(17) F. Hunziker and F. X. Müllner, *Helv. Chim. Acta*, **41**, 70 (1958).
(18) H. R. Billica and H. Adkins, "Organic Syntheses", Collect. Vol. III, Wiley, New York, N.Y., 1955, p 176.
(19) J. F. Bagli, P. F. Mor, and R. Gaudry, *J. Org. Chem.*, **28**, 1207 (1963).
(20) C. Djerassi and M. A. Kielczewski, *Steroids*, **2**, 125 (1963).
(21) I. Midgley and C. Djerassi, *J. Chem. Soc., Perkin Trans. 1*, 155 (1973).
(22) M. Anastasia, A. Fiecchi, and A. Scala, *J. Chem. Soc., Perkin Trans. 1*, 378 (1976).
(23) W. R. Bamford and T. S. Stevens, *J. Chem. Soc.*, 4735 (1952).
(24) I. Midgley and C. Djerassi, *J. Chem. Soc., Perkin Trans. 1*, 2771 (1972).
(25) H. Audier, M. Fetizon, and W. Vetter, *Bull. Soc. Chim. Fr.*, 1971 (1964).
(26) (a) J. H. Beynón, R. A. Saunders, and A. E. Williams, *Nature (London)*, **204**, 67 (1964); (b) K. R. Jennings, *J. Chem. Phys.*, **43**, 4176 (1965).
(27) L. Tökés and C. Djerassi, *J. Am. Chem. Soc.*, **91**, 5017 (1969).
(28) C. Djerassi and I. Midgley, unpublished results.
(29) C. Djerassi, *Pure Appl. Chem.*, **21**, 205 (1970).
(30) (a) R. F. Zürcher, *Helv. Chim. Acta*, **46**, 2054 (1963); (b) N. S. Bhacca and D. H. Williams, "Applications of NMR Spectroscopy in Organic Chemistry", Holden-Day, San Francisco, Calif., 1964.
(31) R. O. Hutchins, C. A. Milewski, and B. E. Maryanoff, *J. Am. Chem. Soc.*, **95**, 3662 (1973).
(32) N. A. Milas and C. R. Cilone, *J. Am. Chem. Soc.*, **68**, 738 (1946).
(33) H. DeVries and H. J. Backer, *Recl. Trav. Chim. Pays-Bas*, **71**, 719 (1952).
(34) L. Dorfmann, *Chem. Rev.*, **53**, 47 (1953).
(35) L. F. Fieser and S. Rajagopalan, *J. Am. Chem. Soc.*, **71**, 3935 (1949).
(36) E. Berner, A. Lardon, and T. Reichstein, *Helv. Chim. Acta*, **30**, 1542 (1947).

The Occurrence of Permutational Isomerism in the Mechanism of the Thermal Thiaallylic Rearrangement

H. Kwart* and N. A. Johnson

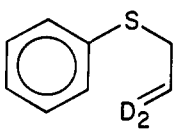
Contribution from the Department of Chemistry, University of Delaware, Newark, Delaware 19711. *Received July 6, 1976*

Abstract: The thermal 1,3 rearrangement of allyl phenyl sulfides has been found to proceed by both unimolecular and bimolecular pathways. Kinetic and product composition studies have yielded the following results: (1) the effect of solvent polarity on rate and molecularity of reaction, (2) comparison of oxyallylic, silaallylic, and thiaallylic rearrangements under thermal and photo conditions, (3) aryl substituent effects on the activation parameters correlated with the charge characteristics of the reaction transition state, (4) substituent effects in the allyl side chain and their significance in assessing the locus of charge development in the course of rearrangement, (5) evidence bearing on a possible ion-pair structure of the reaction intermediate, and other alternatives such as a radical dissociation-recombination process, (6) evidence supporting a cyclic structure of the reaction transition state, (7) a comparison of thermal allylic migration aptitudes of various heteroatoms and its significance for the thiaallylic isomerization, (8) application of the heavy atom isotope effect criterion to distinguish the mechanistic alternatives, and related considerations bearing upon the question of whether a definite reaction intermediate is formed in the course of reaction, (9) the stereochemical factors involved in the structure of the thiaallylic intermediate. These studies suggest that thermal 1,3 rearrangements involving sulfur occur via a transition state of permutational isomerism developing from an intermediate possessing a trigonal-bipyramid structure.

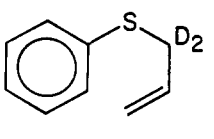
In the course of studies[1] of the thia-Claisen rearrangement, a 1,3 migration of sulfur in α-methylallyl phenyl sulfide (**1**) was observed. The products of thia-Claisen rearrangement could only be understood in terms of the occurrence of a mobile equilibrium with the more stable crotyl phenyl sulfide (**2**) established at lower temperatures. The thiaallylic rearrangement was unsuccessfully sought by Cope and co-workers[2] utilizing refractive index to detect the α-methylallyl to crotyl transformation. In a preliminary communication[3] it has been pointed out that both NMR and GLC can be applied in following the kinetic course of rearrangement. Others[4] have confirmed this reaction pattern in the course of thermolysis of α-methylallylic 2-quinolyl sulfides. This paper presents a full account of the results bearing on the mechanism of this unusual thermal isomerization reaction.

Results and Discussion

The Order of Rearrangement. The isomerization of allyl phenyl sulfide represents a degenerate rearrangement which is detectable by labeling an end of the allyl grouping. Allyl-*3,3-d*$_2$ phenyl sulfide (**3**) was used for this purpose. The rearrangement **3** $\rightleftarrows$ **3a** was kinetically monitored by means of NMR techniques. The rate was found to be independent of the initial concentration of **3** (in the range 0.70–2.50 M) in a thoroughly degassed solution of nitrobenzene. The first-order relation of the logarithm of the concentration change, $(A - A_e)$, was linear with time to more than 80% reaction completion. However, in the less polar solvents such as decalin and *o*-dichlorobenzene, the isomerization of **3** $\rightleftarrows$ **3a** was directly dependent on the initial concentration of substrate even though the apparent first-order plot was linear.



3



3a

Thus it may be assumed that rearrangement could occur by way of competing unimolecular and bimolecular processes. The rate equation for such cases can be shown to reduce to a first-order expression when the attained equilibrium constant K_e is unity, as follows.

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B \qquad \text{unimolecular rearrangement}$$

$$2A \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} 2B \qquad \text{bimolecular rearrangement}$$

$$\frac{k_1}{k_{-1}} = \frac{k_2}{k_{-2}} = 1 = K_e$$

The overall rate is given by

$$-dA/dt = k_1(A) - k_{-1}(A_0 - A) + 2k_2(A)^2 - 2k_2(A_0 - A)^2 \quad (1)$$

where A_0 = the initial concentration of A.
Simplification of 1 produces

Table I. Unimolecular and Bimolecular Rates of Isomerization of **3** ⇌ **3a** in Various Solvents

Solvent	$k_1 \times 10^4$, s^{-1} 413.1 K	423.1 K	433.1 K	443.1 K	453.1 K
Nitrobenzene	0.498	1.29	3.07	7.60	17.2
o-Dichlorobenzene	0.018	0.043	0.109	0.234	0.539
Decalin	0.034	0.082	0.194	0.452	0.53
	$k_2 \times 10^4$, M^{-1} s^{-1}				
Nitrobenzene	Bimolecular rate is negligible at all temperatures				
o-Dichlorobenzene	0.046	0.104	0.225	0.465	0.910
Decalin	0.041	0.080	0.168	0.340	0.735

$$-dA/dt = 2k_1(A) - k_1(A_0) + 2k_2(AA_0) - 2k_2(A_0)^2 \quad (2)$$

At equilibrium, $A = A_e$

$$0 = 2k_1(A_e) - k_1(A_0) + 2k_2(A_eA_0) - 2k_2(A_0)^2 \quad (3)$$

Subtracting 3 from 2 gives

$$-dA/dt = 2k_1(A - A_e) + 2k_2A_0(A - A_e) \quad (4)$$

which reduces to

$$-dA/(A - A_e) = 2(k_1 + k_2A_0)dt \quad (5)$$

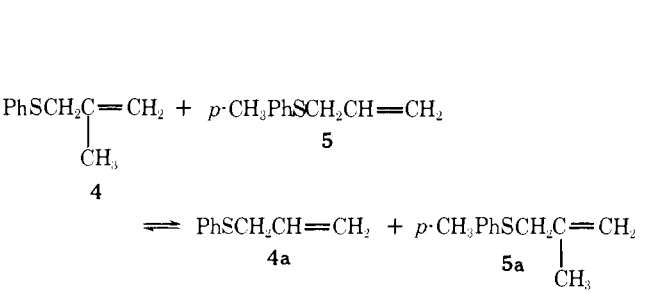
Integration of eq 5 between limits results in

$$-\ln (A - A_e) = 2(k_1 + k_2A_0)t \quad (6)$$

Consequently k_1 and k_2 can be readily determined from a plot of ln $(A - A_e)$ vs. t at a variety of initial concentrations of substrate, wherein the slope k_{obsd} is a linear function of the specific rate constants of the unimolecular (k_1) and bimolecular (k_2) reactions and the magnitude of A_0.

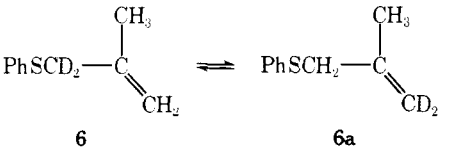
The rate constants k_1 and k_2 for the reaction **3** ⇌ **3a** were determined in solvents of varying polarity, evaluating k_{obsd} at four different concentrations, A_0, spanning at least a fivefold change. The values of the rate constants were calculated by applying a regression analysis[5] to the plot of k_{obsd} vs. A_0. Such determinations carried out at five different temperatures (over a 40 °C range) permitted calculation of the activation parameters by standard procedures.[6] Typical data are listed in Tables I and II.

Proof of the occurrence of the competing bimolecular process was obtained from an appropriate cross product experiment. Substrates **4** and **5**, which differ in both the aryl moiety and in the nature of substitution in the allyl side chain, should undergo completely degenerate self-rearrangement, in that in both unimolecular and bimolecular reaction of substrate molecules with themselves the occurrence of rearrangement is undetectable. However, an intermolecular-bimolecular rearrangement (such as is shown below) can give rise to products which represent crossing of allylic side chain and aryl moieties. After an equimolecular mixture of **4** and **5** in decalin was heated to 160 °C for 3 h, two new products were separated by GLC. Their structures, **4a** and **5a**, respectively, were assigned on the basis of NMR and IR comparisons with authentic samples.



Effect of Solvent Polarity on Rate and Molecularity. Although the unimolecular activation energies for isomerization in various solvents are similar, there are two factors which clearly distinguish the reactions in polar and nonpolar media; the $\Delta S^{\ddagger}$ for the nonpolar solvents decalin and *o*-dichlorobenzene is considerably more negative than that in the polar solvent nitrobenzene (Table II). The bimolecular reaction, however, is almost completely suppressed in nitrobenzene relative to the unimolecular. The bimolecular mechanism has been termed[3] "antipolar". These solvent effects will be clarified by further evidence that an intermediate is formed along the path of isomerization stemming from the interaction of the olefin center of the allyl group with the bivalent sulfur. Solvation or complexation of the substrate by solvent molecules does not interfere as much with formation of the unimolecular intermediate within the solvent cage.

It was possible to demonstrate the validity of this conclusion in cases where the reaction can only occur via the bimolecular intermediate, namely, in the cross product reaction by which **4** and **5** produce **4a** and **5a.** In the absence of a visible, competing unimolecular process, nitrobenzene affords the bimolecular cross reaction products at a rate which is only ca. one-tenth as great as the same reaction in decalin at 150 °C. This result is to be compared with the unimolecular reaction converting **3** ⇌ **3a,** which takes place 10–20 times faster in nitrobenzene than in decalin at all temperatures in the range 140–180 °C. Evidently the work expended in stripping obstructive solvent molecules and then organizing others around the reaction centers in the bimolecular process is associated with a large negative entropy in the case of a polar solvent, but this also results in a diminished activation requirement for formation of the bimolecular complex. These data illustrate the competition of unimolecular and bimolecular processes in a given solvent. They also predict the occurrence of cases where substitution effects have lowered $\Delta H^{\ddagger}$ to an extent where both processes are competitive in nitrobenzene within the accessible temperature range. An illustration fulfilling this prediction is found in the isomerization of β-methylallyl phenyl sulfide (**6** ⇌ **6a**) (see Table IIA). Comparison with the reaction **3** ⇌ **3a**



shows that a significant lowering of $\Delta H^{\ddagger}$, which presumably is also true for the comparison with the invisible bimolecular **3** ⇌ **3a** process in nitrobenzene, sufficiently offsets the very

Table II. Activation Parameters for Isomerization **3** ⇌ **3a**

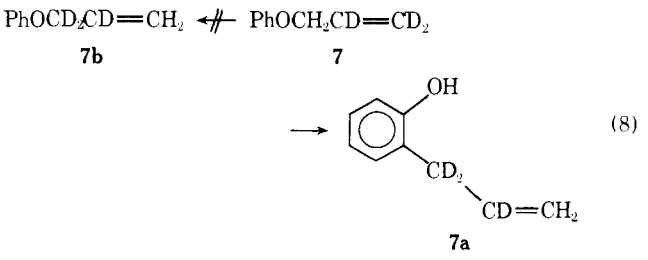
Solvent	E_a, kcal Unimolec	Bimolec	$\Delta H^{\ddagger}$, kcal Unimolec	Bimolec	$\Delta S^{\ddagger}$ (443 K), eu Unimolec	Bimolec
Nitrobenzene	32.9 ± 0.2		32.1 ± 0.2		−1.3 ± 0.4	
o-Dichlorobenzene	31.5 ± 0.2	27.9 ± 0.4	30.6 ± 0.2	27.0 ± 0.4	−11.4 ± 0.5	−18.7 ± 0.4
Decalin	31.9 ± 0.2	27.1 ± 0.9	31.0 ± 0.3	26.2 ± 0.9	−9.2 ± 0.8	−21.4 ± 1.4

Table IIA, Activation Parameters for Isomerization **6** ⇌ **6a** in Nitrobenzene

	E_a, kcal	$\Delta H^{\ddagger}$, kcal	$\Delta S^{\ddagger}$ (428 K), eu
Unimolecular process	28.5 ± 0.9	27.7 ± 0.9	−13.3 ± 2.2
Bimolecular process	24.1 ± 1.9	23.3 ± 1.0	−23.4 ± 2.3

large, negative $\Delta S^{\ddagger}$. The latter is interpreted to be the result of strong solvation by nitrobenzene retarding the formation of the bimolecular intermediate.

Comparison of Oxyallylic, Silaallylic, and Thiaallylic Rearrangements under Thermal and Photo Conditions. The corresponding rearrangement of allyl phenyl ether was found to be inactive at temperatures permitting rapid and complete transformation of the sulfide. When **7** was heated (neat) at 160

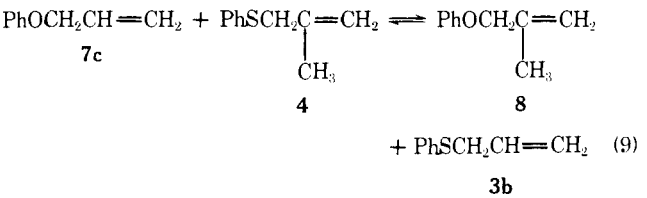


(8)

°C for more than 5 h, no **7b** could be detected. Moreover, when **7** was heated to 195 °C for 16 h, the only substance that could be detected was that arising from normal oxy-Claisen rearrangement (**7a**), and a small amount of the chroman from some subsequent ring closure. Under more severe conditions the γ-^{14}C allyl ether of 2,4,6-trimethylphenol experiences some distribution of its radioactivity between the α and γ carbon of the allyl group. However, this result has been accounted for, not by an assumed oxyallylic rearrangement, but rather by a stepwise ortho–ortho mechanism.[7]

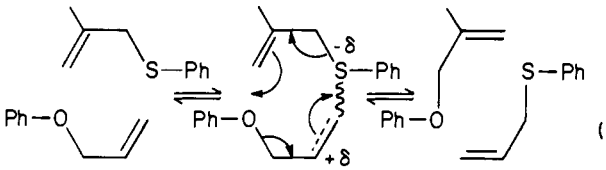
The photooxyallylic rearrangement at ambient temperatures also could not be realized. When **7**, thoroughly degassed in CCl_4 solution, was irradiated at 2557 Å in a quartz tube for 5 h, no measurable reaction could be verified by NMR. Under the same conditions, the sulfur analogue **3** was completely isomerized to the equilibrium mixture with **3a**.

Evidently neither a thermal or photooxyallylic rearrangement can occur by itself in either of the modes (unimolecular or bimolecular) characterized for the analogous thiaallylic processes. The origins of this ineptitude of the oxygen substrate can be perceived in the results of the cross product experiments expressed in eq 9.



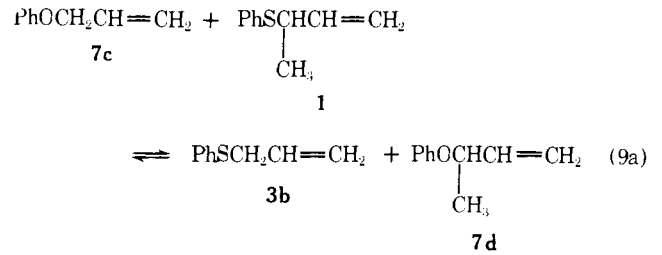
(9)

When equimolar (ca. 1 M) concentrations of **7c** and **4** were heated at 160 °C in decalin solution, approximately 4% conversion to **8** and **3b** was realized in 24 h. Clearly, an oxyallylic rearrangement does take place via a bimolecular route, although somewhat more slowly and only with the assistance of 1 mol of aryl allylic sulfide. These requirements suggest that bimolecular thermal allylic rearrangements occur through formation of a preliminary complex or reaction intermediate at an energy level not too far from the transition state. This complex or intermediate could result from the ability of the sulfur or an equivalent atom capable of octet expansion to coordinate with the olefin end of the donor substrate which could be an allyl phenyl ether. The succession of bond-making and bond-breaking events in the transition state following this step apparently does not depend to a crucial extent on the presence in the donor substrate of an atom having the capability of valency expansion, and therefore the allyl phenyl ether can fulfill this role in the eight-centered process outlined in eq 10.



(10)

The possibility has been considered that this reaction could be effected in a six-membered transition state in which only one net rearrangement of the allylic skeletons takes place in a single step. This is illustrated in eq 9a for the reaction analogous to eq 9. Failure to detect any **7d** among the products after



(9a)

reaction had proceeded to the extent of about 4% appears to exclude this mechanism.[8] In addition to the evidence presented up to this point in the discussion, as well as additional evidence to be considered subsequently which strongly supports the assumption of a definite intermediate or donor–acceptor complex in both the unimolecular and bimolecular cases, this result would also argue against the bimolecular isomerization occurring by any conceivable planar, pericyclic, orbital symmetry conserved process.

In considering the necessity of forming such a donor–acceptor complex it is of value to contrast the properties of the oxyallylic and thiaallylic rearrangements with those reported for the silaallylic rearrangement.[9] There is no evidence for a bimolecular course of the latter reaction. It appears to be completely concerted and totally independent of solvent and polar substituent effects, and gives no evidence of intermediate complex formation involving a hypervalent state of silicon, a point which will receive further discussion in a subsequent section of this report. Thus, when phenyl allyl ether (**7c**) is heated with phenyldimethylallylsilane no evidence of oxyallylic rearrangement could be found in contrast to the cross product result confirmed for the reaction in eq 9. Moreover, it can be shown that the bimolecular thiaallylic mode is not merely a simple series of thiophilic S_N2' displacements[10] by sulfide sulfur. This possibility can be ruled out by the observation that molar equivalents of thioanisole had no effect on either the rate or product composition of either the bimolecular or unimolecular isomerizations of **1**.

Aryl Substituent Effects. Charge Characteristics of the Reaction Intermediate. The Hammett equation criterion was applied to a series of para-substituted allyl-*3,3-d*$_2$ phenyl sulfides undergoing rearrangement via a unimolecular mechanism in nitrobenzene solvent. The activation parameters for each of five such substrates were determined for the reaction **3** ⇌ **3a**. The rate constants at 25 °C computed by means of the relation $k_{(X)} = A \exp(-E_a/RT)$ are listed in Table III. Inspection of the data compiled in Table IV indicates that the best correlation is obtained using the σ_p^- (PhSH) constants, while the poorest fit results from application of σ_p^+ constants.

Table III

X (para)	E_a, kcal mol^{-1}	$\Delta H^{\pm}$, kcal mol^{-1}	$\Delta S^{\pm}$ (413 K), eu	$k_f \times 10^{11}$ (25 °C), s^{-1}
NO_2	28.0 ± 0.2	27.2 ± 0.2	−15.9 ± 0.4	2.43
Cl	31.2 ± 0.6	30.4 ± 0.6	−5.2 ± 1.4	2.27
H	32.9 ± 0.2	32.1 ± 0.2	−1.3 ± 0.4	0.941
CH_3	33.8 ± 0.2	33.0 ± 0.2	+1.3 ± 0.4	0.721
OCH_3	33.2 ± 0.8	32.4 ± 0.8	−0.4 ± 2.0	0.852

For the ionization of para-substituted thiophenols the value of ρ^- is reported[10b] to be 2.58 in 48% alcohol at 25 °C. Thus the thiaallylic rearrangement appears to respond less to a change in the polar character of the substituent than does the ionization of thiophenol in which a full negative charge is developed on sulfur.

A much larger degree of (negative) transition state charge may reside on the sulfur than is indicated merely by the size of $\rho^- = 1.15$. For a reaction which is neither isoentropic or isoenthalpic it is frequently found that the true magnitude of transition state charge cannot be correlated with the magnitude of ρ. For instance, Coward and Sweet[13] have recently presented data demonstrating that ρ (1.60 → 1.74) for an S_N2 displacement in aryldimethylsulfonium ions is independent of whether the transition state involves destruction or dispersion of charge, in cases of such widely different charge characteristics as the reactions of the sulfonium ions with hydroxide ion and with amines. This conclusion is also evident (Table III) from the large difference (ca. 5 kcal) in $\Delta H^{\pm}$ between the p-NO_2 and p-OCH_3 cases, which is a true reflection of the large difference in negative charge stabilization. The magnitude of ρ^-, however, is controlled also by the $\Delta S^{\pm}$ factor in the rate. In the polar solvent, nitrobenzene, the negative transition state charge induces a large extent of organization, resulting in an unfavorable entropy term. Therefore, the rate, and consequently the value of ρ^-, is not a unique indication of the magnitude of the transition state charge. The comparison of activation parameters in Table III is much more informative; in going from p-NO_2 to p-CH_3 $\Delta(\Delta H^{\pm}) \approx 6$ kcal/mol, and $\Delta(\Delta S^{\pm}) \approx 16$ eu.

The necessity for some kind of electron-withdrawing substituent on sulfur is made quite clear by two additional observations: (1) The homologous compound $PhCH_2SCH_2CH{=}CD_2$, where the electron withdrawal by phenyl is somewhat diminished, undergoes thiaallylic rearrangement at rates which are 10–100 times slower at the temperatures of measurement in nitrobenzene. (2) The thiaallylic rearrangement occurs only at an immeasurably slow rate (under these conditions) in the case of cyclohexyl allyl sulfide where no electron withdrawal is exerted by the sulfur substituent.

One possible explanation of the accelerating influence of electron-withdrawing substituents to be considered is that sulfur is utilizing a d orbital to accommodate charge accepted through interaction with the olefin (donor) moiety of the allyl side chain. The view that the d orbitals possess dimensions which are favorable for this type of bonding has had support from Mulliken[14] and Jaffe.[15] More recent calculations by Craig and Thirunamachandran[16a] favor a requirement of d orbital contraction for maximum orbital overlap. An electronegative substituent attached to the phenyl ring may enforce contraction of the sulfur d orbitals and lowering of the energy for orbital overlap.[16b] Based on the latter considerations, the lower activation energy for electron-withdrawing substituents and their sign and magnitude may not be due entirely to stabilization of partial negative charge on sulfur, but rather to lowering of the energy requirement for overlap by regulation of the size of the sulfur d orbitals. Valence expansion and formation of a complex of trigonal bipyramid structure may also be conceived to occur without participation of d orbitals. This alternative,[16c] involving the development of three center–four electron, coaxial bonding to the central atom, may realize stabilization by an electronegative phenyl substituent through resonance interaction with the unshared electron pairs of the sulfur.

Table IV. Various Possible Correlations of Hammett-Type Rate Parameters

σ_{para}[a]	ρ[b]	Corr coeff	std dev
c	1.15	0.993	± 0.10
d	0.92	0.895	±0.30
e	0.92	0.895	±0.30
f	0.35	0.628	±0.30

[a] Type of σ constant applied. [b] Calculated from the Hammett equation by least-squares treatment. The p-nitro substituent was not included in this treatment owing to specific solvation effects by nitrobenzene solvent as evidenced by the large negative $\Delta S^{\pm}$ in this case. [c] Determined by dissociation of substituted thiophenols.[10] [d] Determined by dissociation of substituted benzoic acids.[11] [e] Determined by dissociation of substituted phenols.[12] [f] Determined by the solvolysis of substituted 2-phenyl-2-propyl chloride.[11]

Table V. Summary of Activation Parameter Changes Accompanying Methyl Substitution on the Allyl Side Chain in the Unimolecular Thiaallylic Rearrangement

Substrate	Solvent medium	$\Delta H^{\pm}$, kcal/mol	$-\Delta S^{\pm}$, eu 420–450 K
Unsubstituted	Nitrobenzene	32.1 ± 0.2	1.3 ± 0.4
$PhSCH_2CH{=}CD_2$ (**3**)	o-Dichlorobenzene	30.6 ± 0.2	11.4 ± 0.5
	Decalin	31.0 ± 0.3	9.2 ± 0.8
α-Methyl	o-Dichlorobenzene	29.8 ± 0.5	18.5 ± 0.9
$PhSCH(CH_3)$-$CH{=}CH_2$ (**1**)	Decalin	29.1 ± 0.4	19.3 ± 0.8
β-Methyl $PhSCH_2C(CH_3){=}CD_2$ (**6**)	Nitrobenzene	27.7 ± 0.9	13.3 ± 2.2
α,α-Dimethyl	Nitrobenzene	30.3 ± 0.4	7.2 ± 1.0
$PhS{-}C(CH_3)_2$-$CH{=}CH_2$ (**9**)	Decalin	29.4 ± 0.8	14.5 ± 1.7

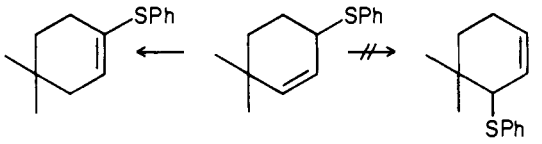
Substituent Effects in the Allyl Side Chain. The rearrangement of compounds **1** and **9**, listed in Table V, represents nondegenerate rearrangements ($K_{eq} = 1$); consequently, the derived rate expression for the degenerate rearrangement of compounds **3** and **6** is not applicable to compounds **1** and **9**. Therefore the kinetic complexities arising from the competition of unimolecular and bimolecular processes were circumvented by running the reactions at very high dilution. Thus, at elevated concentrations of **1** or **9**, ca. 1 M, the first-order plot of ln ($A - A_e$) vs. t was highly curved, while at concentrations below 0.03 M the bimolecular component became negligible as indicated by the linearity of the first-order plot.[17]

In well-established, concerted, isomerization processes, where gross steric factors are of no importance, and where substitution introduces a large degree of stabilization of the product relative to the reactant, a useful generalization has been documented.[18] Since in such a symmetrical transition state there is some resemblance to both products and reactants, this factor is reflected in a lowering of E_a without a significant change in $\Delta S^{\pm}$. The applicability of this generalization finds its best illustration in the case of the structurally analogous

silaallylic rearrangement,[8] which has been identified as a concerted, sigmatropic migration of silicon by means of both stereochemical[19] and kinetic criteria.[8,19] The activation parameters of this reaction are constant (E_a = 47.7 ± 0.3 kcal and $\Delta S^{\ddagger}$ = −6.6 ± 0.3 eu) for all kinds and degrees of methyl substitution in the allyl side chain and for all variations of methyl and phenyl substitution on the migratory silicon center. Moreover, the reaction rate is totally independent of solvent effects.

If the thiaallylic rearrangement possesses an analogous concerted, symmetrical transition state, the following could be anticipated on the basis of this generalization: (1) The activation energy order could be **9** ≪ **1** < **3** ≈ **6**; (2) there should be little difference in $\Delta S^{\ddagger}$ = −6 → −11 eu; (3) significant solvent effects on the activation parameters could not be expected. Instead, the facts to be deduced from the data in Table V represent almost the contrary of these expectations for a typical sigmatropic rearrangement of bivalent sulfur. The rates and activation parameters appear to vary with the nature of the aprotic solvent in such a way as to suggest that extensive solvent coordination can occur in both the ground and transition states, and that considerable change in solvent structure attends the activation process. These effects can be interpreted as confirmation of the development of charge separation in a dipolar intermediate or activated complex representing electron donation to the sulfur from the terminal atom of the olefin center. This was also indicated in earlier considerations (above) of the significant rate effects resulting from variation of the substituent on sulfur, in contrast to the lack of substituent effects in the silaallylic isomerization.

Further Evidence in Support of a Cyclic Structure of the Transition State. As an additional test of the validity of the proposed intermediates in the thiaallylic rearrangement, a substrate was synthesized in which the strain involved in attaining the four-membered ring would be appreciable and the eight-membered bimolecular transition state would experience conformational difficulties. The compound chosen, 4,4-dimethyl-2-cyclohexenyl phenyl sulfide (**12**), is clearly responsive to this test. All efforts to rearrange **12** to **12a** under the usual

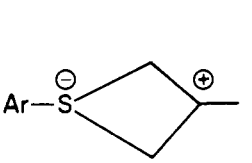


12b **12** **12a**

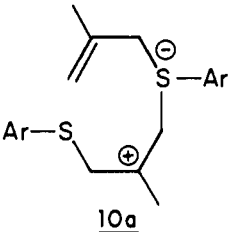
unimolecular thiaallylic isomerization conditions were unsuccessful. However, dilute solutions of **12** in decalin did undergo a thermal reorganization at temperatures above 250 °C to produce **12b**; E_a = 39.4 ± 0.4 kcal/mol, $\Delta S^{\ddagger}$ = −5.2 ± 0.8 eu. A mechanism of bond breaking–recombination of the carbon–sulfur bond to form either ion or radical pair intermediates should have produced **12a**, since these pathways create no special steric requirements for isomerization. The assumption that **12** provides no steric difficulties for a bond breaking–recombination mechanism is deducible from the nearly quantitative conversion of **12** to **12b**. This symmetry forbidden[20a] 1,3 migration of hydrogen, which is not observed in simple thiaallylic substrates, suggests that a nonconcerted process is involved which is made possible through the agency of the phenylthio substituent.[20b]

Expressed most simply, hydrogen migration is faster than thiaallylic isomerization. This is often a factor in rearrangement reactions involving sulfur. For instance, propenylization is found to be much faster than thia-Claisen rearrangement of phenyl allyl sulfides.[1,21] The latter reaction, in fact, is not visible unless it can be accelerated by catalysis to a point where it competes favorably with the "forbidden" α hydrogen migration.

Mechanistic Possibilities. Thus far, the evidence considered has supported what might be defined as an *associative mechanism*, involving a transition state in which considerable negative charge has emerged on the sulfur[22a] and a corresponding degree of positive charge at the β-allyl center. The degree of charge development indicated by these data is so great as to suggest the formation of similarly structured intermediates represented for the unimolecular process by **10** and the bimolecular process by **10a**. However, several alternative



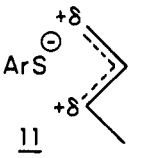
10



10a

mechanisms involving intermediates with increased electron density on sulfur may also be evaluated.

A. Considerations Bearing on a Possible Ionic *Dissociative Mechanism*. Why not a structure (for the unimolecular process) such as **11** formed by ionization of the sulfur–carbon



11

bond? There are at least two compelling arguments against **11**. The first stems from the expectation that α-methyl substitution should strongly stabilize this intermediate and β-methyl substitution should be comparatively without effect. The data in Table V, however, indicate that a (single) β-methyl substituent in **6** lowers $\Delta H^{\ddagger}$ by approximately 4.5 kcal, which is more than 2.5 kcal greater than the effect of dimethyl substitution in **9**. The second argument against **11** correlates with the solvation effects noted earlier in the discussion. For a classical process[22,23] of ionization of a covalent C–S bond represented by **11**, theory predicts that reaction will be accelerated in more polar solvents as a consequence of the activation energy decreasing in proportion to the degree of ionization. Though partially counteracted by the entropy of solvation the enthalpy change will dominate the rate change. These predictions have been amply documented in recent studies[24] of the ionization of α-halo ethers in a long range of aprotic solvents as well.

Solvation effects opposed to those expected on the basis of reaction intermediate **11** can be perceived from the data in Tables II and V. Thus, an increase in both E_a (ca. 1–2 kcal) and $\Delta S^{\ddagger}$ (ca. 8 eu) as the polarity of the aprotic solvent is increased is not to be anticipated in the course of forming an ion pair intermediate at energy levels close to the transition state. Finally, an ion pair structure would not be an appropriate description of the bimolecular intermediate. It is difficult to conceive of a bimolecular activation for the ionization of the C–S bond. Moreover, as stated earlier, the absence of any effect of added thioanisole on either the bimolecular or unimolecular rate confirms the absence of a step involving nucleophilic attack by bivalent sulfur at the olefinic center of the substrate.

B. Considerations Bearing on a Possible Radical Dissociation–Recombination Mechanism. A mechanism involving the intermediate formation of a radical pair could be conceived. However, under the high-temperature reaction conditions this could not be completely prevented from even partial dissociation, and can be consequently disqualified on the following grounds: (1) Analysis of the normal reaction mixtures shows

no traces of products arising from radical coupling, such as disulfides, which are formed characteristically in typical cases. (2) Homolytic bond cleavage of a neutral molecule into radical pairs usually produces positive entropies of activation,[25] contrary to the data in Table V. (3) A stepwise process of radical dissociation–recombination might produce CIDNIP effects.[26] In this regard, the possibility has been considered of a radical pathway analogous to what has been established by Baldwin and Brown for rearrangements in a somewhat similar allylic system.[27] However, no NMR emissions of any kind could be detected at temperatures up to 200 °C in trichlorobenzene as solvent, where it is known that the thiaallylic rearrangement is quite mobile. (4) The addition of galvinoxyl, a stable free radical, had no effect on the rate of rerrrangement. (5) Evidence against a chain reaction initiated by arylthiyl radicals formed by initial radical dissociation of a substrate molecule and involving an intermediate ($R'SCH_2CH_2SR$) of the type characterized by Krusic and Kochi[28a] and Huyser and Kellogg[28b] will be discussed in a subsequent article. However, at this juncture it must be emphasized that the failure (noted above) of cyclohexyl and other alkyl allyl sulfides to undergo the thermal thiaallylic isomerization is not in keeping with the reported[28] ease of addition of alkylthiyl radicals to alkyl allyl sulfides and the stability of the resulting β-mercaptoalkyl radical in general.[29]

The Heavy Atom Isotope Effect Probe of Mechanism. This is the most direct approach to distinguishing the associative and dissociative mechanisms discussed above. Moreover, the Bigeleisen–Mayer analysis, which comprises the theoretical basis for this mechanistic probe, should also afford a measure of the degree of bonding to the central sulfur atom in the transition state. Clearly, data of this nature would be of great aid as well in assessing the possibility of an intervening reaction intermediate.

Listed in a preliminary communication,[30] also describing the means of realizing the high precision measurements of k_{34}/k_{32}, the relative reactivity of corresponding ^{34}S and ^{32}S isotopic substrates, are the results of the calculations applying the Bigeleisen–Mayer equation to the transition state models of the respective *associative* and *dissociative* mechanisms discussed above. The calculated value of the isotope effect, based on a transition state structurally related to an *associative mechanism* intermediate like **10**, was $k_{32}/k_{34} = 1.004$. The corresponding calculated value for the dissociative mechanism related to the intermediate **11** was $k_{32}/k_{34} = 1.012$. The average value of the sulfur isotope effect at the same temperature (198 °C) computed from the experimental fractionation and equilibrium data was $k_{32}/k_{34} = 1.004 \pm 0.0016$.

Giving due consideration to the uncertainties, both experimental and theoretical, these findings afford unequivocal support for the associative mechanism. Since the model used for the calculated value involved the assumption of a full additional bond to the central sulfur atom, and since the agreement of calculated and experimental values was so close, it may be inferred with some confidence that a reaction intermediate similar in structure to **10** lies astride the path of the thiaallylic rearrangement. By the same token, ion-pair intermediates like **11** and radical dissociation–recombination mechanisms must be excluded. Moreover, since the k_{32}/k_{34} value was independent of solvent (decalin or nitrobenzene) it is evident that the unimolecular and bimolecular processes are governed by very similar mechanistic parameters.

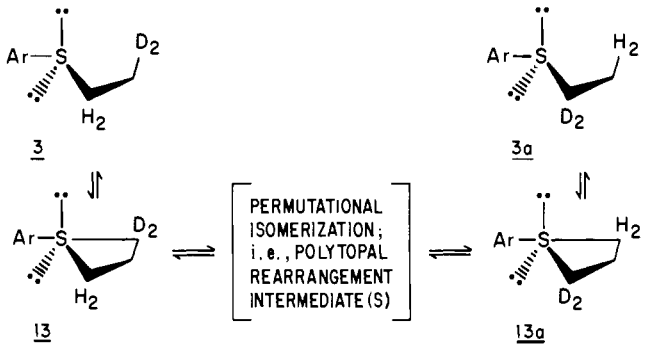
A Comparison of Allylic Migration of Various Heteroatoms and Its Significance for the Thiaallylic Isomerization Mechanism. It has been shown that the unimolecular oxyallylic rearrangement fails to occur, probably because of the inability of oxygen to expand its octet, or attain a hypervalent state as is possible for sulfur. This reaction does occur in the bimolecular manner in conjunction with a host mole of thiaallylic substrate. This mechanism requires the formation of a complex in which the heteroatom must bear negative charge conveyed from the terminal carbon of the olefin. Where this is possible rearrangement occurs as a step subsequent to or concomitant with the formation of this dipolar complex. Other heteroatom allylic systems have also been examined in these laboratories. Although these studies are yet incomplete, the nearest indications may be usefully summarized as follows. Nitrogen, like oxygen, does not undergo a unimolecular (direct) thermal allylic isomerization. Trivalent phosphorus does undergo such a rearrangement reaction but with much higher activation requirements than sulfur. Tetravalent silicon also experiences a 1,3 thermal allylic isomerization[8,19] but by a mechanism possessing distinctively different features than are apparent for the thiaallylic rearrangement. The silaallylic rearrangement takes place as a sigmatropic change in which the silicon is employing a 3p orbital[19] in a symmetrical, concerted transition state of migration in accordance with orbital symmetry conservation rules.[20] There is no evidence suggesting a dipolar intermediate in the silaallylic, as has here been noted for the thiaallylic rearrangement.

These differences in ease and mode of 1,3 rearrangement characterizing the various heteroatoms considered are understandable in terms of a single reaction factor, namely, the ability of the heteroatom to expand its octet or reach some equivalent hypervalent state via electron acceptance and its tolerance of the consequent negative charge development. The sulfur is best equipped to provide such valency growth and negative charge stabilization. The less electronegative phosphorus can experience valency expansion but is less tolerant of the negative charge and therefore shows a higher activation demand. The considerably diminished facility of silicon in accepting negative charge causes it to prefer a process (although of higher activation energy; ca. 45 kcal vs. ca. 30 kcal for sulfur) in which a 3p orbital is utilized in a concerted sigmatropic mode, but one which is much more efficient than carbon utilizing a 2p orbital similarly.

The Stereochemistry of the Thiaallylic Rearrangement. It is possible to conceive both the unimolecular and bimolecular thiaallylic intermediates as involving utilization of a 3d orbital of sulfur to accommodate the electron donation from the olefin center. Alternatively, one may avoid invoking d orbitals by assigning hypervalent character[31] to the reaction intermediate having a trigonal bipyramid or right-pyrimidal configuration featuring two collinear, apical bonds. A similar model has been described[32-37] as a three-center-four-electron bonded structure. The fundamental consideration in the stability of the hypervalent bonding is the extent to which the combination of three atomic orbitals lowers the energy of the bonding orbital. A sufficient decline in energy has been calculated[38,39] to occur when the ligands of a low ionization potential heteroatom (like sulfur) have high electron affinities. The aromatic ring and the double bond appear to be appropriate[38,39] ligands for hypervalent bonding in sulfur.

Whether d orbital or some form of hypervalent bonding is concerned with formation of the essential thiaallylic intermediate, the trigonal bipyramid (TBP) configuration appears to account for the indispensability of an aryl substituent on sulfur. The resistance of cyclohexyl allyl sulfide to form the TBP may be due to either or both of the following considerations: (1) cyclohexyl is insufficiently electronegative to occupy an apical position, and (2) a cyclohexyl group as an equatorial ligand cannot afford the resonance interaction with the unshared pairs on sulfur which, in the case of a phenyl ligand, provides considerable stabilization of the TBP.

A suitable representation of the TBP intermediate in the rearrangement of **3** $\rightleftharpoons$ **3a** is given in **13** $\rightleftharpoons$ **13a**. Since the energy of an equatorial bond in **13** differs from that of an apical bond,[40] a process in which an equatorial bond is broken and



PROPOSED THIA-ALLYLIC (UNCATALYZED) REARRANGEMENT MECHANISM

an apical bond made in the conversion of **13** to **13a** can be seen as a violation of the principle of microscopic reversibility. In other words, both bond making and breaking *must occur* in the apical orientation of the intermediate. This criterion is only satisfied in a pathway which involves intramolecular ligand exchange via a process of permutational isomerism,[41] i.e., some kind of polytopal bond rearrangement of the nature of Berry pseudorotation[42] or turnstile rotation.[41] The activation energy for the overall thiaallylic rearrangement is visualized as the sum of the E_a for formation of the TBP intermediate and the activation barrier for the polytopal rearrangement.

Given that the thiaallylic reaction proceeds through formation of a dipolar intermediate with octet expansion, there is apparently only one alternative to TBP disposition of the sulfur substituents and rearrangement by permutational isomerism of the TBP, namely, a tetragonal pyramid. But this is equivalent to the Berry pseudorotation intermediate structure, and is thus to be regarded as a moot distinction which does not of itself exclude the mechanism of permutational isomerism proposed.

The occurrence of rapid, ligand interchange processes in sulfuranes, by analogy to phosphoranes,[43] has been the focus of considerable disagreement and widely conflicting interpretations. While rapid pseudorotation has been invoked by Sheppard,[38] Trost,[44] and Mislow[45] in possible explanations for reaction products presumed to be formed via tetraarylsulfurane intermediates, and a pseudorotating dioxysulfurane intermediate has been suggested for the HCl-catalyzed rearrangement of sulfoxides, evidence against sulfurane intermediates has also been advanced.

The failure to establish pseudorotation in the course of a reaction process such as solvolysis of sulfurane derivatives[46] and in stable, unsymmetrical sulfuranes[47] may be attributed to rapid ligand exchange with hydroxylic substances unavoidably present.[47] It has also been anticipated[42,48] that pseudorotation times in sulfur would be much longer than in phosphorous.[43] Reich[49] has proposed that the activation barrier to pseudorotation in related seluranes must be greater than 27 kcal. However, in light of the recent report by Martin[50] that rapid ligand interchange is found in a tetraoxysulfurane over a very low barrier ($\Delta G^{\ddagger} \approx 7.5$ kcal), the occurrence of such processes, as the evidence presented above indicates to be the case for the rate-determining step in the thiaallylic rearrangement, can be accepted with some confidence.

Experimental Section

General Comments. Nuclear magnetic resonance spectra were recorded on a Varian Associates A-60A spectrometer. Spectral data are recorded in parts per million with reference to Me_4Si (δ 0) and in CCl_4 solution. Infrared spectra were obtained on a Perkin-Elmer Model 137B spectrometer. Mass spectral analyses were performed on a C.E.C. 21-110B double-focusing high-resolution spectrometer. Melting points were determined in sealed capillary tubes using a Mel-Temp melting point block and are uncorrected.

Kinetics. The solvents used were all purified according to the procedures of Weissberger and Proskauer.[51] The kinetic runs were carried out in a silicone oil bath equipped with a stirrer and a power proportionating temperature controller. Temperatures were controlled to within ±0.05 °C. At temperatures above 225 °C, tubes were placed into 8-mm o.d. holes which had been drilled into an aluminum block assembly. The temperature of the block was controlled to within ±0.2 °C as determined potentiometrically using an iron-constantan thermocouple. Kinetic measurements were performed either by NMR or GLC as the case may be. A typical kinetic procedure, for the NMR case, was as follows.

The deuterium labeled sulfide solutions (0.25 mL) of specified molarity were transferred by syringe into standard NMR tubes. The contents were then thoroughly degassed on a high vacuum system by freeze-pump-thaw cycling, sealed under vacuum, and immersed in a constant-temperature oil bath. The tubes were removed at various time intervals, quenched in cold H_2O, and analyzed by NMR. The disappearance of the SCH_2 absorption (δ 3.30 ppm) and the appearance of the CH_2=C absorption (δ 4.90 ppm) were monitored. Multiple integrations of the corresponding peak areas, using a digital voltmeter, enabled the determination of substrate concentrations with satisfactory precision. The kinetic procedure used with substrates analyzed by GLC was essentially the same except that the sample size used was considerably reduced. Using the above procedures, all rate constants were reproducible with ±2% precision.

Analysis. The GLC analyses were performed using an F and M Model 700 flame ionization gas chromatograph. An injection port temperature of 250 °C, detector temperature of 270 °C, and helium flow rate of 40 mL/min was maintained throughout. The specified liquid phases were supported on Chromosorb WAW, 80–100 mesh in the amount of 10% by weight and then vacuum packed into 0.125 in. o.d. copper tubing. Analytical samples were collected at the thermal conductivity detector exit port of an F and M Model 500 gas chromatograph using a 12 ft × 0.25 in. copper tube packed with a specified liquid phase on Chromosorb WAW.

Deuterium Content. All deuterated compounds had an isotopic purity of at least 95% as determined by both NMR and mass spectrometry.

Preparation of Allyl-*3,3-d*$_2$ Chloride. Allyl-*3,3-d*$_2$ alcohol[52] (5 g, 0.0835 mol) and pyridine (7.1 g, 0.090 mol) were combined in a 25-mL round-bottom flask equipped with a small Vigreux column and dropping funnel. The flask was cooled to −60 °C with a dry ice–acetone bath and $SOCl_2$ (10.7 g, 0.090 mol) was added dropwise. After addition was complete (ca. 15 min), the contents of the flask were slowly warmed in a small oil bath to 45 °C. About 4 g of allyl-*3,3-d*$_2$ chloride were obtained by distillation: bp 40 °C (760 mm) (lit.[53] undeuterated allyl chloride 40 °C (760 mm)). The allyl-*3,3-d*$_2$ chloride was observed to be essentially pure by GLC (10-ft SE-30 column) and to have the same retention time as the undeuterated allyl chloride as determined by peak enhancement: NMR δ 3.85 (d, 2, J = 6 Hz, CH_2Cl), 5.49–6.18 (m, 1, CH), <5% 4.48–5.32 (m, 2, CH_2=C).

Preparation of Allyl-*3,3-d*$_2$ *p*-X-Phenyl Sulfides (3). The following general (modified) procedure of Kwart and Evans[54] was used to prepare all of the para-substituted allyl-*3,3-d*$_2$ phenyl sulfides. The corresponding para-substituted thiophenols were purchased from the Aldrich Chemical Co. and were used without further purification. The thiophenol (0.10 mol) was added to sodium hydroxide (4 g, 0.10 mol) in 250 mL of H_2O and the mixture shaken vigorously in a separatory funnel until all of the thiophenol was dissolved. The aqueous solution was washed three times with CH_2Cl_2 to remove any unreacted thiophenol and disulfides formed. The allyl-*3,3-d*$_2$ chloride (3 g, 0.055 mol) was added and the solution again shaken vigorously. The aqueous solution was extracted three times with 25-mL portions of CH_2Cl_2 and the combined extracts washed twice with 5% NaOH and three times with H_2O, dried over Na_2SO_4, and concentrated under vacuum. Distillation through a small Vigreux column under high vacuum yielded 80–85% of the para-substituted allyl-*3,3-d*$_2$ phenyl sulfide. The *p*-nitro derivative was purified by repeated recrystallizations from a mixture of ether–petroleum ether (1:4) to yield pale yellow crystals, mp 40–41 °C (lit.[55] undeuterated 40–41 °C). The analyzed and calculated molecular weights were identical as determined by mass spectrometry. Analysis by GLC showed that all compounds used in the kinetic runs were of ≥99% purity.

Thermolysis of 4 in the Presence of 5. Equal concentrations of **4** and

5 (ca. 1 M) in decalin solvent were degassed and reacted in sealed tubes in the usual manner at 160 °C for 3 h. Analysis by GLC showed that two new products had been formed, namely **4a** and **5a**. Analytical samples of **4**, **4a**, **5**, and **5a** were obtained from the reaction mixture by preparative GLC using a diethylene glycol adipate column.

Preparation of 2-Methylallyl-*1,1-d*$_2$ Alcohol. A 250-mL round-bottomed flask fitted with a mechanical stirrer, dropping funnel, and the thermometer was charged with lithium aluminum deuteride-d_4 (2 g, 0.0476 mol) (99% D) and 125 mL of dry ether, distilled from lithium aluminum hydride just before use. The reaction mixture was cooled in a dry ice-acetone bath until the temperature of the ether slurry was between −15 and −20 °C. Methyl methacrylate (8 g, 0.080 mol) dissolved in 30 mL of dry ether was added dropwise to the slurry at such a rate as to maintain the temperature between −15 and −20 °C. After the addition was complete (ca. 1 h) the reaction mixture was warmed to room temperature and 2 mL of H_2O, 2 mL of 15% NaOH, and 6 mL of H_2O were cautiously added with cooling. The solution was suction filtered using partial vacuum and the residual inorganic salts were washed three times with 15-mL portions of ether. The washings were combined, dried over K_2CO_3, and concentrated under vacuum. Distillation through a small Vigreux column at atmospheric pressure yielded 5 g of 2-methylallyl-*1,1-d*$_2$ alcohol, bp 114 °C (760 mm) (lit.[53] undeuterated 114 °C). This product was observed to be essentially pure by GLC (10-ft SE-30 column) and to have the same retention time as the undeuterated 2-methylallyl alcohol as determined by peak enhancement: NMR δ 1.68 (d, 3, J = 1.5 Hz, CH_3), 4.32 (br s, 1, OH), 4.68-4.98 (m, 2, CH_2=C), <5% 3.35-3.68 (CH_2O); IR (neat), 3.00 s (OH), 6.05 m, and 11.20 μ, s (vinyl).

Preparation of 2-Methylallyl-*1,1-d*$_2$ Chloride. A 25 mL round-bottom flask fitted with a small Vigreux column and dropping funnel was charged with 2-methylallyl-*1,1-d*$_2$ alcohol (4 g, 0.054 mol) and pyridine (4.8 g, 0.060 mol). After cooling to −50 °C with a dry ice-acetone bath, $SOCl_2$ (7 g, 0.060 mol) was added dropwise. This addition required about 15 min after which the flask was heated to 80 °C by a small oil bath with slow distillation of the 2-methylallyl-*1,1-d*$_2$ chloride, yield 75%, 3.5 g, bp 73 °C (760 mm) (lit.[53] undeuterated 73 °C). This product was essentially pure by GLC (10-ft SE-30 column) and had the same retention time as the undeuterated 2-methylallyl chloride as determined by peak enhancement: NMR δ 1.85 (d, 3, J = 1.5 Hz, CH_3), 4.86-5.12 (m, 2, CH_2=), <5% 3.98 (CH_2Cl).

Preparation of 2-Methylallyl-*1,1-d*$_2$ Phenyl Sulfide (6). The 2-methylallyl-*1,1-d*$_2$ chloride was reacted with sodium thiophenolate according to previous procedures: NMR δ 1.82 (d, 3, J = 1 Hz, CH_3), 4.70-4.82 (m, 2, CH_2=), 7.00-7.42 (m, 5, Ar), <5% 3.41 (SCH_2); IR (neat) 6.80 s and 7.30 m (methyl), 6.10 m, 7.02 s, and 11.20 s (geminal disubstituted alkene), 13.60 s and 14.52 μ, s (monophenyl); mass spectrum mol wt anal. 166, calcd 166.

Preparation of Propargyl-*3-d* Phenyl Ether. Sodium hydride (5 g of 57% oil dispersion), washed twice with *n*-hexane, was added to propargyl phenyl ether[56] (10 g, 0.076 mol) in 150 mL of *n*-hexane. After stirring for 8 h at room temperature D_2O (5 mL of 99.9%) was slowly added with cooling and stirring continued for an additional 8 h. The solution was filtered, and the hexane layer separated, dried over K_2CO_3, and concentrated under vacuum to yield propargyl-*3-d* phenyl ether, 9 g: NMR δ 4.52 (s, 2, OCH_2), 6.72-7.40 (m, 5, Ar), <5% 2.35 (tr, 1, J = 2 Hz, C=CH_2).

Preparation of Allyl-*2,3,3-d*$_3$ Phenyl Ether (7). A mixture of propargyl-*3-d* phenyl ether (2 g), Pd/$BaSO_4$ (20 mg of 5%), and quinoline (10 drops) dissolved in 15 mL of *n*-hexane was deuterated at 1 atm for 2 h using a typical Brown hydrogenation apparatus.[57] Deuterium (D_2) was generated by dropping D_3PO_4 (P_2O_5 plus D_2O) over Mg turnings suspended in D_2O. Filtration and evaporation of the solvent under vacuum yielded a pale yellow oil. Distillation through a small Vigreux column under high vacuum yielded allyl-*2,3,3-d*$_3$ phenyl ether, 1.5 g. The ether was essentially pure by GLC (10-ft SE-30 column) and had the same GLC retention time as the undeuterated allyl phenyl ether: NMR δ 4.58 (s, 2, OCH_2), 6.68-7.51 (m, 5, Ar), <5% 5.19-5.70 (CH_2=C), and 5.86-6.53 (C=CH).

Thermolysis of 4 in the Presence of 7c. Equal concentrations of **4** and **7c** (ca. 1 M) in decalin solution were degassed and then heated at 160 °C overnight. Analysis by GLC indicated approximately 4% conversion to **8** and **3b**. Products were readily determined by peak enhancements using a 12-ft diethylene glycol adipate column as well as a nonpolar 10-ft SE-30 column.

Preparation of 1-Methylallyl Phenyl Sulfide (1). The 3-chloro-1-butene, contaminated with about 15% 1-chloro-2-butene, was reacted with sodium thiophenolate according to the procedure of Cope et al.[2] to yield a mixture consisting of 65% of the desired 1-methylallyl phenyl sulfide. This was separated from the mixture by careful vacuum distillation using a Nester-Faust 18-in. spinning band column, bp 54 °C (0.4 mm).

Thermolysis of 1-Methylallyl Phenyl Sulfide to *cis*- and *trans*- (1:3) Crotyl Phenyl Sulfide. 1 Converted to 2. The rearrangement of **1** to **2** was followed by GLC using a 12-ft diethylene glycol adipate column at 130 °C and 1,2,4-trichlorobenzene as an internal standard. The two isomers were separated by preparative GLC using a 12 ft × 0.25 in. diethylene glycol adipate column and were distinguished from each other by comparison of their IR spectra. The trans isomer had a strong bond at 960 cm^{-1} which is characteristic of a trans double bond. This assignment is also consistent with the observation that the trans isomer should be sterically preferred and thus present in the greater amount.

Preparation of 1,1-Dimethylallyl Phenyl Sulfide (9). A mixture of 1,1-dimethylpropargyl phenyl sulfide[58] (2 g, 0.012 mol) and 1 g of 10% Pd/C suspended in 25 mL of dimethylformamide was hydrogenated at 1 atm and 25 °C for 12 h. The mixture was filtered, 100 mL of H_2O added, and the solution extracted twice with 25-mL portions of pentane. The combined extracts were dried over Na_2SO_4 and concentrated under vacuum to yield 2 g of a pale, viscous, yellow oil. Purification by preparative GLC using a 12 ft × 0.25 in. 3,3-(2,2-bis-2-cyanoethoxymethyltrimethylenedioxy)dipropionitrile (Eastman) column yielded pure 1,1-dimethylallyl phenyl sulfide: NMR δ 1.39 (s, 6, dimethyl), 4.55-5.08 (m, 2, CH_2=), 5.77-6.29 (m, 1, CH), 7.18-7.65 (m, 5, Ar); IR (neat), 3.45 m, 6.80 m, 6.95 m, (methyl), 10.90 s (vinyl), 13.28 s, and 14.40 μ, s, (monophenyl); mass spectrum mol wt anal. 178, calcd 178.

Thermolysis of 1,1-Dimethylallyl Phenyl Sulfide to 3,3-Dimethylallyl Phenyl Sulfide. 9 Converted to 9a. The kinetic analyses were performed on a 6-ft UC-W98 column at 160 °C using 1,2,3,4-tetrachlorobenzene as an internal standard. Compound **9a** was separated by preparative GLC and identified by its NMR spectrum: NMR δ 1.62 (d, 6, J = 8 Hz, dimethyl), 3.42 (d, 2, J = 8 Hz, SCH_2), 5.22 (tr, 1, J = 8 Hz, CH), 7.18 (s, 5, Ar).

Preparation of 4,4-Dimethyl-2-cyclohexenol. This was prepared by a modification of the procedure of Julia et al.[59] A 500-mL round-bottom flask fitted with a mechanical stirrer, dropping funnel, and thermometer was charged with lithium aluminum hydride (12 g, 0.0316 mol) and 250 mL of dry ether. The reaction mixture was cooled in a dry ice-acetone bath until the temperature of the ether slurry was between −15 and −20 °C. The 4,4-dimethyl-2-cyclohexenone[60] (10 g, 0.080 mol) dissolved in 100 mL of dry ether was added dropwise to the lithium aluminum hydride slurry at such a rate as to maintain the temperature between −15 and −20 °C. After the addition was complete, the reaction mixture was warmed to room temperature and 1.5 mL of H_2O, 1.5 mL of 15% NaOH, and 3 mL of H_2O were cautiously added with cooling. The solution was filtered and the residual salts were washed three times with 15-mL portions of ether. Combined filtrate and washings were dried over K_2CO_3 and concentrated under mild vacuum to yield 9.5 g of 4,4-dimethyl-2-cyclohexenol: IR (neat) 3.05 s (OH), 13.35 μ s (alkene); no carbonyl absorption could be detected.

Preparation of 4,4-Dimethyl-2-cyclohexenyl Chloride. A 100-mL round-bottom flask fitted with a condenser and dropping funnel was charged with 4,4-dimethyl-2-cyclohexenol (5 g, 0.040 mol) and pyridine (4 g, 0.050 mol). The flask was cooled to −50 °C using a dry ice-acetone bath and $SOCl_2$ (6 g, 0.050 mol) was added dropwise. After addition was complete, the reaction was warmed to room temperature, chloroform (40 mL) added, and the resulting mixture refluxed until the evolution of SO_2 had ceased (ca. 1 h). The cooled solution was washed twice with 100 mL of 5% $NaHCO_3$, dried over K_2CO_3, and concentrated under vacuum. Distillation through a small Vigreux column yielded 3 g of 4,4-dimethyl-2-cyclohexenyl chloride: NMR δ 1.00 (s, 6, dimethyl), 1.09-2.25 (m, 4, CH_2CH_2), 4.25 -4.58 (m, 1, ClCH), 5.30-5.76 (m, 2, CH=CH); IR (neat) 12.66 μ s (C-Cl).

Preparation of 4,4-Dimethyl-2-cyclohexenyl Phenyl Sulfide (12). A 25-mL round-bottom flask fitted with a condenser and dropping funnel was charged with thiophenol (3 g, 0.025 mol) and NaOH (1 g, 0.025 mol) dissolved in 15 mL of ethanol. After refluxing for 30 min, 4,4-dimethyl-2-cyclohexenyl chloride (1.5 g, 0.0 mol) was added in one portion and the solution refluxed for an additional 1 h. The cooled solution was shaken with NaOH (100 mL of 10%) and extracted twice

with 25-mL portions of CH_2Cl_2. The combined extracts were dried over Na_2SO_4 and concentrated under vacuum to yield 2 g of crude 4,4-dimethyl-2-cyclohexenyl phenyl sulfide. Further purification by preparative GLC using a 12-ft 3,3-(2,2-bis-2-cyanoethoxymethyltrimethylenedioxy)dipropionitrile column yielded pure material: NMR δ 0.98 (s, 6, dimethyl), 1.25–2.08 (m, 4, CH_2CH_2), 3.52–3.81 (m, 1, SCH), 5.48–5.60 (m, 2, CH=CH), 7.02–7.45 (m, 5, Ar); IR (neat), 12.75 s (cis alkene), 13.64 s and 14.55 μs (monophenyl); mass spectrum mol wt anal. 218, calcd 218.

Thermolysis of 4,4-Dimethyl-2-cyclohexenyl Phenyl Sulfide to 4,4-Dimethyl-1-cyclohexenyl Phenyl Sulfide, 12 to 12b. The kinetic analyses were carried out using a 12-ft 3,3-(2,2-bis-2-cyanoethoxymethyltrimethylenedioxy)dipropionitrile column at 150 °C. Compound **12b** was separated by preparative GLC and identified by its NMR and IR spectra: NMR δ 0.95 (s, 6, dimethyl), 1.09–2.32 (m, 6, CH_2), 5.82–6.10 (m, 1, SCH), 7.24 (s, 5, Ar); IR (neat), 7.35 m (*gem*-dimethyl), 12.30 m (cis alkene), 13.56 s, and 14.55 μs (monophenyl).

References and Notes

(1) H. Kwart and M. H. Cohen, *Chem. Commun.*, 319 (1968).
(2) A. C. Cope, D. E. Morrison, and L. Field, *J. Am. Chem. Soc.*, **72**, 59 (1950).
(3) H. Kwart and N. A. Johnson, *J. Am. Chem. Soc.*, **92**, 6064 (1970).
(4) Y. Makisumi and Murabayashi, *Tetrahedron Lett.*, 1975 (1969).
(5) H. D. Young, "Statistical Treatment of Experimental Data", McGraw-Hill, New York, N.Y., 1962, Chapter IV.
(6) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism", Wiley, New York, N.Y., 1961, pp 98–1.
(7) P. Fahrni and H. Schmid, *Helv. Chim. Acta*, **42**, 1102 (1959).
(8) There is much additional evidence and argument of kinetic nature against the intervention of a six-centered transition state of bimolecular isomerization which cannot be considered here in full detail. For example, a six-centered process (eq 9a) would require kinetic consideration of the steps $2A \rightleftharpoons A + B$ and $2B \rightleftharpoons A + B$. This leads to an integrated form of the rate law which can be shown to be inconsistent with the phenomenological equation (6) when there is a large extent of bimolecular reaction, i.e., when $k_2A_0 \gg 2k_1$.
(9) H. Kwart and J. Slutsky, *J. Am. Chem. Soc.*, **94**, 2515 (1972).
(10) (a) F. G. Bordwell, *Acc. Chem. Res.*, **3**, 281 (1970); (b) F. G. Bordwell and H. M. Anderson, *J. Am. Chem. Soc.*, **75**, 6019 (1953).
(11) H. C. Brown and Y. Okamoto, *J. Am. Chem. Soc.*, **80**, 4979 (1958).
(12) H. H. Jaffe, *Chem. Rev.*, **53**, 197 (1953).
(13) J. K. Coward and W. D. Sweet, *J. Org. Chem.*, **36**, 2337 (1971); see also R. J. Basalay and J. C. Martin, *J. Am. Chem. Soc.*, **95**, 2565, 2572 (1973).
(14) R. S. Mulliken, *J. Am. Chem. Soc.*, **72**, 4493 (1950).
(15) H. H. Jaffee, *J. Chem. Phys.*, **58**, 185 (1954).
(16) (a) D. P. Craig and T. Thirunamachandran, *J. Chem. Phys.*, **43**, 4183 (1965); (b) K. A. R. Mitchell, *Chem. Rev.*, **69**, 159 (1969); (c) J. Musher, *Angew. Chem., Int. Ed. Engl.*, **8**, 54 (1969), discusses this matter in some detail.
(17) It should be understood that no detectable rearrangement occurred during the GLC analysis, as determined by valid, internal standard techniques. Moreover, since our preliminary communication (see ref 3), it was noted that only scrupulous degassing through cycles of freezing and thawing under vacuum resulted in a minimum, steady value of the isomerization rate. As a consequence, some of the activation parameters reported in ref 3 must be regarded with caution. The most reliable values for the uncatalyzed reaction are those presented in this report. The catalytic effects of added oxygen and other oxidizing agents will be discussed in a future report.
(18) H. M. Frey and R. Walsh, *Chem. Rev.*, **69**, 103 (1969).
(19) J. Slutsky and H. Kwart, *J. Am. Chem. Soc.*, **95**, 8678 (1973).
(20) (a) R. Hoffmann and R. B. Woodward, *Acc. Chem. Res.*, **1**, 17 (1968), and subsequent articles by these authors; (b) For evidence of other thermal 1,3 hydrogen migrations in heterocyclic systems see D. M. A. Armitage and C. L. Wilson, *J. Am. Chem. Soc.*, **81**, 2437 (1959).
(21) H. Kwart and C. M. Hackett, *J. Am. Chem. Soc.*, **84**, 1754 (1962).
(22) (a) However, this would allow for some degree of covalent bonding between C_β–S. (b) E. D. Hughes and C. K. Ingold, *J. Chem. Soc.*, 244 (1935).
(23) R. W. Gurney, "Ions in Solution", Cambridge University Press, New York, N.Y., 1936, Chapter 1.
(24) H. Kwart and P. A. Silver, *J. Org. Chem.*, **40**, 3019 (1975).
(25) P. D. Bartlett and R. R. Hiatt, *J. Am. Chem. Soc.*, **80**, 1958 (1958); **76**, 1425 (1954).
(26) H. R. Ward, R. G. Lawler, and R. A. Cooper, *J. Am. Chem. Soc.*, **91**, 747 (1969); A. R. Lepley, *ibid.*, **90**, 2710 (1968); H. R. Ward and R. G. Lawler, *ibid.*, **89**, 5518 (1967).
(27) J. E. Baldwin and J. E. Brown, *J. Am. Chem. Soc.*, **91**, 3647 (1969).
(28) (a) P. J. Krusic and J. K. Kochi, *J. Am. Chem. Soc.*, **93**, 846 (1971); (b) E. S. Huyser and R. M. Kellogg, *J. Org. Chem.*, **30**, 2867 (1965); (c) S. N. Lewis, J. J. Miller, and S. Winstein, *ibid.*, **37**, 1478 (1972).
(29) (a) P. S. Skell, *Chem. Soc., Spec. Publ.*, **No. 19**, 131 (1965); (b) S. N. Lewis, J. J. Miller, and S. Winstein, *J. Org. Chem.* **37**, 1478 (1972); (c) C. Walling and W. Helmreich, *J. Am. Chem. Soc.*, **81**, 1144 (1959).
(30) H. Kwart and J. J. Stanulonis, *J. Am. Chem. Soc.*, **98**, 4009 (1976).
(31) (a) W. C. Agosta, *Tetrahedron Lett.*, 2681 (1965); (b) J. I. Musher, *J. Am. Chem. Soc.*, **90**, 7371 (1968); (c) J. I. Musher in "Conformational Analysis", G. Chiurdoglu, Ed., Academic Press, New York, N.Y., 1971, p 177.
(32) E. E. Havinga and E. H. Wiebinga, *Recl. Trav. Chim. Pays-Bas*, **78**, 724 (1959).
(33) G. C. Pimentel, *J. Chem. Phys.*, **19**, 446 (1951).
(34) R. J. Hack and R. E. Rundle, *J. Am. Chem. Soc.*, **73**, 4321 (1951).
(35) R. E. Rundle, *J. Am. Chem. Soc.*, **85**, 112 (1963).
(36) R. E. Rundle, *Surv. Prog. Chem.*, **1**, 81 (1963).
(37) I. C. Paul, J. C. Martin and E. F. Perozzi, *J. Am. Chem. Soc.*, **94**, 5010 (1972).
(38) W. A. Sheppard, *J. Am. Chem. Soc.*, **93**, 5597 (1971).
(39) (a) K. S. Pitzer, *Science*, **139**, 414 (1963); (b) J. I. Musher, *ibid.*, **141**, 736 (1963).
(40) W. C. Hamilton, S. J. LaPlaca, F. Ramirez, and C. P. Smith, *J. Am. Chem. Soc.*, **89**, 2268 (1967).
(41) P. Gillespie, P. Hoffman, H. Klusacek, D. Marquarding, S. Pfohl, F. Ramirez, E. A. Tsolis, and I. Ugi, *Angew. Chem., Int. Ed. Engl.*, **10**, 687 (1971).
(42) R. S. Berry, *J. Chem. Phys.*, **32**, 933 (1960).
(43) See F. H. Westheimer, *Acc. Chem. Res.*, **1**, 70 (1968); F. Ramirez, *ibid.*, **1**, 168 (1968).
(44) R. W. LaRochelle and B. M. Trost, *J. Am. Chem. Soc.*, **93**, 6077 (1971); B. M. Trost and H. C. Arndt, *ibid.*, **95**, 5288 (1973).
(45) D. Harrington, J. Weston, J. Jacobus, and K. Mislow, *J. Chem. Soc., Chem. Commun.*, 1079 (1972).
(46) K. Mislow, *Acc. Chem. Res.*, **3**, 321 (1970).
(47) J. C. Martin and R. J. Arhart, *J. Am. Chem. Soc.*, **93**, 2339 (1971); **94**, 4997 (1972).
(48) E. L. Meutterties and W. D. Phillips, *J. Chem. Phys.*, **46**, 2861 (1967); *J. Am. Chem. Soc.*, **81**, 1084 (1959).
(49) H. J. Reich, *J. Am. Chem. Soc.*, **95**, 964 (1973).
(50) G. W. Astrologes and J. C. Martin, *J. Am. Chem. Soc.*, **98**, 2895 (1976).
(51) A. Weissberger and E. Proskauer, "Organic Solvents", Oxford University Press, London, 1935.
(53) "Handbook of Chemistry and Physics", Chemical Rubber Publishing Co., Cleveland, Ohio, 1969–1970.
(54) H. Kwart and E. R. Evans, *J. Org. Chem.*, **31**, 413 1966).
(55) H. J. Backer and N. Dost, *Recl. Trav. Chim. Pays-Bas*, **68**, 1143 (1949).
(56) I. Iwai and J. Ide, *Chem. Pharm. Bull.*, **11**, 1042 (1963).
(57) H. C. Brown, K. Sivasankaran and C. A. Brown, *J. Org. Chem.*, **28**, 214 (1963).
(58) T. L. Jacobs and W. L. Petty, *J. Org. Chem.*, **28**, 1360 (1963).
(59) S. Julia, M. Julia, H. Linares, and J. C. Blondel, *Bull. Soc. Chim. Fr.*, 1952 (1962).
(60) E. L. Eliel and C. A. Lukach, *J. Am. Chem. Soc.*, **79**, 5986 (1957).