Thermally Initiated Reactions of Allyl *sec*-Butyl Sulfone. Observation of a [1,3]-Allylic Rearrangement†

Sun Ok Myong, Linus W. Linder, Jr., Stephen C. Seike, and R. Daniel Little*‡

Department of Chemistry, University of California, Santa Barbara, Santa Barbara, California 93106

Received October 16, 1984

Allyl alkyl sulfones undergo thermal rearrangement to afford alkenes and sulfur dioxide. Details of the mechanism were investigated by studying the thermolysis of allyl *sec*-butyl sulfone (1). Gas-phase pyrolysis of 1 afforded propene, butenes, isopentane, 1,5-hexadiene, and 4-methyl-1-hexene (3) as major products. The activation energy for the process was determined to be 41.4 ± 2.3 kcal/mol in the temperature range 220–272 °C. As the temperature for the pyrolysis was lowered from 560 °C to 192 °C, the ratio of 1,5-hexadiene to 4-methyl-1-hexene (3) changed from 3.89 to 0.04. Furthermore, pyrolysis of allyl-α,α-d_2 *sec*-butyl sulfone (1-d_2) at 580 °C gave a 1:1 mixture of 1,1- and 3,3-dideuterio-4-methyl-1-hexene, but the ratio changed to 1:4.2 at 278 °C. Control experiments illustrated that at least some of the observed deuterium scrambling was due to the existence of a [1,3]-allylic rearrangement within the starting sulfone. Pyrolysis of optically active allyl *sec*-butyl sulfone ((*R*)-1*) at 580 °C and 278 °C afforded racemic 4-methyl-1-hexene (3). A control experiment demonstrated that recovered sulfone was not racemized. These results suggest that the mechanism for the rearrangement changes from a free radical to a more selective and perhaps concerted mechanism as the temperature for the pyrolysis is lowered. Taking this factor into account, it was possible to convert the observed rate constants into contributions from the two competing pathways, k_c and k_r. In this way, it was determined that the activation energies for the concerted and free radical pathways were 39.6 (log A = 11.8) and 48.1 kcal/mol (log A = 14.9), respectively. Kinetic simulation provided a good fit to the existing data and allowed a determination of the rate constant for the [1,3]-allylic rearrangement; good agreement with the existing literature value was obtained.

A variety of cyclic and acyclic sulfones lose sulfur dioxide upon heating or exposure to ultraviolet irradiation.[1-4] The

$$RSO_2R' \rightarrow R{-}R' + SO_2$$
$$R,R' = \text{alkyl, aryl}$$

extrusion reaction has been of interest to organic chemists for decades, and some facinating examples can be found in the review by Vogtle and Rossa and also in recent monographs.[1,2] In 1961, LaCombe and Stewart reported the results of their pioneering research dealing with thermally initiated rearrangement of allylic sulfones.[3] They found that the temperature required to affect the extusion of sulfur dioxide was structure dependent and demonstrated that many functional groups were unaffected by the conditions of the pyrolysis, making it possible to prepare olefinic chloro and fluoro compounds, nitriles, esters, alcohols, acids, and ketones.

Two of the experiments reported by these authors are germane to the work reported herein. First, at 200 °C (atmospheric pressure), benzyl 1-methylallyl sulfone eliminates SO_2 and is converted to 5-phenyl-2-pentene in 32%; no symmetric products indicative of a radical mechanism were detected. Secondly, at 350 °C (atmospheric pressure), neopentyl allyl sulfone is converted to 5,5-dimethyl-1-hexene, propene, and 2-methyl-1-butene. Interestingly, the ratio of 5,5-dimethyl-1-hexene to the other two products increased as the temperature used to effect rearrangement was decreased. From the results of these two experiments, the authors suggested that an intramolecular, four-center, cyclic mechanism predominates at lower temperatures and that a free radical mechanism is operable at higher temperatures.

Several years after the report of La Combe and Stewart first appeared, Hendrickson and Bergeron communicated their results concerning the thermally initiated rearrangement of allylic sulfones.[4a] They noted that the reaction was useful for the production of a quaternary carbon center, that it could be used to convert aryl sulfones to arylalkenes, and that nothing was known concerning the stereochemistry of bond formation.

A number of years ago, we initiated an investigation of both the thermally and photochemically initiated rearrangement of allylic sulfones.[4b] Like Hendrickson and Bergeron, we too were hopeful that the reactions might provide a versatile, synthetically useful method for the creation of carbon–carbon bonds. However, prior to beginning synthetic efforts based upon the existing knowledge of the reaction, we felt it would be wise to carry out a more detailed mechanistic study, the results of which might prove useful in planning future synthetic ventures. In this paper we report the results of a mechanistic investigation of the rearrangement of allyl *sec*-butyl sulfone (1) over the temperature range 192–560 °C.

Preparation of Starting Materials. Allyl *sec*-butyl sulfone (1) was prepared in high yield by oxidation of the corresponding sulfide with *m*-chloroperoxybenzoic acid. The sulfide, in turn, was prepared from 2-butanethiol and allyl bromide by using standard procedures. Dideuterated sulfone 1-d_2 could be prepared by repetitive treatment of 1 with LDA in THF at −70 °C followed by quenching with D_2O. Optically active sulfone (*R*)-1* was prepared from (*S*)-2-butanol which in turn was prepared by asymmetric hydroboration of *cis*-2-butene according to the procedure of Brown.[5]

[†] Taken in part from the Ph.D. Thesis of Sun Ok Myong.

[‡] Alfred P. Sloan Foundation Fellow.

(1) Vogtle, F.; Rossa, L. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 515. Magnus, P. D. *Tetrahedron* **1977**, *33*, 2019. Field, L. *Synthesis* **1978**, 713. For an interesting comparison of thermal and photochemical processes, refer to: Wylie, P. L.; Prowse, K. S.; Belill, M. A. *J. Org. Chem.* **1983**, *48*, 4022 and references therein.

(2) Oae, S., Ed. "Organic Chemistry of Sulfur"; Plenum Press: New York, 1977; pp 527–602. Block, E. "Reactions of Organosulfur Compounds"; Academic Press: New York, 1978. Suter, C. M. "The Organic Chemistry of Sulfur. Tetravalent Sulfur Compounds", Wiley: New York; 1944; pp 658–773. Kharasch, N., Meyers, C. Y., Eds. "The Chemistry of Organic Sulfur Compounds"; Pergamon Press: New York, 1966; Vol. 2, pp 115–136 and 171–153. Barton, S. D.; Ollis, W. D. "Comprehensive Organic Chemistry. The Synthesis and Reactions of Organic Compounds"; Pergamon Press: New York, 1979; Vol. 3, pp 171–213.

(3) La Combe, E.; Stewart, B. *J. Am. Chem. Soc.* **1961**, *83*, 3457.

(4) (a) Hendrickson, J. B.; Bergeron, R. *Tetrahedron Lett.* **1973**, 3609. (b) Little, R. D.; Wolf, S.; Smested, T.; Seike, S. C.; Linder, L. W., Jr.; Patton, L.; *Synth. Commun.* **1979**, *9*, 545.

0022-3263/85/1950-2244$01.50/0

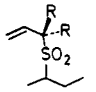
Chart I

$$1 \xrightarrow[\text{flow}]{562\text{-}564\ ^\circ\text{C}} \left\{ \begin{array}{r} \text{ethane + ethylene + propylene + 2-methylbutane +} \\ \text{1,5-hexadiene + butenes + 4-methyl-1-hexene } (\mathbf{3}) + \\ \text{3,4-dimethylhexane + } SO_2 \end{array} \right\}$$

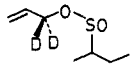
product	ethane	ethylene	propylene	2-methylbutane	1,5-hexadiene
% composition	3.0	6.6	45.5	3.2	8.7

product	butenes	4-methyl-1-hexene (3)	3,4-dimethylhexane
%composition	30.7	2.2	0.08

Finally, 3,3-dideuterio-1-propenyl-2-butyl sulfinate (**2**) was prepared according to the method of Grieco and workers.[6] This sequence required the preparation of the corresponding allylic alcohol. After exploration of several alternative methods, the deuterated alcohol was found to be conveniently prepared by treating the Diels–Alder cycloadduct of anthracene and methylacrylate with lithium aluminum deuteride followed by a retro-Diels–Alder reaction.[7] In this way, the product could be conveniently isolated by distillation as the retro-Diels-Alder reaction was proceeding, thereby avoiding a water workup.



1, R = H
1-d_2, R = D

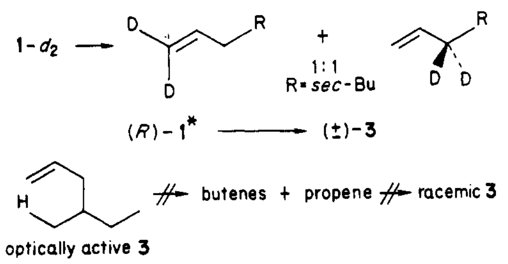


2

Results and Discussion

Flow pyrolysis (nitrogen carrier) of sulfone **1** to complete conversion at 562–566 °C and 4.3 torr led to the extrusion of SO_2. Careful gas chromatographic analysis revealed the presence of at least eight products, the nature and composition of which is indicated below. It is interesting to note that under these conditions 4-methyl-1-hexene (**3**), the product of greatest interest from the viewpoint of possible synthetic applications, constitutes only 2.2% of the total product composition (Chart I). Pyrolysis in the presence of the free radical initiator benzoyl peroxide did not affect the product composition. Furthermore, no significant change in the product composition was observed when the surface to volume ratio was changed by using either empty or quartz chip packed pyrolysis tubes.

When the dideuterated sulfone **1**-d_2 was subjected to the same reaction conditions, a one-to-one mixture of 3,3- and 1,1-dideuterio-4-methyl-1-hexene was observed. Furthermore, pyrolysis of optically active sulfone (*R*)-**1*** afforded racemic 4-methyl-1-hexene (**3**). To rule out the somewhat unlikely possibility that racemization might have occurred via the retroene–ene reaction sequence illustrated below, two experiments were performed. In the first, 4-methyl-1-hexene was pyrolyzed; no detectable amount of propene or butenes were formed. In the second, a flow pyrolysis of a mixture of propene, *cis*- and *trans*-2-butene, and 1-butene failed to produce **3**.



On the basis of the results presented thus far, the reaction of sulfone **1** under the flow pyrolysis conditions can be explained in terms of a free radical mechanism wherein the first, and rate-determining, step involves the homolytic cleavage of the allyl–sulfur bond to form the allyl and 2-butanesulfonyl radical. Subsequent breakdown of the 2-butanesulfonyl radical leads to the formation of sulfur dioxide and the allyl and 2-butyl radicals. Since the bond dissociation energy for the allyl–sulfur bond is lower than that for the alkyl–sulfur bond (13 kcal/mol for allyl-2-propyl),[8] one would expect the cleavage to the allyl–sulfur bond to occur prior to that of the 2-butyl carbon–sulfur bond. The concerted two-bond cleavage to give sulfur dioxide and the allyl and 2-butyl radical is considered unlikely on the basis of the results obtained by Busfield for the free radical decomposition of allyl methyl sulfone.[8] He found that the magnitude of the frequency factor ($\log A = 14.10$) was within the "normal" range for unimolecular reactions involving breakdown into two fragments, i.e., a one-bond cleavage reaction. Furthermore, the activation energy ($E_a = 47.7 \pm 0.7$ kcal/mol) was 22 kcal/mol lower than the sum of the two-bond dissociation energies (viz., that for the C_3–S plus the S–CH_3 bonds). In other words, the activation energy required for two-bond cleavage is greater than the observed activation energy. It is reasonable to assume that these same considerations apply to the chemistry of allyl *sec*-butyl sulfone.

The possibility of the 2-butanesulfonyl radical reacting intermolecularly, prior to its fragmentation into sulfur dioxide and the 2-butyl radical, can be ruled out from a consideration of the conditions used for the pyrolysis (gas phase, 560 °C) and the instability of the alkanesulfonyl radicals at high temperatures. Assuming that the dissociation energy for the 2-butanesulfonyl radical can be approximated by the dissociation energy for the 2-propanesulfonyl radical, which has been estimated to be 22.1 ± 3.6 kcal/mol,[8] and assuming $\log A = 13$, then the half-life for the decomposition of the 2-butanesulfonyl radical can be calculated to be a very short 4×10^{-8} s at 560 °C.[9] Furthermore, Good and Thynne[10] studied the gas-phase reaction of sulfur dioxide with methyl radicals in the temperature range 25–164 °C and found that the methanesulfonyl radicals become increasingly unstable as the temperature increases. For example, at 164 °C, no methanesulfonyl radical was detected in the reaction

$$\cdot CH_3 + SO_2 \rightleftharpoons CH_3SO_2\cdot$$

Combination and disproportionation reactions of the allyl and the 2-butyl radicals result in the formation of the butenes, propene, biallyl, and 4-methyl-1-hexene (**3**) as major products. The formation of only a trace amount (<1%) of 3,4-dimethylhexane, the coupling product of two *sec*-butyl radicals, may be explained when one considers the relative amounts of coupling (AA, BB) and cross-coupling (AB) products which would be expected from the combination of two nonpolar radicals A and B. Trotman-Dickensen reported[11] that $(AB)/[(AA)(BB)]^{1/2} = 2$. Assuming that this equation holds for the allyl and 2-butyl radicals, and knowing the amounts of biallyl (AA = 0.137

---

[5] Brown, H. C.; Yoon, N. M. *Israel J. Chem.* **1976/77**, *15*, 12. (*R*)-(+)-Allyl *sec*-butyl sulfone, $[\alpha]^{25}{}_D$ +7.68° (*c* 0.02, chloroform), was found to be optically pure by ^1H NMR analysis using tris[3-[(heptafluoropropyl)hydroxymethylene]camphorato]europium(III) shift reagent; unpublished result of L. Linder.

[6] Grieco, P. A.; Boxler, D. *Synth. Commun.* **1975**, *5*, 315.

[7] Bartlett, P. D.; Tate, F. A. *J. Am. Chem. Soc.* **1953**, *75*, 91.

[8] Busfield, W. K.; Ivin, K. J. *Trans. Faraday Soc.* **1961**, *57*, 1044.

[9] Chatgilialoglu, C.; Lunazzi, L.; Ingold, K. U. *J. Org. Chem.* **1983**, *48*, 3588.

[10] Good, A.; Thynne, J. C. J. *Trans. Faraday Soc.* **1967**, *63*, 2708.

[11] Trotman-Dickenson, A. F. *Annu. Rev. Phys. Chem.* **1959**, *10*, 53.

Table I. Effect of Temperature upon the Product Composition from the Pyrolysis of Sulfone 1

		products[a] (% composition)									mass balance
run	T, °C	A	B	C	D	E	F	G	H	I	(%)
1	562–564		4.8 (3.0)	10.4 (6.6)	72.0 (45.5)	5.1 (3.2)	13.7 (8.7)	48.7 (30.8)	0.1 (0.06)	3.5 (2.2)	77
2	364	332.6	0.58 (18.2)		0.21 (6.58)		0.1 (3.1)	0.9 (28.2)		1.4 (43.9)	94
3	379	0.3			1.2 (11.3)		2.2 (20.8)	3.6 (34.0)		3.6 (34.0)	64
4	278	2.4			0.1 (3.2)		0.3 (9.7)	1.0 (32.3)		1.7 (54.8)	76
5	192	5.0					0.03 (2.4)	0.2 (16.3)		1.0 (81.3)	93

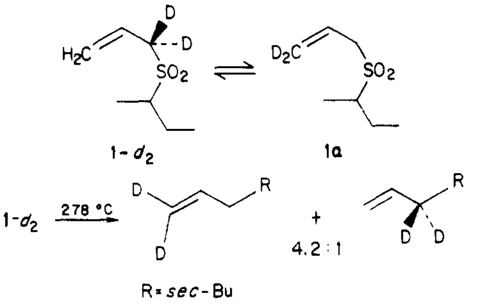
[a] A = recovered sulfone 1, B = ethane, C = ethylene, D = propylene, E = 2-methylbutane, F = 1,5-hexadiene, G = butenes, H = 3,4-dimethylhexane, I = 4-methyl-1-hexene (**3**). Numbers must be multiplied by 10^{-5} to obtain the composition in moles.

Table II. Biallyl (B) to 4-Methyl-1-hexene (3) Ratio as a Function of Temperature

	flow method	static method, T		
	T = 560 °C	379 °C	278 °C	192 °C
B/**3**	3.89	0.60	0.20	0.04

mmol) and 4-methyl-1-hexene (AB = (**3**) = 0.035 mmol) formed in the pyrolysis, the expected amount of 3,4-dimethylhexane (BB) is estimated to be (0.25AB)/AA = 2×10^{-3} mmol = 0.2% yield. Thus, one would in fact expect the formation of only a trace amount of 3,4-dimethylhexane, as observed.

The formation of 2-methylbutane could occur via the combination of a 2-butyl and a methyl radical; the methyl radical, in tern, was presumably formed via fragmentation of the 2-butyl radical.[12]



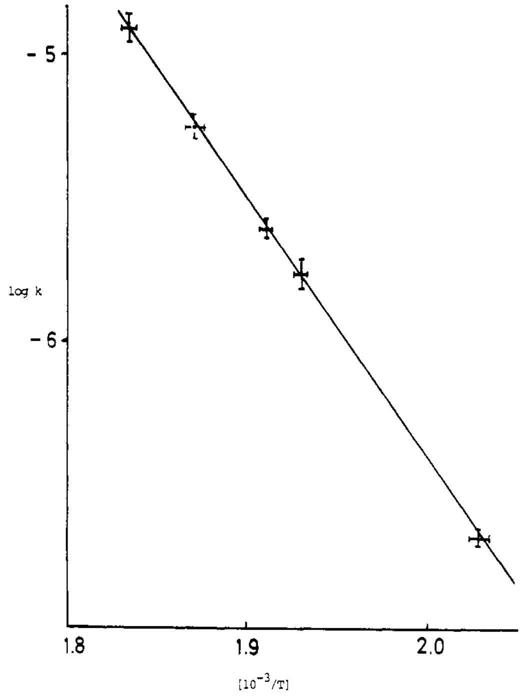


Figure 1. Arrhenius plot for the disappearance of sulfone 1.

Table III. Rate Constants for the Disappearance of Sulfone 1

T, °C	rate constants, s^{-1}
220.0 ± 1.2	2.11×10^{-6}
245.0 ± 1.6	1.75×10^{-5}
250.0 ± 1.0	2.48×10^{-5}
262.0 ± 0.2	5.75×10^{-5}
271.8 ± 1.6	1.22×10^{-4}

Effect of Temperature. To examine the chemistry of sulfone 1 in greater detail, dideuterated sulfone 1-d_2 was pyrolyzed to incomplete conversion at 278 °C (3.8 h, gas phase, sealed tube). Two significant observations were made. First, ^1H NMR analysis of the recovered sulfone indicated the presence of the isomerized sulfone **1a**, the product of a formal [1,3]-shift of the alkanesulfonyl unit across the allylic portion of the molecule; this reaction will be discussed in some detail later. Second, in contrast with the 1:1 ratio of 1,1- to 3,3-dideutereo-4-methyl-1-hexene which was observed at the higher temperature, the ratio changes to 4.2:1 at 278 °C. These results clearly suggest that the thermal chemistry of sulfone may be more complex than has been assumed thus far.

To study the dependence of the reaction upon temperature, the gas-phase pyrolysis of sulfone 1 was studied over a temperature range of 192–560 °C. The results are summarized in Table I. At lower temperatures, although the products arising via free radical process are present, the amount of 4-methyl-1-hexene (**3**) relative to the other products has increased considerably. In particular, the ratio of biallyl to 4-methyl-1-hexene (**3**) changes from 3.89 to 0.04 upon lowering of the temperature from 564 °C to 200 °C (Table II). The change in the product composition is unlikely to be the result of a radical cage formation since the pyrolyses were carried out in gas phase. Finally, it is

---

(12) (a) Bywater, S.; Steacie, E. W. R. *J. Chem. Phys.* **1951**, *19*, 172. (b) In principle, fragmentation of the 2-butyl radical could lead to a change in the B/**3** ratio. However, the following considerations suggest that this is probably not the case. The Arrhenius parameters for fragmentation of the 2-butyl radical are $E_a = 32.6$ and log $A = 14.6$.[12c] Therefore, at 833 K, $k_f \sim 2.8 \times 10^{5.6}$, while at 465 K, $k_f \sim 4.8 \times 10^{-1.4}$, i.e., as expected, the rate of fragmentation increases dramatically as the temperature is increased. However, if one makes the reasonable assumption that the Arrhenius activation energy for the combination of allyl and 2-butyl radicals is zero and that log $A \sim 10$, then the rate constant for the combination of these two radicals, k_c, is 10^{10}. Similarly, from the known[12d] Arrhenius parameters for dimerization of the allyl radical, viz., $E_a = 0$, log $A = 9.93$, it is easy to see that $k_d = 10^{9.93}$, i.e., that the rate is comparable to that for the combination of allyl and 2-butyl radicals and both processes are significantly faster than fragmentation. (c) Kerr, J. A.; Parsonage, M. J. "Evaluated Kinetic Data on Gas Phase Addition Reactions: Reactions of Atoms and Radicals with Alkenes, Alkynes, and Aromatic Compounds"; Butterworths: London, 1972. (d) van den Bergh, H. E.; Callear, A. B. *Trans. Faraday Soc.* **1970**, *66*, 2681.

interesting to note that at 192 °C the yield of 4-methyl-1-hexene (**3**) has increased to 76%.

The decrease in the biallyl to 4-methyl-1-hexene (**3**) ratio and the observance of some regioselectivity in the formation of deuterated 4-methyl-1-hexene can be considered as evidence for the occurrence of another mechanism, perhaps a concerted pathway, at lower temperatures. Moreover, if the difference in the enthalpy of activation, $\Delta\Delta H^{\ddagger}$, for the two pathways is small, then the possibility exists that both process occur simultaneously over some temperature range.

To test this idea quantitatively, the kinetics of the reaction was studied in the temperature range of 220–272 °C. The first-order rate constants derived from the disappearance of the sulfone **1** are presented in Table III; the Arrhenius plot is shown in Figure 1. The Arrhenius parameters, determined by the least-squares method, are given by

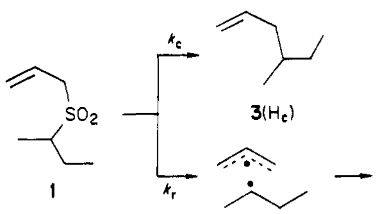
$$\log k = (12.7 \pm 1.0) - (41.4 \pm 2.3/2.303RT)$$

Since the kinetics were carried out in the temperature range where both mechanisms are presumed to be operable, the observed activation energy describes the combined free radical and concerted pathways, and the experimental rate constant is the sum of the rate constant for the concerted and free radical processes:

$$k_{\text{obsd}} = k_c + k_r$$

If the ratios of the rate constants, k_r and k_c, are known, then the activation energy for the concerted and the free radical process can be derived. The ratios of the rate constants, in turn, can be obtained from the product composition as described below.

Consider the partitioning of sulfone **1** between the free radical and concerted pathways illustrated. Let H_c = the amount of 4-methyl-1-hexene (**3**) formed by way of the concerted pathway, R = the amount of free radical products formed, S_0 = the amount of sulfone **1** at time zero, and $S_t = S_o - H_c - R$ = the amount of sulfone **1** at some time, t. Then it follows that



$$d(H_c)/dt = k_c(S_t) = k_c(S_o - H_c - R)$$

and

$$d(R)/dt = k_r(S_t) = k_r(S_o - H_o - R)$$

Therefore, $k_c/k_r = H_c/R$. To determine H_c, recognize that $H_c = H_T - H_r$, where H_T = the total amount of 4-methyl-1-hexene (**3**) formed, and H_r = the amount of **3** formed via the free radical pathway. If one assumes that the ratio of 1,5-hexadiene (biallyl, B) to 4-methyl-1-hexene (**3**) produced by way of the free radical mechanism remains constant over a wide range of temperatures (192–560 °),[12] then by knowing that ratio at a temperature wherein only the free pathway is operating one can determine H_r at a different temperature. It is known that B/**3** = 3.89 at 560 °C, a temperature which fits the criterion set forth above. Therefore, at 287 °C, H_r = B/3.89, and since both H_T and B can readily be measured at any temperature, it follows that $H_c = H_T - \text{B}/3.89$.

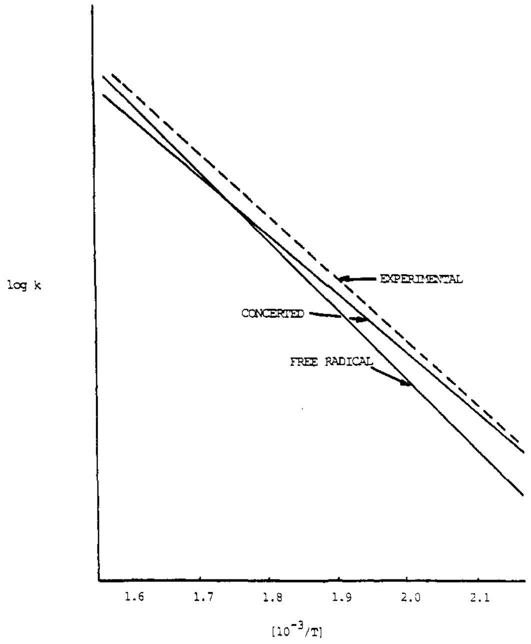


Figure 2. Arrhenius plot comparing the concerted and free radical components with experiment.

Table IV. Estimated Rate Constants

rate constant, s^{-1}	T = 278 °C	T = 192 °C
k_r	6.54×10^{-5}	1.93×10^{-8}
k_c	1.18×10^{-4}	1.48×10^{-7}
k_{obsd}	1.83×10^{-4}	1.66×10^{-7}

Table V

proposed mechanism	T, °C	$\Delta H^{\ddagger}$ (kcal/mol), $E_a - RT$	$\Delta G^{\ddagger}$ (kcal/mol), $-RT \ln kh/KT$	$\Delta S^{\ddagger}$ (eu), $(\Delta H^{\ddagger} - \Delta S^{\ddagger})/T$
concerted	192	38.7	42.2	−7.4
	278	38.5	42.8	−7.9
	560	37.9	45.1	−8.6
radical	192	47.2	44.0	+6.8
	278	47.0	43.5	+6.4
	560	46.4	41.8	+5.6

To determine R, the amount of sulfone **1** which reacts by the free radical pathway, one needs to use care to account for the fact that all of the carbon atoms in the products have a common source, that being the seven carbon atoms in sulfone **1**. For example, the six carbons of biallyl (B), the four carbons in the butenes, the three carbons of propene, etc., all have their origin in sulfone **1**. As a result, the number of mmol of biallyl (B) must be multiplied by $^6/_7$, the amount of propene by $^3/_7$, etc. Finally, the resulting values can be summed to assure conservation of mass and determine that

$$R = \tfrac{1}{7}[6(\text{B}) + 4(\text{butenes}) + 3(\text{propene}) + 7(\text{B}/3.89)]$$

By using the product composition obtained experimentally (note Table I), the ratio of rate constants, k_c/k_r, was calculated to be 1.8 and 7.6 at 278 °C and 192 °C, respectively. From these ratios, the rate constants for the free radical and concerted process were determined to be those presented in Table IV.

The estimated rate constants are shown in the form of an Arrhenius plot in Figure 2. From these rate constants, the activation energies for the two processes were determined to be 39.6 kcal/mol (log A = 11.8) and 48.1 kcal/mol (log A = 14.9) for the concerted and free radical process, respectively. The activation parameters obtained from these activation energies are shown in Table V.

Table VI. Deuterium Scrambling of Sulfone 1-d_2

T, °C	time, s	% deuterium scrambling
320	*a*	4 ± 2
278	6440	5 ± 2
278	13 800	20 ± 2
175	25 200	28 ± 2

[a] Flow pyrolysis; contact time <1 s.

Notice that over the entire temperature range, the difference in enthalpies of activation strongly favor the concerted pathway. However, the difference in free energies of activation vary from 1.8 kcal/mol in favor of the concerted pathway at 192 °C to a large 3.3 kcal/mol in favor of the radical pathway at 560 °C. Examination of the last column in Table V clearly reveals that difference in entropies of activation are responsible for these observations. Obviously, for the free radical process wherein $\Delta S^\ddagger > 0$, an increase in temperature will decrease $\Delta G^\ddagger$ whereas for the concerted process wherein $\Delta S^\ddagger < 0$, a decrease in temperature will decrease $\Delta G^\ddagger$.

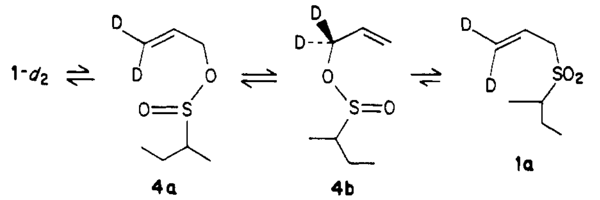
[1,3]-Allylic Rearrangement of Allyl-α,α-d_2 *sec*-Butyl Sulfone (1-d_2). As presented in the preceding section, the deuterated sulfone 1-d_2 rearranges thermally to form sulfone **1a**. The amount of rearranged sulfone, determined by ^{1}H NMR is shown in Table VI.

While the analogous rearrangement in allylic sulfides and sulfoxides has been studied in detail, the sulfone rearrangement has only recently been studied in any detail, although it was first reported as long ago as 1950.[13c] The recent reports of Baechler et al., Kocienski, and Lim and Whitham are particularly noteworthy.[14] In contrast with our gas-phase work, each of the other groups examined only solution-phase chemistry. A variety of mechanisms, ranging from radical chain to tight ion pair have been suggested. Our efforts to provide an adequate description of the gas-phase process are described below.

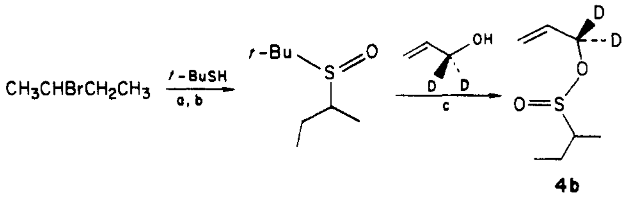
Sulfinate Equilibration. Allylic sulfinates are well-known to undergo [2,3]-sigmatropic rearrangement to form allylic sulfones.[15] The reverse reaction, namely, the rearrangement of an allylic sulfone to form a sulfinate, has not been observed. However, considering that the corresponding sulfenate has not been detected spectroscopically in the analogous [2,3]-sigmatropic rearrangement involving allylic sulfoxides[16,17] despite the fact that it can be intercepted with a variety of thiaphiles, it is not unreasonable to invoke the reversibility of the allylic sulfinate–sulfone rearrangement.

Consideration of the sulfone to sulfinate transformation becomes significant in conjunction with the equilibration of deuterated sulfones 1-d_2 and **1a** if there were to exist a pathway wherein the allylic sulfinates **4a** and **4b** could completely, or partially, equilibrate prior to undergoing conversion to the corresponding deuterium-scrambled sulfones 1-d_2 and **1a**.

To test this possibility, the sulfinate **4b** was prepared by following the sequence shown below.[6,7]



4a **4b** **1a**

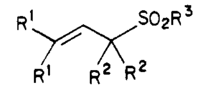


(a) NaOEt, EtOH, room temperature, 4h; (b) NaIO$_4$, H$_2$O-MeOH, 0 °C → room temperature 18 h; (c) NCS, CHCl$_3$, 0 °C, 7h.

^{1}H NMR analysis of the products obtained from the pyrolysis (254 °C, sealed tube, 41 and 105 s) of sulfinate **4b** failed to indicate the presence of the isomerized sulfinate **4a** or sulfone 1-d_2; only sulfone **1a** was detected. We therefore conclude that the sulfinates do not equilibrate under the pyrolysis conditions wherein the sulfone deuterium scrambling occurs.

Coupling of Allyl and 2-Butanesulfonyl Radicals. A Crossover Experiment. An alternative mechanism for the allylic rearrangement might involve homolytic cleavage of sulfone 1-d_2 to afford the allyl and 2-butanesulfonyl radicals followed by recombination to form the deuterium-scrambled product. However, as was stated earlier, the half-life of the 2-butanesulfonyl radical at 560 °C is estimated to be 10^{-8} s (vide supra). As a result of this factor and the fact that the allylic rearrangement was observed in the gas phase at low pressures, we consider it is unlikely that the radicals, once formed, would survive long enough in the gas phase to allow recombination.

To examine this possibility in greater detail, a simple crossover experiment was conducted. Thus, a mixture of allyl isopropyl sulfone and 1-d_2 was pyrolyzed in the gas phase at 174 °C. Assuming that any radicals which might be formed are free to diffuse and recombine, the mixture of recovered sulfones would be expected to contain the following six isomers: Careful mass spectrometric analysis of the recovered allyl *sec*-butyl sulfone mixture indicated the absence of a peak corresponding to the parent for **1**. However, the peak at *m/e* 108.0229 (100% relative abundance) corresponding to $CH_2CHCD_2SO_2H^+$ and consistent with that expected for 1-d_2 and **1a**, along with the peak at 106.0089 (2.41% relative abundance) corresponding to $CH_2CHCH_2SO_2H^+$ and consistent with that expected for **1** and $R^1 = R^2 = H$, $R^3 = i$-Pr, suggest the possibility of crossover. Thus, within the error limits of the analytical techniques used, it can be concluded that if crossover occurs, then it does so in <3% under the present set of reaction conditions.



a, $R^1 = R^2 = H$; $R^3 = i$-Pr
1-d_2, $R^1 = H$; $R^2 = D$; $R^3 = sec$-Bu
b, $R^1 = H$; $R^2 = D$; $R^3 = i$-Pr
1, $R^1 = R^2 = H$; $R^3 = sec$-Bu
1a, $R^1 = D$; $R^2 = H$; $R^3 = sec$-Bu
c, $R^1 = D$; $R^2 = H$; $R^3 = i$-Pr

Kinetic Simulation. In 1982, Baechler and co-workers reported the first and, to the best of our knowledge, only study which allows a direct comparison of the rates and

---

[13] (a) Sulfide: Kwart, H.; Johnson, N. A. *J. Am. Chem. Soc.* **1977**, *99*, 3441. (b) Sulfoxide: Kwart, H.; Benko, D. A. *Ibid.* **1979**, *101*, 1273. (c) Cope, A. C.; Morrison, D. E.; Field, L. *Ibid.* **1950**, *72*, 59.

[14] (a) Baechler, R. D.; Bentley, P.; Deuring, L.; Fisk, S. *Tetrahedron Lett.* **1982**, *23*, 2269. (b) Kocienski, P. *J. Chem. Soc., Perkin Trans 1* **1983**, 943. (c) Lin, P.; Whitman, G. H. *J. Chem. Soc., Chem. Commun.* **1983**, 1102.

[15] Braverman, S. *Int. J. Sulfur Chem. C* **1971**, *6*, 149.

[16] Tang, R.; Mislow, K. *J. Am. Chem. Soc.* **1970**, *92*, 2100. Bickart, P.; Carson, F. W.; Jacobus, J.; Miller, E. G.; Mislow, K. *Ibid.* **1968**, *90*, 4849.

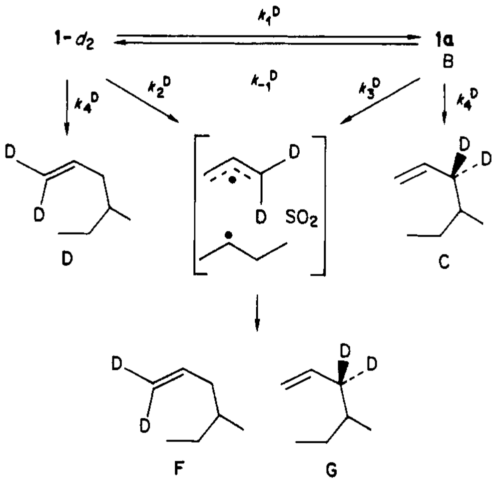
[17] Evans, D. A.; Andrews, G. C. *Acc. Chem. Res.* **1974**, *7*, 147. Evans, D. A.; Andrews, G. C.; Fujimoto, T. T.; Wells, D. *Tetrahedron Lett.* **1973**, 1385 and 1389.

Table VII. Kinetic Data

T, °C	time, s	rate constant (k), s^{-1}	no. of half-lives	correl coeff
220.0 ± 1.2	0 74 272 238 260	2.11×10^{-6} ($\pm 0.22 \times 10^{-6}$)	0.74	0.9930
245.0 ± 1.6	0 16 191 41 052 81 257	1.75×10^{-5} ($\pm 0.22 \times 10^{-5}$)	2.05	0.9991
250.0 ± 1.0	0 6947 52 216	2.48×10^{-5} ($\pm 0.19 \times 10^{-5}$)	1.94	0.9955
262.0 ± 0.2	0 5183 17 757 22 052	5.75×10^{-5} ($\pm 0.15 \times 10^{-5}$)	1.89	0.9984
271.8 ± 1.6	0 5529 11 793	1.22×10^{-4} ($\pm 0.15 \times 10^{-4}$)	2.08	0.9983

activation parameters for the thermal [1,3]-allylic rearrangement of a sulfide, sulfoxide, and sulfone (for the series $PhSXCD_2C(CH_3){=}CH_2$ where the nature of X is variable).[14] Their results confirm qualitative observations which indicate that k(sulfoxide) > k(sulfide) > k(sulfone).

To complete our study and allow comparison with the results of Baechler, we carried out a kinetic simulation for the processes shown below.[18] The free radical and concerted rate constants, k_r (k_2 and k_3) and k_c (k_4 and k_5) obtained at 278 °C and listed in Table IV, were utilized. Since the rate constants for the sulfone isomerization (k_{+1} and k_{-1}) were unknown, they were varied until the results of kinetic simulation agreed with the experimentally determined values for the ratios of A/B (3.5 ± 0.5) and H/I (4.2 ± 0.5) at 13 800 s and 278 °C. The amount of dideuterated 4-methyl-1-hexene (F + G) formed via the free radical pathway was assumed to be 3.5% of total free radical product, E, in accord with the results illustrated in Table I. Thus, since F = G, H = [(3.5%)E(0.5) + D] and I = [(3.5%)E(0.5) + C].



where
H = D + F and I = C + G

An adequate fit, viz, A/B = 3.2 and H/I = 4.8, was obtained by assuming that a secondary equilibrium isotope effect equal to that which has been used in Claisen rearrangement is applicable to the free radical and concerted pathways as well as to the isomerization.[19] In this way k_{+1} was calculated to be 5.4×10^{-5} s^{-1}. At 150 °C, Baechler and co-workers reported a value of 0.39×10^{-5} s^{-1} for the isomerization of $PhSO_2CD_2C(CH_3){=}CH_3$. Use of their activation parameters allows one to calculate a rate constant of 4.2×10^{-5} s^{-1} at 270 °C, in good agreement with that which we have obtained.

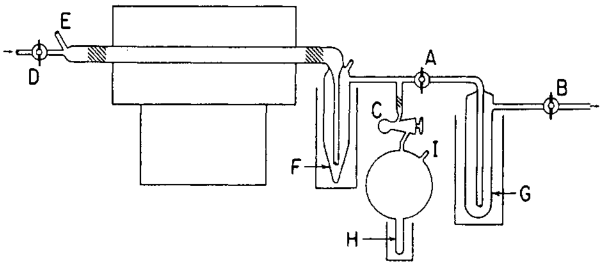


Figure 3. Flow pyrolysis apparatus.

Experimental Section

Proton magnetic resonance spectra were obtained on a Varian T-60 or an XL-100 spectrometer. Chemical shifts are given as parts per million (ppm) downfield from tetramethylsilane (Me_4Si) in δ units, and coupling constants are given in cycles per second (hertz). The ^1H NMR data are reported in the order chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets, bs = broad singlet), number of protons, coupling constants, and assignments.

Infrared spectra (IR) were obtained on a Perkin-Elmer 283 or 337 spectrometer. High-resolution mass spectra were obtained by Dr. M. Pedley on an AEI MS 902 or a ZAB 2-F mass spectrometer. Low-resolution mass spectra were obtained from a Hewlett Packard 5992A GC/MS system by Dr. R. Petty. Elemental analysis were performed by Chemalytics, Inc., Tempe, AZ. Melting points were obtained on a Mel-Temp capillary melting point apparatus and are uncorrected; boiling points are also uncorrected.

Optical rotations were taken on a Bendix automatic polarimeter Model 1169 (2-cm path length cell) or a Perkin-Elmer 141 polarimeter. ORD measurements were obtained with a Cary 60 spectropolarimeter using a 5-cm path length cell.

Analytical gas chromatography was performed on a Hewlett-Packard HP 5830A gas chromatograph equipped with a flame ionization detector (300 °C) and nitrogen carrier gas (30 mL/min). Peak areas were measured with an HP 18850 GC integrator terminal. The injection port temperature was maintained at 190 °C. Preparative gas chromatography was done on a Varian Aerograph Model A-90 or a Loenco 15C-E gas chromatograph equipped with a thermal conductivity detector and helium carrier gas. Medium-pressure liquid chromatography (MPLC) was performed on a variety of Altex columns (2 × 21 cm, 2 × 46 cm, 2 × 96 cm, 3 × 96 cm) packed with E. Merck Silica Gel 60 (230–400 mesh ASTM). The distilled solvents were passed through the system with an FMI Model RPS 4 lab pump. The pressure was kept at 100–120 psi. The eluent was monitored at 280 nm on an Altex Model 150 monitoring system, and the products were

---

(18) Shindell, D. M.; Magagnosc, C.; Purich, D. L. *J. Chem. Educ.* **1978**, *55*, 708.

(19) (a) Gajewski, J. J.; Conrad, N. D. *J. Am. Chem. Soc.* **1979**, *101*, 2747. (b) McMicheal, K. D. *Ibid.* **1967**, *89*, 2943.

collected with an ISCO Model 273 fraction collector.

Reagent grade solvents were used for all reactions. *N,N*-Dimethylformamide (DMF) was distilled from either barium oxide or calcium hydride at atmospheric pressure. Tetrahydrofuran (THF) was pre-dried by refluxing over calcium hydride prior to distillation from sodium benzophenone ketyl. Pyridine was dried by distillation over a calcium hydride. Brucine dihydrate (Aldrich) was dried in a vacuum oven at 98 °C for 15 h prior to use. (+)-Pinene (98%, Aldrich) was purified by a distillation over lithium aluminum hydride ($LiAlH_4$). Lithium aluminum deuteride ($LiAlD_4$) was purchased from Ventron.

All reactions were run under nitrogen or argon atmosphere. Some of the reactions described were run several times under varying conditions. The procedure given is that which resulted in the highest yield of product and least amount of side reactions.

Kinetic simulation was performed with a microcomputer-based reaction kinetic simulator described by Shindell, Magagnosc, and Purich.[18]

Allyl *sec*-Butyl Sulfone (1). To a stirred solution of 20 g (85%, 95 mmol) of *m*-chloroperoxybenzoic acid in 330 mL of dichloromethane was added 6.0. g (46.3 mmol) of allyl *sec*-butyl sulfide at 0 °C. After 0.5 h, the reaction mixture was allowed to warm to room temperature and was stirred there for 2.5 h. The mixture was filtered and the filtrate washed with 10% sodium bisulfite (1 × 100 mL) and water (1 × 100 mL), dried over magnesium sulfate, and concentrated in vacuo to give an oil. The oil was distilled to yield 6.7 g (89%), bp 100–101 °C (1.1 mm), of 1: ^1H NMR ($CDCl_3$) 5.23 –6.32 (m, 3 H, vinyl), 3.71 (d, 2 H, $J = 6$ Hz, allyl), 2.63–3.26 (m, 1 H, SO_2CH), 1.49–2.63 (m, 2 H, CCH_2C), 1.40 (d, 1 H, $J = 7$ Hz, $CHCH_3$), 1.02 ppm (t, 3 H, $J = 7$ Hz, CH_2CH_3); IR (NaCl, film) 2980, 1640, 1459, 1295, 1130, 935 cm^{-1}. Anal. Calcd for $C_7H_{14}SO_2$: C, 51.56; H, 8.49; S, 19.74. Found: C, 51.85; H, 8.64; S, 19.75.

Allyl-α,α-d_2 *sec*-Butyl Sulfone (1-d_2). To a solution of 4.7 g (29 mmol) of allyl *sec*-butyl sulfone in 10 mL of dry THF was added 29 mmol of LDA (in 40 mL of THF–hexane (1:1)) dropwise at −78 °C with stirring. After the solution was stirred for 25 min at −78 °C, 5.5 mL of 99.8% deuterium oxide was added. The cooling bath was then removed and the mixture was stirred for 40 min. The resulting solution was poured into 50 mL of dichloromethane and 30 mL of 1 N hydrochloric acid. The organic layer was separated, washed with water and brine, dried over magnesium sulfate, and concentrated in vacuo to give a yellow oil. The oil was distilled (Kugelrohr) to yield 3.6 g (78%) of partially (ca. 50%) deuterated sulfone. The same procedure was repeated 3 more times to give 1-d_2: ^1H NMR ($CDCl_3$) 5.23–6.32 (m, 3 H, vinyl), 2.63–3.26 (m, 1 H, SO_2CH), 1.49–2.63 (m, 2 H, CCH_2C), 1.40 (d, 3 H, $J = 7$ Hz, $CHCH_3$), 1.02 ppm (t, 3 H, $J = 7$ Hz, CH_2CH_3); IR (NaCl, film) 2980, 1635, 1295, 1130, 1015, 935 cm^{-1}. Anal. Calcd for $C_7H_{12}SO_2D_2$: 164.0840. Found: 164.0839.

Allyl *sec*-Butyl Sulfide. Method A.[20] To a stirred solution of 17.1 g (0.19 mmol) of 2-butanethiol in 100 mL of 1.98 M ethanolic sodium ethoxide was added dropwise 23.0 g (0.22 mmol) of allyl bromide. After the solution was stirred at room temperature for 15 min, the white precipitate was removed by filtration. Water (100 mL) was added to the filtrate and the organic layer was separated. The aqueous layer was extracted with dichloromethane (2 × 35 mL, 1 × 20 mL). The combined organic layers were washed with water (3 × 100 mL) and brine (2 × 100 mL), passed through a fritted glass disk containing a 1:1:1 mixture of silica gel–charcol–magnesium sulfate, and concentrated in vacuo to afford an oil which was purified by a vacuum distillation to yield 17.6 g (72%), bp 27–29 °C (1.5 mm), of the desired product: ^1H NMR ($CDCl_3$) 5.50–6.20 (m, 1 H, C=CH), 4.90–5.28 (m, 2 H, $H_2C{=}C$), 3.16 (d, 2 H, $J = 8$ Hz, allyl), 2.30–2.98 (m, 1 H, SO_2CH), 1.0–2.0 (m, 2 H, CH_2C), 1.30 (d, 3 H, $J = 6$ Hz, $CHCH_3$), 0.98 ppm (t, 3 H, $J = 6$ Hz, CH_2CH_3); IR (NaCl, film) 2915, 1678, 1375, 1220, 980, 908, 729 cm^{-1}. Anal. Calcd for $C_7H_{14}S$: 130.0817. Found: 130.0822.

Method B.[21] To 5.0 g (104 mmol) of 50% sodium hydride which had been washed with pentane (3 × 30 mL) and dried under a stream of dry nitrogen was added 60 mL of anhydrous DMF. The mixture was cooled to 0 °C and 12 mL (111 mmol) of 2-butanethiol was added dropwise via syringe. After an additional 40 mL of anhydrous DMF was added, the cooling bath was removed and the solution was stirred for 10 min at room temperature. Then, 9.5 mL (108 mmol) of allyl bromide was added dropwise at 0 °C and the solution was stirred for 30 min. The mixture was filtered, and the filtrate was poured into 100 mL of water and extracted with ether (3 × 50 mL). The combined ether extracts were washed with 45% potassium hydroxide (30 mL) and water (2 × 50 mL), dried over magnesium sulfate, and concentrated in vacuo to give an oil which was purified by distillation to yield 12.4 g (92%), bp 156–157 °C (1 atm) of the desired product.

(*S*)-(−)-Allyl *sec*-Butyl Sulfone (1*).[5] One gram (7.7 mmol) of (*S*)-(+)-allyl *sec*-butyl sulfide was oxidized with *m*-chloroperoxybenzoic acid, as described previously, to give 1.1 g (88%) of crude 1* which was purified in sequence, by a vacuum distillation, chromatography (MPLC, silica gel, 10–80% ether in hexane), and vacuum distillation (Kugelrohr) to give 0.71 g (57%), $[\alpha]^{20.2}{}_D$ −7.65° (*c* 0.05, chloroform),[5] of 1*. The infrared and ^1H NMR spectra were identical with those of the racemic sulfone.

(*S*)-(+)-Allyl *sec*-Butyl Sulfide. To 1.0 g (21 mmol) of hexane washed 50% sodium hydride was added 20 mL of dry DMF. The mixture was cooled to 0 °C, and 2 mL (25 mmol) of freshly distilled 2-propenethiol was added dropwise using a syringe. The cooling bath was removed, and the resulting solution was stirred at room temperature for 20 min. After recooling to 0 °C, 4.6 g (20 mmol) of (R)-(−)-2-butyl tosylate, dissolved in dry DMF (5 mL), was added dropwise via syringe. The mixture was warmed to room temperature where it was stirred for 1.3 h. The resulting suspension was filtered, and the filtrate was poured into a mixture of ether (50 mL) and water (50 mL). The organic layer was separated, and the aqueous layer was extracted with ether (5 × 20 mL). The combined ether extracts were washed with water (3 × 30 mL) and brine (3 × 30 mL) and evaporated in vacuo to give an oil which was distilled to yield 2.0 g (79%), bp 22–23 °C (0.8 mm), $[\alpha]^{26.0}{}_D$ +12.99° (*c* 0.69, chloroform), of sulfide.

(*R*)-(−)-2-Butanol.[5] *cis*-2-Butene (10 mL, 111 mmol) was treated with 100 mmol of diisopinocamphenylborane (IPC_2BH), according to the method of Brown,[5] to give 3.9 g (52%) of the desired product (2.8 g at 95–99 °C, 1.1 g at 99 °C (760 mm)), $[\alpha]^{23}{}_D$ −13.1° (*c* 0.03, chloroform); 97% optical purity; ^1H NMR ($CDCl_3$) 3.80 (sextet, 1 H, $J = 6$ Hz, HOC*H*), 3.40 (s, 1 H, OH), 2.83–1.25 (m, 2 H, CCH_2C), 1.21 (d, 3 H, $J = 6$ Hz, $CHCH_3$), 0.95 ppm (t, 3 H, $J = 6$ Hz, CH_2CH_3).

(*R*)-(−)-*sec*-Butyl Tosylate. To a solution of 2.81 g 938 mmol) of (*R*)-(−)-2-butyl alcohol was added 56 mL of dry pyridine at 0 °C with stirring. The resulting solution was kept in the refrigerator for 17 h and was then poured into 300 mL of ice water. The organic layer was separated and the aqueous layer was extracted with ether (3 × 80 mL). The combined ether extracts were washed with cold 30% H_2SO_4 (150 mL), water (100 mL), and brine (100 mL), dried over sodium sulfate–potassium carbonate, and evaporated in vacuo to yield 8.3 g (96%), $[\alpha]^{20.2}{}_D$ −9.28° (*c* 0.10, chloroform), of tosylate: ^1H NMR ($CDCl_3$) 7.60 (m, 4 H, aromatic), 4.59 (sextet, 1 H, $J = 6$ Hz, HCOTs), 2.48 (s, 3 H, aromatic CH_3), 1.80–1.33 (m, 2 H, CCH_2C), 1.29 (d, 3 H, $J = 6$ Hz, CH_3CH), 1.82 ppm (t, 3 H, $J = 6$ Hz, CH_3CH_2); IR (NaCl, film) 2970, 1596, 1350, 1175, 900, 813 cm^{-1}.

***sec*-Butyl *tert*-Butyl Sulfide.** To a solution of 300 mL of 1.1 M (0.33 mol) ethanolic sodium ethoxide and 34 mL (0.30 mmol) of *tert*-butyl mercaptan was added with stirring 33 mL (0.30 mol) of 2-butyl bromide at room temperature. After the reaction mixture was stirred for 4 h at room temperature, 100 mL of ether and 250 mL of water was added. The aqueous layer was separated and extracted with ether (2 × 100 mL). The combined etheral layers were washed with water (4 × 200 mL) and brine (100 mL), dried ($MgSO_4$), and concentrated in vacuo to give crude material which was distilled to yield 21.2 g (50%), bp 20 °C (0.35 mm), lit.[24] bp 50–51 °C (17 mm), of the desired product: ^1H NMR

---

[20] Sato, K. *Nippon Kagaku Zasshi* **1956**, *77*, 1409.

[21] Trost, B. M.; Godleski, S. A.; Ippen, J. *J. Org. Chem.* **1978**, *43*, 4559.

[22] Gorden, A. J.; Ford, R. A. "The Chemist's Companion"; Wiley: New York, 1972; p 449.

[23] Benson, S. W.; O'Neal, H. E. NSRDS-NBS-21, National Bureau of Standards, Washington, D.C., 1970, pp 8–9.

[24] Truce, W. E.; Breiter, J. J. *J. Am. Chem. Soc.* **1962**, *84*, 1621.

($CDCl_3$) 2.38–3.01 (sextet, 1 H, J = 7 Hz, methine), 1.34 (s, 9 H, t-Bu), 0.78–1.84 ppm (m, 8 H, *sec*-Bu); IR (NaCl, film) 2960, 1460, 1365, 1165 cm^{-1}. Anal. Calcd for $C_8H_{18}S$: 146.1127. Found: 146.1133.

***sec*-Butyl *tert*-Butyl Sulfoxide.** To a solution of 22.5 g (105 mmol) of sodium metaperiodate in water (140 mL) and methanol (60 mL) was added with stirring 14.6 g (100 mmol) of *sec*-butyl *tert*-butyl sulfide at 0 °C. The resulting solution was stirred for 6 h at 0 °C and an additional 18 h at room temperature. The reaction mixture was filtered and the filtrate was extracted with chloroform (1 × 200 mL, 2 × 100 mL). The combined chloroform extracts were washed with water (200 mL) and brine (100 mL), dried ($MgSO_4$), and concentrated in vacuo to afford an oil. The oil was distilled to yield 14.5 g (90%), bp 75–76 °C (1.2 mm), of a mixture containing 94% of the sulfoxide and 6% of the corresponding sulfone, as evidenced by gas chromatography (Carbowax, 20 M, temp 1 100 °C, rate 5 °C/min; temp 2 120 °C, time 1 10 min, time 2 30 min, 11.4 min retention time for the sulfoxide, 17.8 min retention time for the sulfone. The mixture was separated by column chromatography (MPLC, silica gel, 70% ether in pentane). The spectral data were as follows: ^1H NMR ($CDCl_3$) 2.29–2.99 (m, 1 H, methine), 1.18 (s, 9 H, *t*-Bu), 0.60–1.87 (m, 8 H, *sec*-Bu); IR ($NaCl_3$) 3450, 2950, 1470, 1040 cm^{-1}. Anal. Calcd for $C_8H_{18}SO$: 162.1078. Found: 162.1100.

Allyl *sec*-Butyl Sulfinate. To a solution of 4.95 g (37 mmol) of *N*-chlorosuccinimide (NCS) in 50 mL of dry chloroform was added 2.6 mL (95% pure, 37 mmol) of allyl alcohol in 20 mL of dry chloroform. After the solution was cooled to 0 °C, 5.0 g (31 mmol) of *sec*-butyl *tert*-butyl sulfoxide was added, and the mixture was stirred for 7 h at 0 °C. The solution was filtered and washed with 5% sodium sulfite (4 × 50 mL) and water (50 mL), dried (Na_2SO_4), and concentrated in vacuo to give 4.1 g (82%) of the desired product: ^1H NMR ($CDCl_3$) 4.43 ppm (d, 2 H, J = 7 Hz, allylic CH_2); IR (NaCl, film) 2960, 1455, 1130 cm^{-1}.

Allyl-α,α-d_2 *sec*-Butyl Sulfinate. As described above, 0.21 g (3.5 mmol) of allyl-α,α-d_2 alcohol was treated with 0.51 g (3.2 mmol) of NCS to afford 0.89 g of product which was purified by preparative thin-layer chromatography (basic alumina, Eastman), 10% ether in hexane (R_f 0.2), to yield 0.13 g (24%) of product: ^1H NMR ($CDCl_3$) 5.95 (dd, 1 H, J = 10, 7.5 Hz, C=CH), 5.38 (m, 1 H, H_2C=C(trans)), 5.30 (m, 1 H, H_2C=C(cis)), 2.82–2.28 (m, 1 H, methine), 1.30–2.08 (m, 2 H, methylene), 1.25 (d, 3 H, J = 7 Hz, CH_3), 1.03 ppm (*t*, 3 H, J = 7 Hz, -CH_3). Anal. Calcd for $C_7H_{14}SO_2$: 162.0714. Found: 162.0721.

Flow Pyrolysis. The apparatus is shown in Figure 3. Pyrolyses were performed in 2.5 cm (o.d.) × 34-cm tubes (empty or quartz-chip filled) heated with a Lindberg tube furnace (Model 55035). The temperature of the oven was measured by using an Omega digital thermometer (Model 2170A) equipped with an iron–constantan thermocouple. The accuracy of the thermometer was checked at the boiling points of water (100 °C) and sulfolane (285 °C) and the temperature of ice water (0 °C) and was found to be correct within ±0.2 °C.

The pressure within the system was set by adjusting the nitrogen flow rate using stopcock D. The reported pressures are measured at the beginning of the pyrolysis using a McLeod gauge. The traps, F and G, were cooled to −196 °C by using liquid nitrogen. Bulb H was evacuated to 10^{-3} torr prior to the pyrolysis; stopcock C was kept closed during the pyrolysis.

The sulfone was added to the system through serum cap E using a syringe (Hamilton, 2 mL) equipped with a three-way stopcock and a stainless steel needle (9 in. × 18 gauge). The sulfone was then distilled into the heated zone using a heat gun. The amount of sulfone placed in the tube was determined by weighing the syringe before and after the injection. After the pyrolysis, the stopcocks B and D were closed and the traps F and G were allowed to warm to room temperature. Most of the products were collected in trap F. Stopcock C was opened to condense the gaseous products in bulb H, which had been cooled (liquid nitrogen, −196 °C) and evacuated (10^{-3} torr). Then, the stopcock C was closed and the internal standard (dry benzene) was added through the septum I using a 10-μL syringe.

Static Pyrolysis. The pyrolyses were done in Pyrex tubes which had been cleaned with a 10% ammonium hydroxide solution and rinsed at least 5 times with deionized water prior to use. The tubes were immersed in a molten salt bath[22] which was heated by a stainless steel shielded Vycor-brand immersion heater (1 KW, Corning) and stirred using a Lightin Model L stirrer. The temperature of the bath was controlled with a Leeds and Northup Electromax II temperature controller (Model 6434) which was connected to the heater and a chromel–alumel thermocouple. The temperature of the bath was measured to ±0.2 °C using the digital thermometer described previously.

The samples were placed in tubes of various sizes by using a syringe (Hamilton, 50 μL or 100 μL). The samples were then degassed (at least 3 freeze–degas–thaw cycles) and sealed under vacuum (10^{-2} torr). After the pyrolysis, the tubes were cooled (liquid nitrogen) and opened. Then, a solvent, either carbon disulfide or diethyl ether, was added to dissolve the products.

The products were indentified by comparison of the GC retention times (Porapak Q column, 5 ft × 0.125 in. 100/120 mesh; temp 1 120 °C, time 1 0 min, rate 10°/min; temp 2 190°, time 2, 15 min) with authentic material and by low-resolution GC/MS. The amount of each product was determined from the integrated GC peak areas using benzene as an internal standard.

The amount of unpyrolyzed sulfone was determined either by weighing the material (flow pyrolysis) or by comparing the GC areas of sulfone to biphenyl (internal standard). The relative FID response factor for the sulfone and biphenyl was determined to be 1.86 (1% Carbowax 20 M, 1 m × 0.125 in; temp 1 90 °C, time 1 10 min, rate 5°/min; temp 2 120 °C, time 2 15 min).

Kinetic Runs. Into 40-mL Pyrex tubes was added 10 μL (via a 25-μL Hamilton syringe) of the stock solution which was prepared by dissolving 0.13 g (0.85 mmol) of biphenyl in 1.75 g (10.78 mmol) of allyl *sec*-butyl sulfone. The samples were freeze-degassed (3×) and were sealed under vacuum (1 × 10^{-2} mm). Then, the tubes were immersed into the molten salt bath described previously. After the pyrolysis was continued for some specific time interval, the tubes were removed from the holder and were quickly plunged into an ice–water bath. The tubes were then opened. The material inside the tube was washed with ether (3 mL), and the ether solution was analyzed at least twice by analytical GC (1% Carbowax 20 M, temp 1 130 °C, time 1 2.0 min, rate 10.00 °C/min; temp 2 150 °C, time 2 10.0 min) for each point, an average of the analyses was used. The kinetic data are presented in Table VII. The error analyses was performed according to the method described by Benson.[23]

Pyrolysis of Allyl-α,α-d_2 *sec*-Butyl Sulfinate. The sulfinate (0.16 mmol) placed in a 40-mL Pyrex tube was pyrolyzed at 254 °C for 41 and 105 s. The material was taken up in $CDCl_3$. ^1H NMR analysis revealed the presence of only **1a** and unreacted sulfinate. The absence of a doublet at δ 4.43 in the ^1H NMR spectrum corresponding to the allylic methylene unit of rearranged sulfinate suggests that the sulfinates do not equilibrate under the reaction conditions.

Copyrolysis of Allyl-α,α-d_2 *sec*-Butyl Sulfone (1-d_2) and Allyl Isopropyl Sulfone. Into the cold finger located at the base of a 2-L spherical Pyrex bulb was placed sulfones 1-d_2 (0.23 mmol, 40 μL) and allyl isopropyl sulfone (0.30 mmol, 40 μL) via a syringe (10 in. × 20 gauge needle, 1 mL, Perfektum); the sulfones were pyrrolyzed at 174 °C for 84.3 h. The recovered sulfones were separated first via preparative thin-layer chromatography (EM silica gel, 0.2 × 20 × 20 cm, 50% ether in pentane, R_f 0.14 (allyl isopropyl sulfone) and 0.23 1-d_2), and then in a final purification step, via preparative gas chromatography (5 ft × $^1/_4$ in., 5% OV-1 on 80/100 Chrom W/AW DMCS, column 190 °C, injector 200 °C, detector 265 °C, flow rate 60 mL/min, 5.5 (allyl isopropyl sulfone), 9.2 min (1-d_2): ^1H NMR ($CDCl_3$) of 1-d_2 showed an 8:1:3 ratio of vinyl:allyl:methine hydrogens, which is consistent with 17% deuterium scrambling of 1-d_2. The mass spectral data (ZAB) for recovered allyl *sec*-butyl sulfone is shown below.

obsd mass	calcd mass	abundance	assignment
106.0089	106.0088	2.41	$C_3H_6O_2S$
108.0229	108.0213	100.00	$C_3H_4O_2D_2S$
121.0326	121.0323	19.04	$C_4H_9O_2S$
164.0862	164.0840	27.18	$C_7H_{12}O_2D_2S$

Acknowledgment. We are grateful to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. We are indebted to Mr. Mark Bridges for able technical assistance.