{O})\text{CD}_2\text{C}(\text{CH}_3)=\text{CH}_2$	69. ^d	1.8×10^2	31.4 ^d	36.6 ± 1.3^e	$+12.4 \pm 3.2^e$
3 $\text{C}_6\text{H}_5\text{S}(\text{O}_2)\text{CD}_2\text{C}(\text{CH}_3)=\text{CH}_2$	0.39 ^f	1.0	35.7 ^f	44.4 ± 4.2^g	$+20.5 \pm 9.7^g$

^a Solvent, nitrobenzene- d_5 . ^b Calculated from values reported^{3a} for ΔH^\ddagger and ΔS^\ddagger .

^c Temperature range, 147-177°C. ^{3a} ^d Calculated from values for ΔH^\ddagger and ΔS^\ddagger .

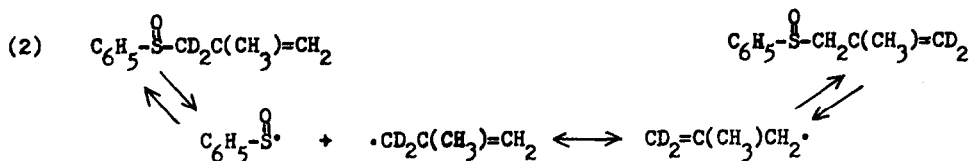
^e Temperature range, 110-130°C. ^f Experimental value at 150°C.

^g Temperature range, 150-170°C.

case of the sulfoxide and sulfone. (a) The negative activation entropy, ΔS^\ddagger , observed for the sulfide supports the proposed^{3a} associative reaction mechanism, whereas the distinctly positive ΔS^\ddagger values for the sulfoxide and sulfone suggest a dissociative process. (b) In sulfides, substitution of a methyl group at the β -allylic position has been found^{3a} to lower the activation enthalpy, ΔH^\ddagger , for rearrangement more effectively than α -methyl substitution, which is in accord with the charge development implied by the proposed reaction intermediate. In marked contrast, α -methyl substitution is far more effective than β -methyl substitution at enhancing the reactivity of allylic sulfoxides toward (1,3)-rearrangement. We have found that α -methylallyl phenyl sulfoxide⁸ undergoes allylic rearrangement to crotyl phenyl sulfoxide at temperatures above 70°, although accompanying decomposition prevented careful kinetic analysis. Moreover, α,α -dimethylallyl phenyl sulfoxide has been reported^{1a} to undergo the (1,3)-rearrangement readily at 40°.⁹ Even more dramatic is the recent report¹⁰ that cinnamyl phenyl sulfenate undergoes a rapid transformation at room temperature to the isomeric cinnamyl phenyl sulfoxide, suggesting that an intermediate α -phenylallyl phenyl sulfoxide (generated by (2,3)-sigmatropic rearrangement) undergoes a (1,3)-allylic rearrangement so rapidly as to preclude the direct spectral detection of the intermediate. (c) In the allylic sulfides, a polar solvent, such as nitrobenzene, was required in order to observe simple first-order kinetics. In less polar solvents, such as *o*-dichlorobenzene and decalin, competing unimolecular and bimolecular reaction mechanisms were encountered.^{3a} We have found that in toluene- d_8 solution, β -methylallyl phenyl sulfoxide (2) undergoes the (1,3)-rearrangement in a clean, first-order manner, with rate constants and activation parameters ($\Delta H^\ddagger = 35.2 \pm 0.8$ kcal/mol; $\Delta S^\ddagger = +10.6 \pm 2.2$ cal/mol·K) very similar to those obtained in nitrobenzene- d_5 .

A simple mechanistic interpretation consistent with the above observations is that allylic sulfoxides, such as 2, undergo thermal (1,3)-rearrangement by a homolytic dissociation-recombination process involving the formation of relatively stable allyl and arylsulfinyl radicals. This process, depicted in equation 2, would account for the positive activation entropy, dramatic rate acceleration upon substitution at the α -allylic position, and relative insensitivity to changes in solvent polarity. It is also noteworthy that the thermal racemization of benzyl aryl sulfoxides in the temperature range 130-160° has been explained on the basis of a radical

dissociation mechanism.¹¹ Such a dissociative process is also compatible with a recent study of a sulfoxide rearrangement employing heavy atom, kinetic isotope effects.¹²



The somewhat higher activation enthalpy observed for 3, together with the positive activation entropy, suggest that a homolytic dissociation mechanism may be operating in the sulfone system also. The fact that rearrangement occurs almost as readily in the sulfone as in the sulfoxide demonstrates conclusively that a pseudopericyclic mechanism⁴ requiring a valence shell non-bonding electron pair on sulfur can not be involved. However, any further conclusions regarding the nature of the thermal (1,3)-allylic rearrangement in sulfones must be viewed with some reservation at this time. Since compound 3 is the first sulfone subjected to a thorough kinetic analysis of the rearrangement process, no comparative information is available regarding the effect of structural modifications upon the facility of the reaction. Moreover, we have encountered an unanticipated complexity in our investigation of β -methylallyl phenyl sulfone. In contrast to the sulfoxide (2), a change in reaction solvent from nitrobenzene to toluene resulted in a rate acceleration at 150° of over 100-fold for the sulfone. Furthermore, when the kinetic studies were extended to the lower temperatures of 130 and 140°, pronounced deviations were observed from the linearity expected for a first-order process. This mechanistic complexity in the sulfone system appears to be somewhat reminiscent of that previously encountered^{3a} when the reactions of allylic sulfides were studied in non-polar solvents. Although it might be possible to rationalize the observed deviations from first-order behavior by suggesting contributions from a dissociative radical chain reaction pathway, further speculation regarding the rearrangement of allylic sulfones in non-polar solvents is not justified at this time.

A further conclusion which may be drawn from the results provided by this study is that thermal (1,3)-allylic rearrangement involving sulfur in any of the three oxidation states represented by the series 1 - 3, occurs with considerably more ease than in related phosphorus systems, where evidence substantiates the thermal stability of allylic phosphines¹³ and phosphine oxides¹⁴ at temperatures over 200°.

Acknowledgment The financial support of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged. We also thank Margaret Blohm for assistance with some of the kinetic measurements.

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 6. The samples of β -methylallyl phenyl sulfoxide (2) and sulfone (3) were both prepared by oxidation of the corresponding sulfide (1) with *m*-chloroperbenzoic acid in dichloromethane at -70° , using somewhat less than one equivalent of the oxidant for the sulfoxide synthesis and somewhat more than two equivalents of oxidant for the sulfone synthesis. The products, 2 and 3 respectively, were purified by column chromatography on silica gel followed by low temperature crystallization.
 7. The first-order rate constants were determined by linear regression analysis of individual kinetic runs consisting of between 12 and 20 data points and extending through at least four half-lives. A correlation coefficient of at least 0.99 was obtained in every case.
 8. The α -methylallyl phenyl sulfoxide was obtained via (2,3)-sigmatropic rearrangement of crotyl phenyl sulfenate, which was prepared by the low temperature reaction of benzene-sulfonyl chloride with lithium crotyl alcoholate.
 9. It has been reported that a deuterated sample of allyl *p*-tolyl sulfoxide (possessing an unmethylated allyl moiety) exhibits no evidence of (1,3)-rearrangement at temperatures up to 75° . P. Bickart, F. W. Carson, J. Jacobus, E. G. Miller, and K. Mislow, J. Amer. Chem. Soc., 90, 4869 (1968).
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(Received in USA 28 January 1982)