The proton nmr spectrum of 3-difluoroaminopropylcarbamyl fluoride ($CDCl_3$ solution) consisted of a quintet (J = 7 cps) at δ 1.98 for $CH_2CH_2CH_2$, a broad signal at δ 5.68 for NH, a triplet of triplets (J_{HF} = 29.3 cps) at δ 3.58 for NF_2CH_2CH, and quartet at δ 3.34 for CH_2CH_2NH. The fluorine spectrum showed a triplet (J = 28.5 cps) at ϕ^* −55.3 for NF_2 and a doublet (J = 7.3 cps) at ϕ^* +14.59 (-NHCOF). The infrared spectrum showed NH at 3.0 μ and C=O at 5.60 μ.

Anal. Calcd for $C_4H_7N_2F_3O$: C, 30.77; H, 4.52; N, 17.95; F, 36.51. Found: C, 30.99; H, 4.60; N, 17.5; F, 36.0.

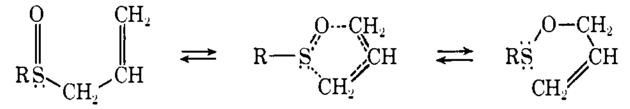
Rates and Equilibria in the Interconversion of Allylic Sulfoxides and Sulfenates[1]

Reginald Tang and Kurt Mislow

Contribution from the Department of Chemistry, Princeton University, Princeton, New Jersey 08540. *Received August 21, 1969*

Abstract: Activation parameters for the thermal racemization of allyl *p*-trifluoromethylphenyl sulfoxide ($\Delta H^{\ddagger}$ = 21 kcal/mol, $\Delta S^{\ddagger}$ = −8 eu) and the thermal rearrangement of allyl *p*-trifluoromethylbenzenesulfenate ($\Delta H^{\ddagger}$ = 19 kcal/mol, $\Delta S^{\ddagger}$ = −5 eu) in combination provide the first complete description of the energy surface for a [2,3] sigmatropic rearrangement. A study of substituent and solvent effects on the rate of racemization of allyl sulfoxides and on the sulfenate–sulfoxide equilibrium constant has revealed that electron-withdrawing groups and nonpolar solvents accelerate the racemization and increase the proportion of sulfenate at equilibrium. It is suggested that these effects originate in changes in the ground-state energy of the sulfoxide.

The thermal racemization of allyl sulfoxides (**1**)[2,3] and the thermal rearrangement of allyl sulfenates (**2**)[3,4] are both manifestations of the same process: the interconversion of **1** and **2** by way of a five-membered ring transition state. The reaction is concerted, reversible, and intramolecular, and may be characterized as a [2,3] sigmatropic process.[5] However, although in one case, that of **1a**, rates and activation parameters were measured[2,3] for the racemization reaction (*i.e.*, for the conversion of **1** to **2**), corresponding parameters for the reverse process, the isomerization of **2** to **1**, have been lacking. The present work was undertaken in order to fill this gap in our information, and thus to complete the description of the energy surface for the interconversion reaction.



1 2

a, R = 4-$CH_3C_6H_4$
b, R = 4-$CF_3C_6H_4$
c, R = 4-$NO_2C_6H_4$
d, R = 2,4-$(NO_2)_2C_6H_3$
e, R = 2-$NO_2C_6H_4$
f, R = C_6F_5

While rearrangement of **2a** is too fast for the convenient measurement of reliable rate constants, it was found that **2b** and **2c** present fewer difficulties in this respect and may be handled at temperatures near −20° without extensive rearrangement. At temperatures above 0°, rearrangement to the corresponding sulfoxides, **1b** and **1c**, proceeds at rates which can be followed conveniently by ultraviolet absorption spectroscopy, since absorption bands of **2** are located at substantially longer wavelengths than the corresponding bands of **1**. The reliability of these measurements is vouchsafed by the presence of isosbestic points, which indicate the absence of side reactions, and good precision is obtained by the appreciable decrease in absorbance which accompanies the change from sulfenate to sulfoxide, even at the low concentrations (*ca.* 10^{-4} *M*) employed. The rearrangement of **2b** and **2c**, like that of **2a**, is essentially complete (>99%), to judge by the spectroscopic (ir, nmr, uv) evidence. Benzene was chosen as the solvent in order to provide a match for the racemization studies described below. Our findings are summarized in Table I. It should be noted that the negative entropy of activation is consistent with the cyclic concerted mechanism of the rearrangement.[3]

Table I. First-Order Rate Constants and Activation Parameters for the Rearrangement of Allyl Arenesulfenates (**2**) to Allyl Aryl Sulfoxides (**1**) in Benzene

Sulfenate	T, °C	$k_{rearr} \times 10^4$, sec^{-1}	Activation parameters
2b	6.9	10.8 ± 0.3	$\Delta H^{\ddagger}$, 18.8 ± 0.3 kcal/mol
	12.4	20.2 ± 0.6	$\Delta S^{\ddagger}$, −4.8 ± 0.1 eu
	20.1	48.4 ± 0.1	
	25.1	92.3 ± 0.3	
2c	6.8	9.1 ± 0.1	$\Delta H^{\ddagger}$, 17.6 ± 0.3 kcal/mol
	12.3	16.8 ± 0.2	$\Delta S^{\ddagger}$, −9.6 ± 0.1 eu
	20.0	40.0 ± 0.6	

The counterpart for the rearrangement of **2b**, *i.e.*, the racemization of **1b**, was studied as part of a general

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(1) This work was supported by the Air Force Office of Scientific Research under Grant No. AF-AFOSR-1188-B.

(2) D. R. Rayner, E. G. Miller, P. Bickart, A. J. Gordon, and K. Mislow, *J. Amer. Chem. Soc.*, **88**, 3138 (1966).

(3) K. Mislow, *Rec. Chem. Progr.*, **28**, 217 (1967); P. Bickart, F. W. Carson, J. Jacobus, E. G. Miller, and K. Mislow, *ibid.*, **90**, 4869 (1968).

(4) (a) E. G. Miller, D. R. Rayner, and K. Mislow, *ibid.*, **88**, 3139 (1966); (b) S. Braverman and Y. Stabinsky, *Chem. Commun.*, 270 (1967).

(5) A. Jefferson and F. Scheinmann, *Quart. Rev.* (London), **22**, 391 (1968).

inquiry into the effect of substituents on the rates of racemization of allyl aryl sulfoxides. Inspection of the results, collected in Table II, reveals that the rate constants of racemization are not very sensitive to changes in the *para* substituent, and even the extreme variation between the strongly electron-withdrawing trifluoromethyl and the electron-donating methoxy groups only produces a six- to sevenfold change in the rate constants. The observed changes in rate constants of racemization appear to reflect parallel changes in the enthalpy of activation, and correlate satisfactorily with the equation[6] $\log k_\alpha = 0.6\sigma_p^+ - 3.63$ for a spread of $1.39\sigma_p^+$ units (correlation coefficient $r = 0.9814$). The value of ρ_p^+ (+0.6) confirms that electron-withdrawing substituents have the effect of slightly lowering the barrier to racemization, and is consonant with the view that electron depletion in the arene moiety adjacent to the positive end of the sulfoxide dipole is energetically unfavorable in the ground state of the sulfoxide. In the transition state leading to the sulfenate, the dipolar character of the S=O bond is reduced, and the effect of electron supply and withdrawal by the arene moiety is thereby lessened. Consequently, the destabilization of the sulfoxide in the ground state appears to be principally responsible for the rate acceleration[7] accompanying electron withdrawal. Similar conclusions may be drawn from a study of the effect of changes in solvent polarity, as measured by E_T,[9] on the rate of racemization of **1b** and the rate of rearrangement of **2b** (Figure 1). The rates of racemization of **1b** and of **1a**[3] may be expressed by $\log k_\alpha = -0.063E_T - 0.40$, and $\log k_\alpha = -0.078E_T - 0.58$, *i.e.*, both racemizations are significantly decelerated by an increase in solvent polarity. As previously pointed out,[3] this deceleration reflects the increased stabilization of the highly polar sulfoxide with increasing solvent polarity, and the concomitant increase in energy required to break the solvent-solute bonds on the way to the transition state leading to the less polar sulfenate. Conversely, and in harmony with this interpretation, the rearrangement of the sulfenate **2b** is essentially insensitive to changes in solvent polarity ($\log k_{\text{rearr}} = 0.006E_T - 2.3$). Accordingly, in terms of S–O bond polarity, the transition state for the interconversion of **1** and **2** resembles the ground state of **2** more closely than that of **1**.

Table II. First-Order Rate Constants and Activation Parameters for the Racemization of Allyl Aryl Sulfoxides (**1**) in Benzene[a,b]

Aryl group	T, °C	$k_\alpha \times 10^5$, sec^{-1}	Activation parameters
4-$CH_3OC_6H_4$	49.6	8.9 ± 0.1	$\Delta H^\ddagger$, 23.1 ± 0.1 kcal/mol
	58.8	24.4 ± 0.1	$\Delta S^\ddagger$, −5.6 ± 0.1 eu
	68.3	67.5 ± 0.5	
C_6H_5	49.6	18.7 ± 0.8	$\Delta H^\ddagger$, 22.5 ± 0.8 kcal/mol
	58.8	46.6 ± 2.2	$\Delta S^\ddagger$, −6.2 ± 0.1 eu
	68.3	135 ± 6.3	
4-ClC_6H_4	49.6	29.3 ± 0.2	$\Delta H^\ddagger$, 22.9 ± 1.3 kcal/mol
	58.8	70.2 ± 0.6	$\Delta S^\ddagger$, −4.0 ± 0.2 eu
	68.3	220 ± 17	
4-$CF_3C_6H_4$ (**1b**)	39.8	20.5 ± 0.3	$\Delta H^\ddagger$, 21.2 ± 0.2 kcal/mol
	49.6	60.9 ± 0.7	$\Delta S^\ddagger$, −8.0 ± 0.1 eu
	58.8	152 ± 2	

[a] **1a** has $\Delta H^\ddagger = 23.1 \pm 0.1$ kcal/mol and $\Delta S^\ddagger = -4.9 \pm 0.1$ eu (ref 3). [b] In every case the amount of detectable sulfenate (**2**) present was negligibly small (<1%).

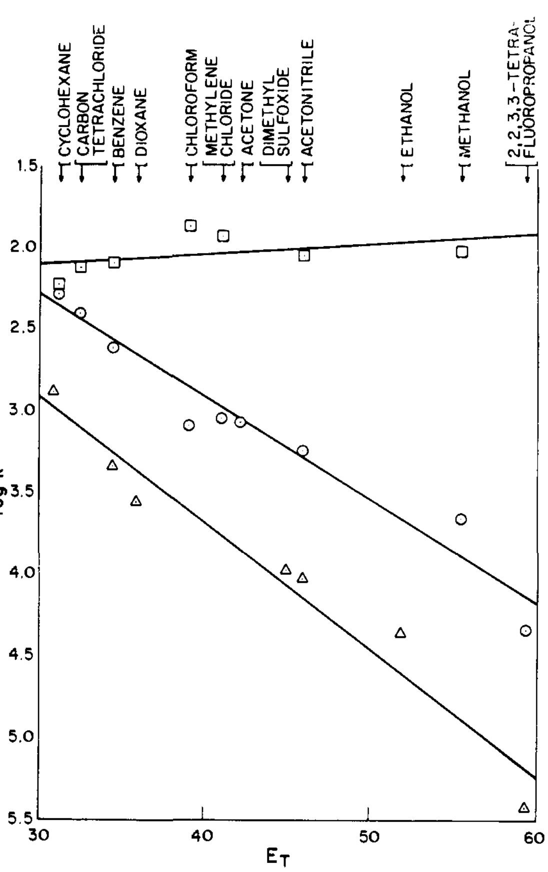

Figure 1. Plots of $-\log k$ *vs.* solvent polarity parameter E_T for the racemization of allyl *p*-tolyl sulfoxide (**1a**) at 60.7° (△), the racemization of allyl *p*-trifluoromethylphenyl sulfoxide (**1b**) at 60.7° (○), and the rearrangement of allyl *p*-trifluoromethylbenzenesulfenate (**2b**) at 25.1° (□).

In combination, the rearrangement of **2b** and the racemization of **1b** provide the first complete picture of the energy surface of this reaction.[10] Since the rearrangement is concerted, a single transition state separates **1** and **2**. Enantiomeric sets of sulfoxides, *e.g.*, **1b** and $\overline{\textbf{1b}}$, are interconverted by way of the *effectively* (in the kinetic sense) achiral sulfenate, *e.g.*, **2b**. Conformers of the intermediate, **2b**, which owe their chirality to dihedral angles of twist between C-S-O and S-O-C planes,[3] are readily interconverted by torsion

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[6] J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," John Wiley & Sons, Inc., New York, N. Y., 1963, p 172 ff.

[7] The small substituent effect in the racemization of **1** has its analogy in the related *ortho*-Claisen rearrangement of allyl phenyl ethers, a thermal [3,3] sigmatropic process also involving six π-electrons,[5] for which $\rho_p^+ = -0.51$ has been reported.[8]

[8] H. L. Goering and R. R. Jacobson, *J. Amer. Chem. Soc.*, **80**, 3277 (1958).

[9] C. Reichardt and K. Dimroth, *Fortschr. Chem. Forsch.*, **11**, 1 (1968).

[10] An analogous process with phosphorus as the chiral center was reported by W. B. Farnham, A. W. Herriott, and K. Mislow, *J. Amer. Chem. Soc.* **91**, 6878 (1969).

about the S–O and other single bonds: none of the barriers which separate the conformational enantiomers of the sulfenate are expected to exceed *ca.* 5–10 kcal/mol. Accordingly, k_α reflects the conversion of *either* chiral **1b** *or* **1b̄**, *via* an achiral intermediate (**2b**), into a racemic mixture of **1b**/**1b̄**, whereas k_{rearr} reflects the conversion of achiral **2b** into the same racemic mixture. Since the rearrangement results in a partitioning of products into **1b** and **1b̄**, the rate constants of the forward (**1b** → **2b**) and reverse (**2b** → **1b**) processes, which share a single transition state, are therefore expressed by k_α and $0.5k_{\text{rearr}}$, respectively. From the values in Tables I and II, and correcting for the statistical factor (R ln 2) in the entropy of activation of the rearrangement, the thermodynamic driving force for the rearrangement, $\Delta G°$ ($=\Delta\Delta G^{\ddagger} = \Delta\Delta H^{\ddagger} - T\Delta\Delta S^{\ddagger}$), is 2.9 kcal/mol at 25°, corresponding to no more than 1% of **2b** in equilibrium with the racemic mixture of **1b**. This result is in accord with the observation that less than 1% of **2** is present during the racemization of **1**, and that rearrangements of **2** (**a**–**c**) are essentially complete (>99%).

In the rearrangement of allyl benzenesulfenate and *para*-substituted derivatives, the extent of the conversion (>99%) to the corresponding sulfoxides has been ascribed[3,4a] to the formation of the strong (D = 90 kcal/mol) S=O bond. However, as shown in the present study, although the equilibrium lies on the side of the sulfoxide, the difference in free energy between the two forms is of the order of 3 kcal/mol at room temperature, and one might therefore expect to observe the presence of a significant proportion of sulfenate at equilibrium, given appropriate structural modifications of the system.[11] A combination of steric and polar factors appears to be effective in shifting the equilibrium. Thus, α-methylallyl trichloromethyl sulfoxide and crotyl trichloromethanesulfenate coexist in roughly equimolar amounts (the equilibrium constant is solvent dependent),[3,12] whereas less than 5% of the corresponding sulfenates exist in equilibrium with α-methylallyl *p*-tolyl and allyl trichloromethyl sulfoxides. Similarly, reaction of 2,4-dinitrobenzenesulfenyl chloride with lithium allyl-1,1-d_2 alcoholate gives mainly allyl-1,1-d_2 2,4-dinitrobenzenesulfenate,[3] whereas the corresponding reaction with *p*-nitrobenzenesulfenyl chloride results in virtually complete (>99%) rearrangement to the sulfoxide, **1c**/**c̄** (present work). However, when a single nitro group is located in the *ortho* position, the ratio (K) of sulfenate (**2e**) to sulfoxide (**1e**/**ē**) approaches unity. The solvent dependence of all these equilibria is such that with an increase in solvent polarity, the proportion of the more highly polar sulfoxide is increased. Thus, in going from carbon disulfide (E_T 32.6) to DMSO (E_T 45.0), the ratio of crotyl trichloromethanesulfenate to α-methylallyl trichloromethyl sulfoxide decreases from 1.9 to 0.3.[3] Similarly, in carbon tetrachloride (E_T 32.5), chloroform (E_T 39.1), and acetonitrile (E_T 46.0), the ratio of **2d** to **1d**/**d̄** decreases with values of $K \geq 100$, 19, and 4.6, respectively. The decrease in the ratio of **2e** to **1e**/**ē** with solvent polarity is shown in Table III; the value of **2e** to **1e**/**ē** in chloroform is out of line (log K roughly correlates[9] with E_T; a = *ca.* −0.04) and suggests the operation of special solvent–solute interactions, presumably of the hydrogen bonding type. The same comments apply to the pair of pentafluorophenyl derivatives, **2f** and **1f**/**f̄** (Table III; a = *ca.* −0.09). The equilibrium constant is unity (within less than 10%) for **2e** to **1e**/**ē** in benzene (E_T 34.5) and for **2f** to **1f**/**f̄** in cyclohexane (E_T 31.2).

Table III. Ratio of Components in Sulfenate–Sulfoxide Equilibria as a Function of Solvent Polarity, at 25°

Solvent	E_T[a]	**2e**:**1e**/**ē**[b]	**2f**:**1f**/**f̄**[b]
CCl_4	32.5	1.43 ± 0.03	0.63 ± 0.01
$CHCl_3$	39.1	0.39 ± 0.01	0.11 ± 0.03
$(CH_3)_2CO$	42.2	0.68 ± 0.01	0.17 ± 0.04
CH_3CN	46.0	0.40 ± 0.03	0.08 ± 0.05
CH_3OH	55.5	0.19 ± 0.03	

[a] See ref 9. [b] Equilibrium constants, obtained by direct measurement or by interpolation from values obtained at other temperatures.

Evidently, inductive effects are of overriding importance in determining the position of the equilibrium between **1** and **2**. In every case where there is an appreciable proportion of **2** at equilibrium, R is strongly electron withdrawing (R = trichloromethyl, 2-nitrophenyl,[13] 2,4-dinitrophenyl,[13] and pentafluorophenyl). The observed effect presumably originates in the destabilization of the sulfoxide ground state which accompanies electron withdrawal, and which is also reflected in the accelerated racemization.

Experimental Section[15]

(−)-Menthyl *p*-Trifluoromethylbenzenesulfinate (3). A solution of *p*-trifluoromethylphenylmagnesium bromide was prepared from *p*-trifluoromethylphenyl bromide (25 g. 0.22 mol) and magnesium turnings (5.5 g, 0.22 g-atom) in 180 ml of ether. The Grignard solution was filtered through glass wool and chilled to −78°, and sulfur dioxide (15 g, 0.22 mol) was condensed into the stirred solution. After slowly warming to room temperature, the gray colored semisolid was diluted with 500 ml of ether and cooled to *ca.* −20°. Thionyl chloride (88 ml, 1.2 mol) was added. After continued stirring for 4 hr at room temperature, the mixture was filtered and the residue was washed with ether. The ether filtrate was flash evaporated and pumped free of thionyl chloride. The residual was diluted with 1 l. of ether, and the solution was chilled to −78°. A solution of (−)-menthol (35 g, 0.22 mol) in pyridine (74 ml, 0.66 mol) was added. After reaction was completed, the pyridine hydrochloride

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(11) The presence of **2a** in equilibrium with **1a**/**ā** has been inferred from the products obtained in the reaction of **1a**/**ā** with piperidine (D. J. Abbott and C. J. M. Stirling, *J. Chem. Soc., C*, 818 (1969)).

(12) S. Braverman and Y. Stabinsky, *Israel J. Chem.*, **5**, 71p (1967); S. Braverman and C. Simons in "Mechanisms of Reactions of Sulfur Compounds," Vol. 2, N. Kharasch, B. S. Thyagarajan, and A. I. Khodais, Ed., Intra-Science Research Foundation, Santa Monica, Calif., 1968, p 102.

(13) In these cases, the additional possibility exists that the sulfenate ground state is stabilized by partial bonding between the sulfur atom and one of the oxygen atoms of the nitro group. Such attractive interactions have been proposed to account for the extraordinarily short S···O distance (2.44 Å; the sum of the van der Waals radii is 3.25 Å) in, and molecular planarity of, methyl *o*-nitrobenzenesulfenate.[14]

(14) W. C. Hamilton and S. J. LaPlaca, *J. Amer. Chem. Soc.*, **86**, 2289 (1964); *cf.* also J. A. Kapecki, J. E. Baldwin, and I. C. Paul, *ibid.*, **90**, 5800 (1968). Evidence for such interaction also comes from kinetic studies (E. N. Givens and H. Kwart, *ibid.*, **90**, 378, 386 (1968)) and ^{18}O tracer experiments (C. Brown, *Chem. Commun.*, 100 (1969)) which indicate that the *o*-nitro group may function as an internal nucleophile in attack on sulfur.

(15) Elemental analyses were performed by Schwarzkopf Microanalytical Laboratories, Woodside, N. Y. Unless otherwise stated, nmr spectra were recorded on a Varian A-60A spectrometer, and refer to *ca.* 10% deuteriochloroform solution, with tetramethylsilane as internal standard.

Table IV. Characteristics of Allyl Aryl Sulfoxides

			Calcd, %				Found, %				Nmr,[d] τ		
Aryl group	Bp (mm)[a] or mp, °C	[α]D, deg[b]	C	H	S	Halogen	C	H	S	Halogen	Aromatic[e]	Vinylic	Methylene
4-$CF_3C_6H_4$ (**1b**)	69.5–72.3	+89[c]	51.27	3.87	13.69	24.33	51.45	3.75	13.93	24.24	2.25 (q)	3.90–5.05 (m)	6.53 (m)
4-ClC_6H_4	120 (0.3)	+207	53.86	4.52	15.97	17.67	53.80	4.32	15.70	17.94	2.50 (q)	3.93–5.07 (m)	6.57 (d)[e]
C_6H_5	100 (0.3)	+230	65.02	6.06	19.29		65.11	6.34	18.92		2.48 (s)	3.93–5.08 (m)	6.60 (d)[e]
4-$CH_3OC_6H_4$[f]	125 (0.3)	+181	61.20	6.16	16.34		61.03	6.30	16.38		2.70 (q)	3.95–5.07 (m)	6.61 (d)

[a] Boiling point is Kugelrohr distillation temperature. [b] Solvent acetone unless otherwise specified. [c] Solvent ethanol. [d] *Ca.* 10% in carbon tetrachloride with TMS as internal standard. [e] Broadened signals. [f] Nmr for CH_3O group: τ 6.17 (s).

was filtered and washed with ether. The yellow filtrate was extracted with 1% hydrochloric acid, sodium bicarbonate, and saturated aqueous sodium chloride. The ether solution was dried (sodium sulfate) and flash evaporated to give a crude oil from which excess menthol was distilled (Kugelrohr, below 100°, 0.3 mm). A small portion of the remaining oil was chromatographed on silica gel to yield, on elution with benzene, a partially crystalline product. The solid was added, as seeding crystals, to the remaining sulfinate ester dissolved in low boiling petroleum ether, and dry HCl was added to the mixture at −78° to effect epimerization.[16] Repeated recrystallization from low boiling petroleum ether yielded a colorless product, (−)-**3**:[17] mp 67–68.5°, $[\alpha]^{24}$D −179° (*c* 0.61, isooctane), the properties of which did not change on further recrystallization. The infrared and nmr spectra were consistent with the assigned structure.

Anal. Calcd for $C_{17}H_{23}F_3O_2S$: C, 58.60; H, 6.65; F, 16.36; S, 9.20. Found: C, 58.70; H, 6.54; F, 16.30; S, 9.27.

The absolute configuration at sulfur was established through *p*-trifluoromethylphenyl *p*-tolyl sulfoxide (**4**). In previous work,[20] (+)-(*S*)-**4** had been generated from the reaction of *p*-trifluoromethylphenylmagnesium bromide with (−)-menthyl *p*-toluenesulfinate,[20] which has the *S* configuration at sulfur.[19] In the present work, the reaction of *p*-tolylmagnesium bromide with (−)-**3** yielded (−)-(*R*)-**4**, mp 42.5–44°, $[\alpha]^{23}$D −55° (*c* 1.0, ethanol); infrared and nmr spectra were identical with those of the enantiomer[20] (lit.[20] mp 40–42°, [α]D +57° (ethanol)). Thus, the chirality at sulfur in (−)-**3** is *S*, in harmony with previous generalizations.[19]

(−)-Menthyl *p*-Chlorobenzenesulfinate (5). This compound was prepared in a manner analogous to that described for the preparation of **3**. Recrystallization from acetone–petroleum ether yielded colorless crystals of (−)-**5**,[17] mp 85–86.5°, $[\alpha]^{23}$D −186° (*c* 0.61, acetone), the properties of which did not change on further recrystallization. The infrared and nmr spectra were consistent with the assigned structure.

Anal. Calcd for $C_{16}H_{23}ClO_2S$: C, 61.03; H, 7.36; Cl, 11.26; S, 10.18. Found: C, 61.02; H, 7.43; Cl, 11.23; S, 10.38.

The absolute configuration at sulfur was established through *p*-chlorophenyl *p*-tolyl sulfoxide (**6**). Previously, (+)-(*S*)-**6** had been generated from the reaction of *p*-chlorophenylmagnesium bromide with (−)-menthyl *p*-toluenesulfinate.[20] In the present work, the reaction of *p*-tolylmagnesium bromide with (−)-**5** yielded (−)-(*R*)-**6**, mp 75–77.2°, $[\alpha]^{22}$D −20.4° (*c* 0.22, acetone); infrared and nmr spectra were identical with those of the enantiomer[20] (lit.[20] mp 76–78°, [α]D 25° (acetone)). Thus the chirality at sulfur in (−)-**5** is *S*, in harmony with previous generalizations.[19]

Preparation of Optically Active Sulfoxides (1). A general method of preparation of optically active sulfoxides by the reaction of allylmagnesium bromide with the corresponding diastereomerically enriched (−)-menthyl arenesulfinate[21] was previously described.[3] In the preparation of the sulfoxides, care was taken to minimize contamination by extracting the sulfoxides into the aqueous layer from the ether solution; in this manner, only a trace of menthol was present in the product sulfoxide. Yields generally ranged from 40 to 80%, depending on the starting sulfinate ester. In the case of **1b**, however, only a 1% yield was realized, for this sulfoxide remained almost totally in the ether layer. Properties of the sulfoxides are described in Table IV. In addition, the following spectral information is noted: for **1c**/**c̄** in acetonitrile λ_{max} 249 (ε 6000), 300 mμ (ε 5200); for **1b**/**b̄** in acetonitrile λ_{max} 261 mμ (ε 4600).

Allyl *p*-Nitrobenzenesulfenate (2c). A solution of *n*-butyllithium (6.3 ml, 1.6 *M* in hexane) was added to a stirred solution of allyl alcohol (redistilled; 0.7 ml, 0.01 mol) in dimethyl ether (20 ml), chilled to −78° under nitrogen. The gelatinous solution formed was poured into a stirred slurry of *p*-nitrobenzenesulfenyl chloride[22] (1.5 g, 0.008 mol) in 10 ml of Freon-11 chilled to −78°,[25] under nitrogen. The mixture was warmed slowly to −35°. A suspension resulted. Chilled aqueous ammonium chloride was added to the basic reaction mixture, together with an additional 30 ml of Freon-11. The mixture was vigorously shaken and the organic layer, containing the product in suspension, was decanted from the frozen aqueous layer. Solvent was removed by evaporation at −35° (0.5 mm), and **2c** remained as a light yellow colored solid. The nmr spectrum of **2c** in acetonitrile-d_3 was recorded at −30° and showed: aromatic AB quartet, τ 2.20 (4 H); vinyl multiplet, τ 3.6–4.4 (3 H); and a broadened doublet corresponding to the methylene protons, τ 5.55 (2 H). When a sample of **2c** in acetonitrile-d_3 was slowly heated in the nmr probe, the signals slowly changed to those of the spectrum of the corresponding sulfoxide, **1c**/**c̄**: aromatic quartet, τ 1.88 (4 H); vinyl multiplet, τ 3.9–5.0 (3 H); and a multiplet of the methylene protons, τ 6.37 (2 H). There was no measurable signal around τ 5.55, indicating that the rearrangement for **2c** is essentially complete.[27] The methylene portion of the nmr spectrum of **1c**/**c̄** showed no appreciable changes when the sample was heated to 100°. Freshly prepared **2c** had λ_{max} 342 mμ (ε ≥9100) in acetonitrile. A sample of **1c**/**c̄** obtained by rearrangement of **2c** was chromatographed on silica gel (elution with ether). The product, an oil which solidified on standing, was recrystallized from ether–cyclohexane. The slightly yellow plate crystals had mp 61.5–64.5°; ir S=O stretch at 1050 cm⁻¹; nmr properties as described above.

Anal. Calcd for $C_9H_9NO_3S$: C, 51.17; H, 4.29; N, 6.63; S, 15.18. Found: C, 51.29; H, 4.25; N, 6.46; S, 14.98.

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(16) H. F. Herbrandson and R. T. Dickerson, Jr., *J. Amer. Chem. Soc.*, **81**, 4102 (1959).

(17) The sign of rotation in the visible region is presumably determined by the chirality of the sulfur atom,[18,19] and the diastereomers which are epimeric at sulfur are expected to have opposite signs of rotation at the D line.[18,19] The rotational prefix refers to this sign. It has been shown[19] that the (−)-diastereomers have the *S* and the (+)-diastereomers the *R* configuration at sulfur.

(18) K. Mislow, M. M. Green, P. Laur, J. T. Melillo, T. Simmons, and A. L. Ternay, Jr., *J. Amer. Chem. Soc.*, **87**, 1958 (1965).

(19) M. Axelrod, P. Bickart, J. Jacobus, M. M. Green, and K. Mislow, *ibid.*, **90**, 4835 (1968).

(20) D. R. Rayner, A. J. Gordon, and K. Mislow, *ibid.*, **90**, 4854 (1968).

(21) Of the (−)-menthyl arenesulfinates used in this work, menthyl *p*-methoxybenzenesulfinate and menthyl benzenesulfinate were described previously,[16] while **3** and **5** are discussed above.

(22) *p*-Nitrobenzenesulfenyl chloride was prepared by the method of Lecher and Hardy[23] and purified by sublimation (90°, 0.5 mm). The crystalline product had mp 42.5–44° (lit.[24] mp 52°). The infrared spectrum (cyclohexane) had absorptions at (cm⁻¹): 1523, 1335 (s), 1590, 1575, 850, 840, and 738 (m). The nmr spectrum featured an aromatic AB quartet centered at τ 2.08.

(23) H. Z. Lecher and E. M. Hardy, *J. Org. Chem.*, 20, 475 (1955).

(24) H. Baganz and H. Peissker, *Arch. Pharm.* (Weinheim), **289**, 262 (1956).

(25) When the reaction was carried out at room temperature, one major by-product (presumably the addition product of the sulfenyl chloride to the olefinic bond) was formed. This is entirely in accord with known reactions of sulfenyl halides.[26] At low temperatures, the substitution product usually predominates.

(26) See I. B. Douglass, "Organic Sulfur Compounds," Vol. I, N. Kharasch, Ed., Pergamon Press, New York, N. Y., 1961, pp 352–355.

(27) Reaction of lithium allyl-3,3-d_2 alcoholate with *p*-nitrobenzenesulfenyl chloride, followed by rearrangement as described for the undeuterated counterpart, gives *p*-$O_2NC_6H_4S(O)CD_2CH{=}CH_2$, for the nmr spectrum of this compound features signals due to aromatic protons (4 H) and a simplified vinyl multiplet (3 H), but exhibits no measurable signal around τ 6.37. It follows that the rearrangement is concerted, as has been demonstrated[3] for the rearrangement of **1a**.

***p*-Trifluoromethylphenyl Disulfide.**[28] A solution of *p*-trifluoromethylphenylmagnesium bromide (generated from 25 g (0.111 mol) of *p*-trifluoromethylphenyl bromide and an excess of magnesium turnings) in ether was added dropwise to a stirred mixture of sulfur (4.5 g, 0.14 mol) in ether, under nitrogen. After addition was completed, the mixture was heated to reflux for 3 hr. Aqueous ammonium chloride was added; evolution of a gas (hydrogen sulfide) was evident. After chloroform extraction, and extraction of the chloroform layer with aqueous sodium chloride solution, the organic layer was dried (sodium sulfate) and flash evaporated to yield a thick red liquid which, upon Kugelrohr distillation (105°, 0.03 mm), gave a partially solidified yellow distillate. Recrystallization with low boiling petroleum ether yielded 5.5 g (27% based on the precursor bromide) of the desired product as colorless, needle-shaped crystals, mp 53–55°. The infrared spectrum (Nujol) showed strong absorptions (cm^{-1}) at 1600 and 1325, a series of five bands at 1175–1020, and a sharp band at 825. The nmr spectrum consisted of a singlet at τ 2.43.

Anal. Calcd for $C_{14}H_8F_6S_2$: C, 47.45; H, 2.28; F, 32.17; S, 18.10. Found: C, 47.61; H, 2.52; F, 32.42; S, 18.31.

Allyl *p*-Trifluoromethylbenzenesulfenate (2b). *p*-Trifluoromethylbenzenesulfenyl chloride, prepared from the disulfide by the method of Lecher and Hardy,[23] purified by distillation (35°, 0.05 mm), was a red liquid with an nmr signal at τ 2.50. The method of preparation of **2b** was analogous to that described for the preparation of **2c**, except as follows. Dimethyl ether was used in place of Freon-11. After addition of the allyl alcoholate to the sulfenyl chloride, the reaction mixture was allowed to warm up to only −50°. The organic layer at the work-up was homogeneous, but the crude product after removal of solvent contained a crystalline impurity which was separated by pipetting off the liquid portion. The liquid product was stored at −78°. The nmr spectrum at −40° showed the characteristic broadened doublet of the sulfenate methylene protons at τ 5.66. The nmr spectrum also revealed the presence of the corresponding sulfoxide, **1b/b̄**, a broadened apparent doublet at τ 6.5 (see Table IV). As the sample was warmed in the nmr probe, the signal corresponding to the sulfenate disappeared, while the sulfoxide signal was enhanced accordingly. Freshly prepared **2b** had λ_{max} 256 mμ ($\epsilon \geq 6600$) in acetonitrile. A sample of **2b** was rearranged to **1b/b̄** on warming in acetone. Recrystallization from low boiling petroleum ether gave a product which had physical and spectral properties identical with those of **1b/b̄** obtained by direct Grignard synthesis (above).

Allyl *o*-Nitrobenzenesulfenate (2e) and Allyl *o*-Nitrophenyl Sulfoxide (1e/ē). Commercial *o*-nitrobenzenesulfenyl chloride was dissolved in hot carbon tetrachloride and insoluble impurities were removed by filtration. A solution of lithium allyl alcoholate in ether was added to the carbon tetrachloride solution until the mixture was basic to wet litmus. The mixture was quenched with aqueous ammonium chloride. The organic layer, after dilution with chloroform, was separated, washed with aqueous sodium chloride, dried (sodium sulfate), and flash evaporated to yield bright yellow crystals of a mixture of **1e/ē** and **2e**. Recrystallization from 95% ethanol resulted in a product, mp 77–82.5°, whose nmr spectrum was solvent and temperature dependent. For example, in deuteriochloroform at 37°, the nmr spectrum showed a complex aromatic multiplet at τ 1.55–3.02 (4 H), a vinylic multiplet at τ 3.67–5.03 (3 H), a broadened doublet (corresponding to the methylene protons in the sulfenate) at τ 5.60, and a multiplet (corresponding to the methylene protons in the sulfoxide) at τ 6.25. The total methylene protons integrated to 2 H. Values for other solvents at 25° are listed in Table III.

Anal. Calcd for $C_9H_9NO_3S$: C, 51.17; H, 4.29; N, 6.63; S, 15.18. Found: C, 51.05; H, 4.13; N, 6.74; S, 15.00.

Allyl Pentafluorobenzenesulfenate (2f) and Allyl Pentafluorophenyl Sulfoxide (1f/f̄). Pentafluorobenzenesulfenyl chloride was prepared from pentafluorothiophenol by the method of Kurzer and Powell.[29] The reaction of the sulfenyl chloride with lithium allyl alcoholate was carried out in the same manner[25] as described for **2c**. Light yellow crystals were obtained after the crude product was chromatographed on silica gel, upon elution with ether. Recrystallization from low boiling petroleum ether yielded a mixture of **2f**[30] and **1f/f̄**[30] (20% yield based on the precursor thiophenol), mp 44.8–46°. The nmr spectrum was solvent and temperature dependent. For example, in deuteriochloroform at 37°, the nmr spectrum showed a complex vinyl multiplet at τ 3.87–5.02 (3 H) and a pair of broadened doublets (2 H) at τ 5.73 (methylene protons of the sulfenate[30]) and 5.92 (methylene protons of the sulfoxide[30]).

Anal. Calcd for $C_9H_5F_5OS$: C, 42.19; H, 1.97; F, 37.08; S, 12.51. Found: C, 42.13; H, 2.09; F, 32.83; S, 13.12.

Allyl 2,4-Dinitrobenzenesulfenate (2d) and Allyl 2,4-Dinitrophenyl Sulfoxide (1d/d̄). A sample of **2d**, mp 87–89.5° (lit.[31] 86–87°), was obtained as previously described.[3] At 37°, there was no measurable nmr signal due to the sulfoxide in carbon tetrachloride. In acetonitrile-d_3, the nmr spectrum exhibited an aromatic multiplet at τ 0.87–2.08 (3 H), a vinyl multiplet at τ 3.46–4.98 (3 H), and a broadened doublet at τ 5.48 (methylene protons of the sulfenate). In addition, there appeared a multiplet at τ 6.15 (methylene protons of the sulfoxide). Relative signal intensities of the methylene signals revealed the presence of 18% of **1d/d̄** in the mixture. In deuteriochloroform, a mixture consisting of 5% of the sulfoxide was measured.

Kinetic Studies. A. Racemization Kinetics. All runs were made with solutions of **1** (*c* 0.2–0.4 g/100 ml) contained in a 1-cm thermostated polarimeter cell, and rotations were continuously recorded as a function of time at 500 mμ, using a Cary 60 spectropolarimeter. Measurements were taken over periods of 1–3 half-lives. Residual rotations were determined by letting racemization proceed for over 15 half-lives. All rotations were corrected for the residual rotation.

For studies of the solvent dependence of the racemization rate of (+)-**1b**, the appropriate solvent was allowed to achieve thermal equilibrium in the cell compartment. Approximately 20 μl of a solution of (+)-**1b** in toluene was injected, the solution was mixed, and rotations were recorded against time as described before. A correction was made for the residual rotation in each run. Contamination by toluene was $\leq 1\%$.

After completion of the racemization runs, the samples were collected and were found to have the same nmr and infrared absorption characteristics as the optically active starting materials. Thus, there was no measurable decomposition.

First-order rate constants (k_α) were calculated as usual.[32] Activation parameters were calculated as previously described.[20] Results are collected in Table II and displayed in Figure 1.

B. Rearrangement Kinetics. All runs were made with solutions of **2** contained in a 1-cm thermostated cell, and absorptions were continuously recorded as a function of time at 340 mμ for **2c** and at 305 mμ for **2b**, using a Cary 14 spectrophotometer. Typically, the cells with the appropriate solvent (*ca.* 2 ml each in reference and sample) were placed in the temperature-stabilized cell-block. After allowing for thermal equilibration, about 10–20 μl of a solution of the sample in toluene was injected, and the solution was mixed. Final concentrations used were less than 0.03 g/100 ml. Measurements were taken over a period of 1–6 half-lives, while residual absorption was determined to constant absorption at the end of each run. For the rearrangement in acetonitrile of **2b**, isosbestic points were at 268 mμ (ϵ 4095) and 278 mμ (ϵ 2500), while that for **2c** was at 310.5 mμ (ϵ 4706).

First-order rate constants (k_{rearr}) were calculated as usual.[32] Activation parameters were calculated as for the racemization, above. The values thus found are collected in Table I.

Equilibrium Studies. Each sample of the sulfoxide–sulfenate mixture of **e** or **f** was prepared in a sealed nmr tube with concentrations *ca.* 0.03 g/0.35 ml of solvent. The samples were allowed to reach thermal equilibrium (*ca.* 10 min) and signal intensities in the methylene region were recorded at least ten times at each temperature, each time as reached by heating *and* by cooling. The ratio of signals of **2**:**1** remained constant, within experimental error, for each temperature and solvent. The arithmetic mean of the ratio of signals was taken as the equilibrium constant. Values thus obtained are given in Table III.

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(28) Method of disulfide preparation was adapted from M. S. Kharasch and O. Reinmuth, "Grignard Reactions of Nonmetallic Substances," Prentice-Hall, Inc., New York, N. Y., 1954, pp 1274–1275.

(29) F. Kurzer and J. R. Powell, "Organic Syntheses," Coll. Vol. IV, N. Rabjohn, Ed., John Wiley & Sons, Inc., New York, N. Y., 1962, p 934.

(30) The deuterated sulfenate prepared by the reaction of lithium allyl-3,3-d_2 alcoholate and pentafluorobenzenesulfenyl chloride, as described for the undeuterated counterpart **2f**, showed a complex vinyl multiplet at τ 3.87–5.02, a doublet at τ 5.70, but no signal corresponding to sulfoxide type methylene protons. This is entirely in accord with the composition of the mixture, *i.e.*, **2f** partially rearranged to **1f/f̄**.

(31) L. Goodman and N. Kharasch, *J. Amer. Chem. Soc.*, 77, 6541 (1955).

(32) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," 2nd ed, John Wiley & Sons, Inc., New York, N. Y., 1961, p 13.