The Thermal Racemization of Allylic Sulfoxides and the Interconversion of Allylic Sulfoxides and Sulfenates. Mechanism and Stereochemistry[1,2]

Paul Bickart,[3a] Frederick W. Carson,[3b] John Jacobus,[3c] Edward G. Miller,[3b] and Kurt Mislow

Contribution from the Department of Chemistry, Princeton University, Princeton, New Jersey 08540. *Received March 4, 1968*

Abstract: The thermal racemization of optically active allyl sulfoxides has been shown on the basis of kinetic evidence and labeling experiments to proceed by way of a facile, reversible, and wholly concerted rearrangement to optically inactive allyl sulfenates. The reaction involves an intramolecular cyclic α,γ shift of the allyl group between the sulfoxide oxygen and sulfur termini. Rearrangement of (*S*)-α-methylallyl *p*-toluenesulfenate to (*S*)-*trans*-crotyl *p*-tolyl sulfoxide proceeds with at least 37% stereospecificity and provides an example of an asymmetric synthesis in which one chiral center (sulfur) is generated at the expense of another (carbon).

Benzyl *p*-tolyl sulfoxide (**1**) racemizes at a significantly faster rate than comparable nonbenzylic sulfoxides, and in the preceding paper[4] we presented arguments for a change in mechanism: whereas diaryl and some alkyl aryl and diaryl sulfoxides racemize by the pyramidal inversion mechanism,[5] the racemization of **1** follows a pathway of homolytic scission and cage recombination which owes its low free energy of activation chiefly to a very positive activation entropy. The bond dissociation energies of benzyl and allyl compounds are very nearly equal,[6] and we therefore anticipated the possibility that racemization of allyl *p*-tolyl sulfoxide (**2**) might also proceed *via* the homolytic scission mechanism of **1**. The work described in this paper received its initial impetus in the need for investigating this possibility.

(+)-Allyl *p*-tolyl sulfoxide ((+)-**2**) was prepared by the Grignard synthesis[7] from allylmagnesium bromide and menthyl *p*-toluenesulfinate ((−)-**3**).[8,9] Reduction of (+)-**2**, $[\alpha]_D$ +212° (ethanol), with diimide[10] afforded a product, $[\alpha]_D$ +211° (ethanol), identical by ir and nmr with (+)-*n*-propyl *p*-tolyl sulfoxide, $[\alpha]_D$ +201° (ethanol), prepared from *n*-propylmagnesium bromide and (−)-**3**. Preliminary experiments indicated that **2** racemizes in benzene or *p*-xylene at conveniently measured rates in a temperature range (50–70°) significantly below that (130–150°) required for the racemization of **1** by the homolytic scission–recombination mechanism,[4] let alone that (190–220°) required for the racemization of sulfoxides by the pyramidal inversion mechanism.[5] It was also noted that the racemization of **2** is not accompanied by decomposition, again in contrast to **1**. These observations signalized the operation of yet another mechanism.

Pertinent rate data are collected in Table I. The

Table I. First-Order Rate Constants and Activation Parameters for the Racemization of Allyl *p*-Tolyl Sulfoxide (**2**)

Solvent	*T*, °C	$k \times 10^5$, sec^{-1}	Period of observn[a]	Activation parameters
Benzene	40.0	4.39	1.5	
	50.9	16.3	2.5	
	60.0	43.9	2.5	$\Delta H^{\ddagger}$, 23.1 ± 0.1 kcal/mol
	69.0	112	3.0	$\Delta S^{\ddagger}$, −4.9 ± 0.1 eu
TFP[b]	60.7	0.38	0.3[c]	
	70.8	1.30	3.0	$\Delta H^{\ddagger}$, 27.6 ± 0.3 kcal/mol
	79.6	3.78	2.5	$\Delta S^{\ddagger}$, −0.7 ± 0.1 eu

[a] Half-lives. [b] 2,2,3,3-Tetrafluoro-1-propanol. [c] 15 hr.

enormous rate acceleration in benzene, $k = 1.63 \times 10^{-4}$ sec^{-1} *at 51°* for **2**, as compared to $k = 0.70 \times 10^{-4}$ sec^{-1} *at 145°* for **1**, results from a 20 kcal/mol lowering in the enthalpy of activation, which is 23.1 kcal/mol for **2**, in contrast to 43.0 kcal/mol for **1**.[4] The large rate acceleration due to the enthalpy effect overcomes the rate deceleration due to the negative entropy of activation for the racemization of **2** (−4.9 eu), which is in marked contrast to the value of 24.6 eu found[4] for **1**; thus $\Delta G^{\ddagger}$ for the racemization of **2** in benzene is 24.7 kcal/mol at 51°, while $\Delta G^{\ddagger}$ for the racemization of **1** is still 32.7 kcal/mol at 145°.

On the basis of evidence adduced below, we have concluded that the racemization of **2** involves the intermediacy of allyl *p*-toluenesulfenate (**4**), an achiral[11] and therefore optically inactive substance which is present in low concentration at equilibrium.

(1) This work was supported by the Air Force Office of Scientific Research under Grant No. AF-AFOSR-1188-67 and by the National Science Foundation under Grant No. GP-3375.

(2) For preliminary accounts of this work, see D. R. Rayner, E. G. Miller, P. Bickart, A. J. Gordon, and K. Mislow, *J. Amer. Chem. Soc.*, **88**, 3138 (1966); E. G. Miller, D. R. Rayner, and K. Mislow, *ibid.*, **88**, 3139 (1966); K. Mislow, *Rec. Chem. Progr.*, **28**, 217 (1967).

(3) (a) National Aeronautics and Space Administration Fellow, 1965–1967; (b) U. S. Public Health Service Postdoctoral Fellow, 1965–1966; (c) U. S. Public Health Service Postdoctoral Fellow, 1966–1967.

(4) E. G. Miller, D. R. Rayner, H. T. Thomas, and K. Mislow, *J. Amer. Chem. Soc.*, **90**, 4861 (1968).

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

(6) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, p 50; J. B. Homer and F. P. Lossing, *Can. J. Chem.*, **44**, 2211 (1966).

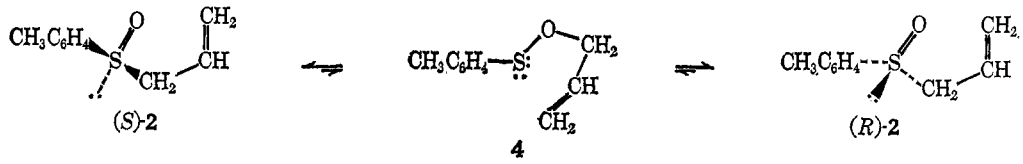
(7) K. K. Andersen, *Tetrahedron Lett.*, 93 (1962).

(8) This ester was prepared from (−)-menthol and *p*-toluenesulfinyl chloride.[9] The diastereomers (epimeric at sulfur) have opposite signs of rotation at the D line and the prefix refers to this sign.

(9) H. F. Herbrandson, R. T. Dickerson, Jr., and J. Weinstein, *J. Amer. Chem. Soc.*, **78**, 2576 (1956); H. F. Herbrandson and R. T. Dickerson, Jr., *ibid.*, **81**, 4102 (1959).

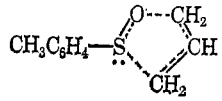
(10) J. W. Hamersma and E. I. Snyder, *J. Org. Chem.*, **30**, 3985 (1965).

(11) On the time scale of racemization of **2**. By analogy with peroxides and disulfides,[12] sulfenates such as **4** should be chiral molecules by virtue of torsion about the S–O bond,[13] with dihedral angles of twist between the C–S–O and S–O–C planes ($0° < \theta < 180°$) and a barrier to torsion about the S–O bond (and thus to interconversion of enantiomeric conformations).



(*S*)-2 4 (*R*)-2

The transition state for the rearrangement of **2** into **4** and *vice versa* corresponds to a concerted, cyclic process, and may be formulated as



The low enthalpy of activation and the negative entropy of activation in benzene are consistent with a concerted cyclic rearrangement mechanism, the former because the energy required to break the α-carbon–sulfur bond is furnished in large measure by the synchronous formation of the γ-carbon–oxygen bond, and the latter because simultaneous partial bonding of α- and γ-carbon atoms to the migration origin and terminus (sulfur and oxygen, respectively) results in a loss of degrees of freedom in the transition state.[14]

The implication in the above mechanism, that a *small* concentration of **4** is in mobile equilibrium with **2**, leads to the corollary that **4**, prepared from *p*-toluenesulfenyl chloride and allyl alcohol labeled in the α position, should rearrange essentially quantitatively to **2** labeled in the γ position under the conditions employed in the racemization of **2**. This prediction has been amply verified by the finding that reaction of *p*-toluenesulfenyl chloride with lithium crotyl alcoholate, lithium α-methylallyl aleoholate, and lithium allyl-α-d_2 alcoholate at 0° in ether or glyme affords α-methylallyl *p*-tolyl sulfoxide, crotyl *p*-tolyl sulfoxide, and allyl-γ-d_2 *p*-tolyl sulfoxide, respectively, and that none of the isomeric sulfoxides which are conceivable as products of a *non*concerted rearrangement, *i.e.*, crotyl *p*-tolyl sulfoxide, α-methylallyl *p*-tolyl sulfoxide, and allyl-α-d_2 *p*-tolyl sulfoxide, respectively, are discernible by nmr. It must be concluded that the initially formed allylic sulfenate is thermally unstable relative to sulfoxide, even under the mild conditions employed (work-up at temperatures not exceeding 25°), and that the α,γ shift is wholly concerted.

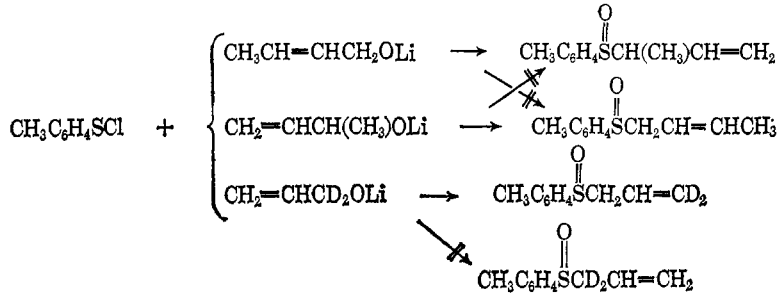
As an intriguing sidelight, the nmr spectrum of allyl-γ-d_2 *p*-tolyl sulfoxide at 75° remains invariant, *i.e.*, no trace of allyl-α-d_2 *p*-tolyl sulfoxide is apparent, even over a period of time during which **2** suffers ten half-lives of racemization. This observation is consistent with our thesis that the lowest energy pathway for racemization of **2** does not involve dissociation into kinetically free allyl and *p*-toluenesulfinyl radicals.

The rate constant of racemization of **2** exhibits a marked solvent dependence (Table II). With increasing solvent polarity, as measured by Z[15] or E_T[16] values, the rate constant decreases, the relationship of log k to either parameter being linear, as exemplified by the plot in Figure 1. The direction of the solvent dependence is in accord with the proposed mechanism, for with increasing solvent polarity the highly polar sulfoxide[17] is expected to be more strongly solvated, while solvation of the less polar sulfenate should be relatively insensitive to changes in solvent polarity.

Table II. Racemization of Allyl *p*-Tolyl Sulfoxide (**2**) at 60.7°

Solvent	Z,[a] kcal/mol at 25°	E_T,[b] kcal/mol at 25°	$k \times 10^5$, sec^{-1}	k_{rel}[c]
Methylcyclohexane	60.1[e]	30.9[d]	126	2.73
Benzene	...	34.5	46.1	1.00
Dioxane	...	36.0	27.6	0.60
Dimethyl sulfoxide	71.1	45.0	10.6	0.23
Acetonitrile	71.3	46.0	9.4	0.20
Ethanol	79.6	51.9	4.34	0.094
2,2,3,3-Tetrafluoro-1-propanol	96.3	...	0.38	0.0083

[a] Reference 15. [b] Reference 16. [c] $k/k_{benzene}$. [d] In *n*-hexane. [e] In isooctane.



It follows that the stabilization of the sulfoxide **2** relative to the sulfenate **4** increases with increasing solvent polarity, and that the energy of the transition state for the process leading from sulfoxide to sulfenate will increase as a result of the contribution of the $\Delta H^{\pm}$ term, which reflects the necessity of breaking in-

(12) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, pp 134–136; O. Foss in "Organic Sulfur Compounds," Vol. I, N. Kharasch, Ed., Pergamon Press, Inc., New York, N. Y., 1961, pp 77–78.

(13) This is the case with methyl *o*-nitrobenzenesulfenate in the solid state (W. C. Hamilton and S. J. LaPlaca, *J. Amer. Chem. Soc.*, **86**, 2289 (1964)).

(14) For example, see A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1961, p 111 ff.

(15) E. M. Kosower, *J. Amer. Chem. Soc.*, **80**, 3253 (1958); E. M. Kosower and G.-S. Wu, *ibid.*, **83**, 3142 (1961).

(16) C. Reichardt, *Angew. Chem. Intern. Ed. Engl.*, **4**, 29 (1965).

(17) The dipole moments of sulfoxides devoid of other functional groups are about 4 D, whereas the corresponding ethers (R_2O) and thioethers (R_2S) have dipole moments in the range 1–2 D (C. W. N. Cumper and S. Walker, *Trans. Faraday Soc.*, **52**, 193 (1956)).

creasingly strong solvent–solute bonds. On the other hand, because the desolvation implicit in the conversion of **2** to **4** is expected to increase the degrees of freedom in the system, a more positive entropy term ($T\Delta S^{\pm}$) is expected to work in the opposite direction and effect a compensating increase in k with increasing solvent polarity. These suppositions are entirely borne out by experiment: at 60.7° the 100-fold increase of k in benzene, as compared to 2,2,3,3-tetrafluoro-1-propanol, is the result of a smaller $\Delta G^{\pm}$ (24.7 kcal/mol *vs.* 27.8 kcal/mol); however, $\Delta H^{\pm}$ is 23.1 kcal/mol in benzene and 27.6 kcal/mol in 2,2,3,3-tetrafluoro-1-propanol, while the corresponding values of $\Delta S^{\pm}$ in the two solvents are −4.9 and −0.7 eu, respectively (Table I).

All of our observations thus accord with the hypothesis that racemization of **2** proceeds by way of a cyclic concerted, reversible intramolecular rearrangement of chiral sulfoxide to achiral[11] sulfenate, with the equilibrium lying far to the side of the sulfoxide. It is worth noting at this juncture that the cyclic rearrangement mechanism is plainly inaccessible to simple dialkyl and diaryl sulfoxides, and that even in **1** an α,γ-shift mechanism would require destruction of the benzene resonance to achieve the intermediacy of a sulfenate which, incidentally, can also be ruled out on other grounds.[4]

Our finding that allyl sulfenates readily undergo rearrangement to allyl sulfoxides prompted us to reinvestigate a report[18] that allyl trichloromethanesulfenate is obtained on reaction of allyl alcohol with trichloromethanesulfenyl chloride. As expected, reaction of lithium allyl-α-d_2 alcoholate with trichloromethanesulfenyl chloride instead gives *exclusively* allyl-γ-d_2 trichloromethyl sulfoxide, as shown by the nmr spectrum of the product, which features a broad triplet (1 H) at τ 4.04, J = 7.6 Hz ($CD_2{=}CHCH_2$–), and, as a portion of an ABX system, a doublet of AB quartets (τ_A 6.07, τ_B 6.47, J_{AB} = −12.7 Hz, $J_{AX} \cong J_{BX}$ = +7.6 Hz, 2 H), consistent with the presence of a pair of diastereotopic protons[19] on carbon adjacent to sulfur ($CD_2{=}CHCH_2$–); no trace of allyl-α-d_2 trichloromethanesulfenate or of the isomeric allyl-α-d_2 trichloromethyl sulfoxide could be detected. This result confirms the specificity of the α,γ shift already established in the exclusive formation of allyl-γ-d_2 *p*-tolyl sulfoxide described above.[20] However, whereas the extent of rearrangement in the formation of allyl *p*-tolyl, crotyl *p*-tolyl, α-methylallyl *p*-tolyl, and allyl trichloromethyl sulfoxides appears to be essentially complete ($\geq$95%) within the precision of our analytical method (nmr), reaction of trichloromethanesulfenyl chloride with lithium crotyl alcoholate yields a mixture of the rearrangement product (α-methylallyl trichloromethyl sulfoxide) and of unrearranged crotyl trichloromethanesulfenate. In carbon disulfide, the mixture consists of

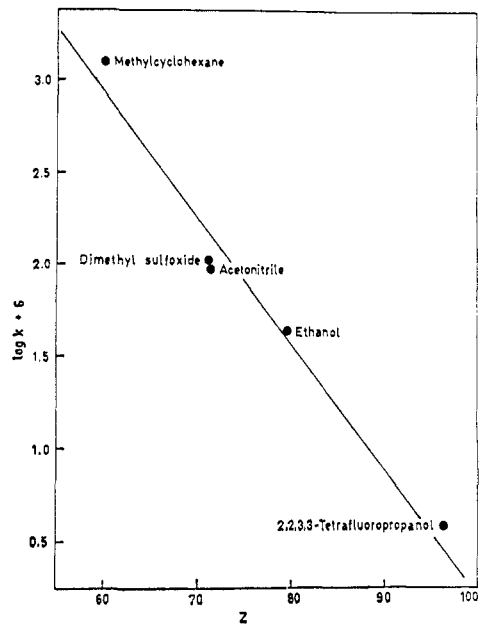


Figure 1.

35% of rearranged sulfoxide and 65% of unrearranged sulfenate, whereas in DMSO-d_6, the mixture consists of 75% of sulfoxide and 25% of sulfenate (by nmr). This observation leads to two conclusions: first, that the equilibrium between sulfenate and sulfoxide is indeed a mobile one, as postulated above, and second, that the equilibrium is solvent dependent, the relatively nonpolar sulfenate predominating in the more nonpolar solvent and the relatively polar sulfoxide in the more polar solvent. Reaction of 2,4-dinitrobenzenesulfenyl chloride with lithium allyl-α-d_2 alcoholate gives only allyl-α-d_2 2,4-dinitrobenzenesulfenate, to the exclusion of the rearrangement product (allyl-γ-d_2 2,4-dinitrophenyl sulfoxide), as shown by the nmr spectrum: the vinyl multiplet (3 H) in the region τ 3.6–4.8 is essentially the same as that of undeuterated material,[21] except that the lowest field portion (attributable to the C-2 vinyl proton) has been simplified to a four-line system (J_{AX} = 9 Hz, J_{BX} = 17 Hz), and the doublet (2 H) at τ 5.53 found in the undeuterated material[21] is absent in the deuterated material. The structural features which determine the extent and generality of the rearrangement of allylic sulfenates to sulfoxides are not yet fully understood.

In the thermal O → S rearrangement of allylic or benzylic[4] sulfenates to sulfoxides, the driving force for the rearrangement has its source in the formation of the S=O sulfoxide bond, whose strength of 90 kcal/mol[22] resides in its multiplicity.[23] This mechanism of bond strengthening is not available to amine oxides, wherein the N–O bond is purely dipolar, and this argument provides the rationale for the obser-

(18) G. Sosnovsky, *J. Chem. Soc.*, 3139 (1956).

(19) K. Mislow and M. Raban, "Topics in Stereochemistry," Vol. 1, N. L. Allinger and E. L. Eliel, Ed., John Wiley and Sons, Inc., New York, N. Y., 1967, Chapter 1.

(20) Following our preliminary report of the sulfenate → sulfoxide rearrangement,[2] S. Braverman and Y. Stabinsky [*Chem. Commun.*, 270 (1967)] also noted that sulfoxide is formed in the reaction of allyl alcohol with trichloromethanesulfenyl chloride, rather than sulfenate as previously claimed.[18] However, these workers employed *unlabeled* allyl alcohol and their postulation that a *cyclic* mechanism *via* the sulfenate is responsible for the observed result thus lacks the support of experimental evidence which is provided by the present work. See also S. Braverman and Y. Stabinsky, *Israel J. Chem.*, **5**, 125 (1967).

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

(22) H. Mackle, *Tetrahedron*, **19**, 1159 (1963).

(23) W. Moffitt, *Proc. Roy. Soc.* (London), **A200**, 409 (1950); L. Pauling, *J. Phys. Chem.*, **56**, 361 (1952); G. Cilento, *Chem. Rev.*, **60**, 147 (1960), and references cited therein; A. B. Burg, "Organic Sulfur Compounds," Vol. 1, N. Kharasch, Ed., Pergamon Press, Inc., New York, N. Y., 1961, pp 35, 36; P. Haake, W. B. Miller, and D. A. Tyssee, *J. Amer. Chem. Soc.*, **86**, 3577 (1964).

vation[24] that allyl phenyl sulfoxide does not undergo thermal rearrangement to allyl benzenesulfenate, even though the S → O shift in a sulfoxide → sulfenate rearrangement is formally analogous to the N → O shift in the Meisenheimer rearrangement of N-allyl- or N-benzylamine oxides to O-allyl- or O-benzylhydroxylamines[25] or in the rearrangement of nitrones to oximes.[26] The same argument serves to account for the direction of other O → S shifts, such as the sulfoxylate → sulfinate[27] and sulfinate → sulfone[28] rearrangements, and for the direction of the thermal O → P shift in the phosphinite → phosphine oxide,[29,30] phosphite → phosphonate,[30,31] and phosphonite → phosphinate[30] rearrangements.[32] The direction of these rearrangements corresponds to a thermodynamic driving force and is independent of mechanism.[33]

The intramolecular character of the concerted cyclic rearrangement of **4** to **2** was borne out in an experiment in which the lithium salt of (+)-(*S*)-3-buten-2-ol,[34] *i.e.*, optically active α-methylallyl alcohol, was allowed to react with *p*-toluenesulfenyl chloride in dimethyl ether at −60 to −70°. When the reaction mixture was allowed to warm to room temperature, the initially formed (*S*)-α-methylallyl *p*-toluenesulfenate (**5**)[39] rearranged to (−)-(*S*)-*trans*-crotyl *p*-tolyl sulfoxide (**6**),[40,43] which rapidly racemized (*e.g.*, at 29°, $\tau_{1/2}$ = 51 min in toluene) and, over a period of days, rearranged to an equilibrium mixture of racemic *trans*- (77%) and *cis*- (23%) crotyl *p*-tolyl sulfoxides.[45] From the rate constants of racemization of **6** in toluene at 28.9, 41.0, and 49.3° ($k \times 10^4$ = 2.24, 8.15, and 18.3 sec^{-1}, respectively), the calculated values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are 19.3 kcal/mol and −11.3 eu, respectively. The activation parameters for the racemization of **6** resemble those of **2**, both in the value of $\Delta H^{\ddagger}$, which is low, and the value of $\Delta S^{\ddagger}$, which is negative, and there can be little question but that the mechanism of racemization of the two compounds is the same.[46] Accordingly, the rearrangement of **5** to **6** and the racemization of **6** share the same mechanistic pathway, *i.e.*, both proceed by way of the reversible, intramolecular, cyclic, concerted mechanism which underlies the rearrangement of **4** to **2** and the racemization of **2**. There is this difference: whereas in the rearrangement of **4** to **2** only the two enantiomers of **2** are interconverted, by reaction of either of the two enantiotopic faces[19] on the sulfur

(24) A. C. Cope, D. E. Morrison, and L. Field, *J. Amer. Chem. Soc.*, **72**, 59 (1950).

(25) J. Meisenheimer, *Ber.*, **52**, 1667 (1919); J. Meisenheimer, H. Greeske, and A. Willmersdorf, *ibid.*, **55**, 513 (1922); R. F. Kleinschmidt and A. C. Cope, *J. Amer. Chem. Soc.*, **66**, 1929 (1944); A. C. Cope and P. H. Towle, *ibid.*, **71**, 3423 (1949); A. C. Cope, T. T. Foster, and P. H. Towle, *ibid.*, **71**, 3929 (1949); A. H. Wragg, T. S. Stevens, and D. M. Ostle, *J. Chem. Soc.*, 4057 (1958); U. Schöllkopf, M. Patsch, and H. Schäfer, *Tetrahedron Lett.*, 2515 (1964); G. P. Shulman, P. Ellgen, and M. Connor, *Can. J. Chem.*, **43**, 3459 (1965).

(26) A. C. Cope and A. C. Haven, Jr., *J. Amer. Chem. Soc.*, **72**, 4896 (1950); E. J. Grubbs, J. D. McCullough, Jr., B. H. Weber, and J. R. Maley, *J. Org. Chem.*, **31**, 1098 (1966); E. J. Grubbs, J. A. Villarreal, J. D. McCullough, Jr., and J. S. Vincent, *J. Amer. Chem. Soc.*, **89**, 2234 (1967).

(27) Q. E. Thompson, *J. Org. Chem.*, **30**, 2703 (1965).

(28) J. Kenyon and H. Phillips, *J. Chem. Soc.*, 1676 (1930); C. L. Arcus, M. P. Balfe, and J. Kenyon, *ibid.*, 485 (1938); A. H. Wragg, J. S. McFadyen, and T. S. Stevens, *ibid.*, 3603 (1958); D. Darwish and R. McLaren, *Tetrahedron Lett.*, 1231 (1962); D. Darwish and E. A. Preston, *ibid.*, 113 (1964); C. J. M. Stirling, *Chem. Commun.*, 131 (1967); S. Braverman and H. Mechoulam, *Israel J. Chem.*, **5**, 71 (1967).

(29) A. E. Arbuzov and K. V. Nikonorov, *Zh. Obshch. Khim.*, **18**, 2008 (1948); R. S. Davidson, R. A. Sheldon, and S. Trippett, *J. Chem. Soc., C*, 722 (1966); M. P. Savage and S. Trippett, *ibid.*, 1842 (1966); D. Dron, M.-L. Capmau, and W. Chodkiewicz, *C. R. Acad. Sci., Paris, Ser. C*, **264**, 1883 (1967).

(30) A. P. Boisselle and N. A. Meinhardt, *J. Org. Chem.*, **27**, 1828 (1962).

(31) V. Mark, *Tetrahedron Lett.*, 281 (1962); A. N. Pudovik, I. M. Aladzheva, and L. N. Yakovenko, *Zh. Obshch. Khim.*, **33**, 3443 (1963); A. N. Pudovik and I. M. Aladzheva, *Dokl. Akad. Nauk SSSR*, **151**, 1110 (1963); *Zh. Obshch. Khim.*, **33**, 3096 (1963); A. L. Lemper and H. Tieckelmann, *Tetrahedron Lett.*, 3053 (1964).

(32) The P=O bond energies lie in the range 120–140 kcal/mol (S. B. Hartley, W. S. Holmes, J. K. Jacques, M. F. Mole, and J. C. McCoubrey, *Quart. Rev.* (London), **17**, 204 (1963)).

(33) (a) We were unable to effect a homoallylic sulfenate → sulfoxide rearrangement: cyclopropylcarbinyl *p*-toluenesulfenate, prepared by reaction of *p*-toluenesulfenyl chloride and lithium cyclopropylcarbinolate, does not rearrange on heating for 1 hr at 150° in benzene. (b) *Cf.* also the related O → C rearrangement of allyl ethers (U. Schöllkopf and K. Fellenberger, *Ann.*, **698**, 80 (1966); Y. Mokisumi and S. Notzumoto, *Tetrahedron Lett.*, 6393 (1966)).

(34) (+)-3-Buten-2-ol has been correlated with (+)-(*S*)-2-butanol[35,36] and with (+)-(*S*)-2-butyl methyl ether,[36,37] both of which have been correlated with (+)-(*S*)-lactic acid.[38]

(35) W. G. Young and F. F. Caserio, Jr., *J. Org. Chem.*, **26**, 245 (1961).

(36) K. B. Wiberg, *J. Amer. Chem. Soc.*, **74**, 3891 (1952).

(37) D. S. Tarbell and M. C. Paulson, *ibid.*, **64**, 2842 (1942).

(38) P. A. Levene, H. L. Haller, and A. Walti, *J. Biol. Chem.*, **72**, 591 (1927); P. A. Levene, A. Walti, and H. L. Haller, *Science*, **64**, 558 (1926).

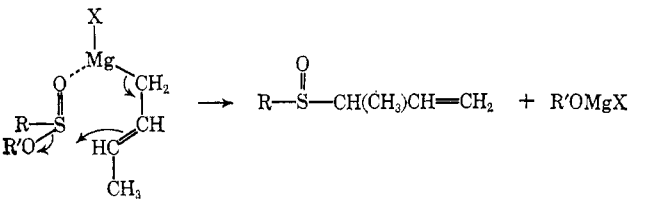
(39) Although **5** was not isolated, the nmr spectrum of the dimethyl ether solution of the reaction product was consistent with this structure.

(40) Diimide reduction of **6** gave *n*-butyl *p*-tolyl sulfoxide, identical in all respects with authentic material prepared by periodate oxidation of *n*-butyl *p*-tolyl sulfide (the rate of diimide reduction of **6** is very slow in comparison with the rate of racemization). The geometry about the double bond was assigned on the basis of the ir spectrum, which exhibited a strong absorption at 970 cm^{-1} (*trans* −CH=CH−) and no absorption at 744 cm^{-1} (*cis* −CH=CH−). The absolute configuration was established on the following grounds. It has been rigorously proven[41] that the Grignard synthesis[7] of sulfoxides occurs with inversion of configuration at sulfur and that (−)-**3** has the *S* configuration at sulfur; consequently, **2** must have the *R* configuration at sulfur. A study[42] of the optical rotatory power of sulfoxides of known absolute configuration has led to the recognition that alkyl *p*-tolyl sulfoxides which have the *R* configuration at sulfur are dextrorotatory in the visible region, and (+)-(*R*)-**2**, which has a positive Cotton effect (a +335) centered at 258 mμ and thus resembles other (*R*)-alkyl aryl sulfoxides,[42] is no exception to this rule. On the reasonable assumption that the terminal methyl group on the crotyl moiety of **6** does not strongly perturb the chromophoric system, signs and configurations of **2** and **6** may thus be safely correlated, and (−)-**6** accordingly has the *S* configuration.

(41) M. Axelrod, P. Bickart, J. Jacobus, M. M. Green, and K. Mislow, *J. Amer. Chem. Soc.*, **90**, 4835 (1968).

(42) K. Mislow, M. M. Green, P. Laur, J. T. Melillo, T. Simmons, and A. L. Ternay, Jr., *ibid.*, **87**, 1958 (1965).

(43) In an attempt to prepare optically active crotyl *p*-tolyl sulfoxide directly from crotylmagnesium chloride and (−)-**3**, only α-methylallyl *p*-tolyl sulfoxide was obtained. By analogy with the cyclic addition mechanism of butenylmagnesium halides to ketones,[44] the reaction of sulfinate esters conceivably involves an allylic rearrangement following coordination of the sulfoxide with oxygen magnesium.

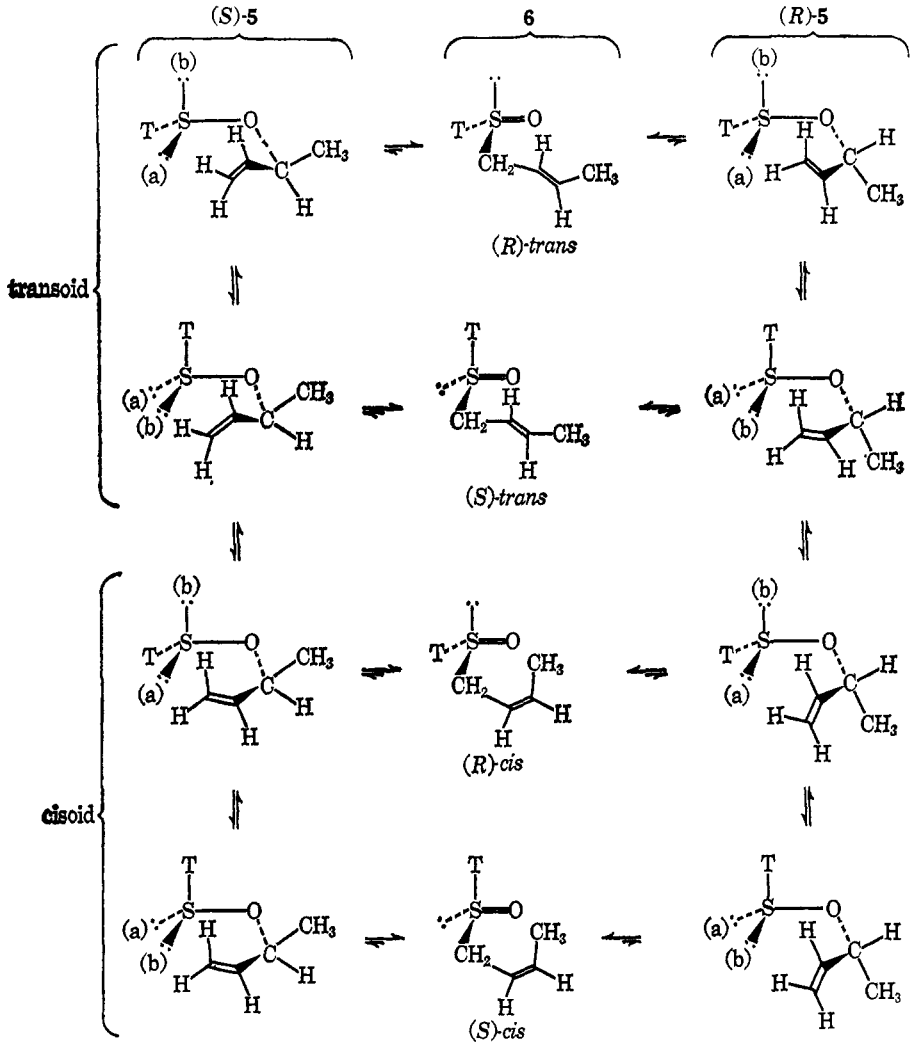


(44) W. G. Young and J. D. Roberts, *J. Amer. Chem. Soc.*, **68**, 1472 (1946); R. H. De Wolfe and W. G. Young, *Chem. Rev.*, **56**, 753 (1956); J. E. Nordlander, W. G. Young, and J. D. Roberts, *J. Amer. Chem. Soc.*, **83**, 494 (1961).

(45) The composition of the mixture was analyzed by nmr since the crotyl methyl and methylene signals are significantly shifted in the *cis* and *trans* form of **6** (Experimental Section).

(46) At 40°, the rate of racemization of **6** exceeds that of **2** by a factor of about 10, corresponding to $\Delta G^{\ddagger}$ values of 22.8 and 24.6 kcal/mol, respectively. A similar effect was noted by S. G. Smith, *J. Amer. Chem. Soc.*, **83**, 4285 (1961), who found that substitution of α- and γ-methyl groups enhances the rate of rearrangement of allyl thionbenzoate by a factor of *ca.* 55 and *ca.* 6, respectively.

Chart I[a]



[a] T = *p*-tolyl.

atom of **4** with the terminal allyl methylene carbon, the interconversion of **5** and **6** involves four stereoisomers of **6**, which differ in configuration at the asymmetric sulfur atom and/or at the double bond. The interconversion of these four isomers proceeds as indicated by the arrows in Chart I. Eight conformations of **5** are shown, divided into transoid and cisoid types depending on whether rearrangement of **5** to **6** affords *trans*- or *cis*-**6**. For each of the resulting conformational types (*i.e.*, (*S*)-transoid-**5**, (*S*)-cisoid-**5**, (*R*)-transoid-**5**, (*R*)-cisoid-**5**), two modes of ring closure are possible, depending on whether rearrangement of **5** to **6** affords (*R*)- or (*S*)-**6**. In reactions yielding (*R*)-**6**, the reacting face is characterized by the unshared electron pair labeled a, whereas in reactions yielding (*S*)-**6**, the reacting face is characterized by the unshared electron pair on sulfur labeled b. Remembering that (*S*)- and (*R*)-cisoid and -transoid forms of **5** differ only in conformation and are therefore readily interconvertible, and that the sulfenate → sulfoxide rearrangement is reversible, the racemization as well as the *trans–cis* interconversion of **6** are readily understandable on the assumption that the various transition states corresponding to the reactions of Chart I, though not isoenergetic, are nevertheless at least comparable in energy. A mechanism is thereby provided for loss of configurational purity through leakage *via* competitive diastereomeric transition states; this includes starting **5** which is seen by this mechanism to lose optical purity alongside with **6**. In consequence, the stereospecificity of the transformation, which is 37% based on the optical purity of starting **5** (52.3%) and the estimated optical purity of initially formed **6** (19.4%),[47] is to be considered a lower limit.

The present asymmetric synthesis belongs to the not uncommon variety in which one chiral center, here sulfur, is generated at the expense of another, here carbon,[48] and in which an allylic α,γ inversion is an integral part of the asymmetric synthesis.[49] Given our knowledge of the configurations of starting material and kinetically determined (*i.e.*, initially formed) prod-

(47) Assuming that the terminal methyl group on the crotyl moiety of **6** does not strongly perturb the chromophoric system[40] and thus fails to make a substantial contribution to the molecular rotation, the value of the molecular rotation for optically pure **6** should be closely similar to that found for **2**, $[\phi]_{500}$ 665° (toluene). Since the initially read value of $[\phi]_{500}$ (toluene) for **6** was −129°, the estimated optical purity is 129/665 = 19.4%.

(48) For some recent examples, see R. K. Hill and T. H. Chan, *J. Amer. Chem. Soc.*, **88**, 866 (1966); E. W. Warnhoff and S. V. Lopez, *Tetrahedron Lett.*, 2723 (1967).

(49) E. R. Alexander and R. W. Kluiber, *J. Amer. Chem. Soc.*, **73**, 4304 (1951); F. F. Caserio, G. E. Dennis, R. H. DeWolfe, and W. G. Young, *ibid.*, **77**, 4182 (1955); H. L. Goering and R. W. Greiner, *ibid.*, **79**, 3464 (1957); R. B. Woodward and T. S. Katz, *Tetrahedron*, **5**, 70 (1959); R. P. Lutz and J. D. Roberts, *J. Amer. Chem. Soc.*, **83**, 2198 (1961); H. L. Goering and W. I. Kimoto, *ibid.*, **87**, 1748 (1965); R. K. Hill and N. W. Gilman, *Chem. Commun.*, 619 (1967).

uct, the lowest energy pathway corresponds to that in which the rearrangement of (*S*)-transoid-**5** leads to (*S*)-*trans*-**6** (Chart I) and the diastereomeric transition states leading from (*S*)-**5** to the other three diastereomers accordingly are higher in energy. To provide an *ex post facto* explanation for the direction of the asymmetric synthesis by invoking an assumed topography of diastereomeric transition states and then comparing secondary (nonbonding interaction) forces which are but poorly understood is an exercise in speculative rationalization from which we shall refrain; our opinions in this matter have already found emphatic expression on other occasions.[42,50]

That the mechanism of racemization of allylic sulfoxides is not restricted to *aryl* allyl sulfoxides (such as **2** and **6**) was shown by the observation that (+)-allyl methyl sulfoxide[41] racemizes at 60.7° in benzene with a first-order rate constant of 7.07×10^{-6} sec^{-1}, *i.e.*, 65 times more slowly than **2** (Table II) but still enormously faster than **1**, let alone sulfoxides which racemize by the pyramidal inversion mechanism. It would appear that the mechanism of racemization proposed in this paper is applicable in general to compounds containing an allylic grouping attached to sulfoxide sulfur.

Experimental Section[51]

Racemization Kinetics. For runs at temperatures above 70°, the sealed tube method was used as described before.[5] For runs at temperatures below 70°, the solutions were contained in a temperature-controlled polarimeter cell, and rotations were continuously recorded as a function of time, using a Cary 60 spectropolarimeter. Typical operating conditions: *c* 0.4 g/100 ml, *l* 0.1 dm, λ 500 mμ. Measurements were taken over a period of one to five half-lives, with the exception of **2** in TFP at 60.7° (Table I). First-order rate constants and activation parameters were calculated as before.[5] Residual rotations (α_∞) were determined by letting the racemization proceed for over ten half-lives and to constant rotation. In the racemization of **2**, the infinity value was 0.000 ± 0.001°, whereas in the racemization of **6**, the infinity value at 500 mμ was +0.014° (initial reading α^0_{500} −0.280°) with *l* 0.1 and *c* 4.3. All rotations were corrected for the residual rotation.

(+)-Allyl *p*-Tolyl Sulfoxide ((+)-2). A solution of allylmagnesium bromide was prepared by dropwise addition of 5.0 g (0.041 mol) of allyl bromide to a stirred suspension of magnesium turnings (0.50 g, 0.020 g-atom) in 30 ml of anhydrous ether. When most of the magnesium had dissolved, the mixture was added through a glass wool plug to an ethereal solution of (−)-menthyl *p*-toluenesulfinate[9] ((−)-**3**, 3.5 g, 0.012 mol), $[\alpha]^{25}D$ −198° (*c* 1.0, acetone). The reaction was immediately quenched by addition of saturated ammonium chloride solution and cooled by addition of ice. The ethereal layer was extracted five times with ice water. The combined aqueous portions were saturated with sodium chloride and extracted five times with a total of 700 ml of chloroform. The cold chloroform solution was dried (magnesium sulfate) and concentrated on a rotary evaporator, care being taken to keep the solution at or below 0°. The residue was chromatographed at 5° on 25 g of Florisil. The first fractions, eluted with benzene, were discarded, and material eluted with ethyl acetate was concentrated on a rotary evaporator at temperatures below 0° and pumped free of solvent at 0.02 mm. The yellow oil, $[\alpha]^{27}D$ +212° (*c* 0.26, ethanol), was used without further purification for all experiments; ORD (*c* 0.11, isooctane, 27°) $[\phi]D$ +172°, $[\phi]_{278}$ +13,540°, $[\phi]_{262}$ 0°, $[\phi]_{236}$ −53,500°, $[\phi]_{222}$ 0°, $[\phi]_{217}$ +22,800°. The ir spectrum of the neat material shows the characteristic strong sulfoxide stretching frequency at 1050 cm^{-1}. The nmr spectrum shows four well-separated groups of lines: an aromatic AA′BB′ quartet (4 H) centered at τ 2.60, a complex vinyl multiplet (3 H) centered at τ 4.65, a sharp doublet (*J* = 7 Hz, 2 H) centered at τ 6.50 (–C*H*$_2$SO–), and a sharp singlet (3 H) at τ 7.62 (methyl on the aromatic ring). A sample was purified for analysis by kugelrohr distillation at 100° (0.05 mm).

Anal. Calcd for $C_{10}H_{12}SO$: C, 66.62; H, 6.71; S, 17.79. Found: C, 66.70; H, 6.83; S, 17.67.

(+)-*n*-Propyl *p*-Tolyl Sulfoxide. A. Following a procedure analogous to that described above, this compound was prepared by addition of a solution of *n*-propylmagnesium bromide in ether to an ethereal solution of (−)-**3**. After work-up and chromatography (as above, except that operations were carried out at room temperature), the material was purified by kugelrohr distillation at 90° (0.02 mm) to give a colorless liquid, $[\alpha]^{27}D$ +201° (*c* 1.54, ethanol). The ir spectrum shows the characteristic S=O stretching frequency at 1050 cm^{-1}. The nmr spectrum (in carbon tetrachloride) shows five sets of signals: a four-proton aromatic AA′BB′ quartet centered at τ 2.65, a broad triplet (2 H) centered at τ 7.33 (–C*H*$_2$-SO–), a three-proton singlet at τ 7.63 (aromatic methyl), a two-proton complex multiplet centered at τ 8.35 (CH$_3$C*H*$_2$–), and an asymmetric triplet (3 H) centered at τ 9.00 (C*H*$_3$CH$_2$–).

Anal. Calcd for $C_{10}H_{14}SO$: C, 65.89; H, 7.74; S, 17.59. Found: C, 66.16; H, 7.88; S, 17.64.

B. Potassium azodicarboxylate (4.7 g, 0.024 mol) and 50 ml of dry ether were placed in a 100-ml, round-bottomed flask equipped with magnetic stirrer, addition funnel, and drying tube. Freshly prepared (+)-**2** (0.56 g, 3.1 mmol) was added, and the stirred mixture was cooled to 5°. Dropwise addition of 5 ml of propionic acid over a period of several hours, followed by 48 hr of stirring at 5° and filtration, yielded a colorless solution which was washed with 20 ml of 10% sodium hydroxide solution. The aqueous layer was thrice extracted with chloroform, and the combined organic portions were dried (sodium sulfate) and distilled (kugelrohr, 110°, 0.02 mm) to give a mobile pale yellow oil, $[\alpha]^{25}D$ +211° (*c* 1.97, ethanol), whose nmr spectrum showed no vinyl resonances and which was identical with that of *n*-propyl *p*-tolyl sulfoxide prepared by procedure A.

(±)-Allyl *p*-Tolyl Sulfoxide ((±)-2) by Reaction of *p*-Toluenesulfenyl Chloride with Lithium Allyl Alcoholate. A solution (22.5 ml) of 1.6 *M* *n*-butyllithium in hexane was added at room temperature to a stirred solution of 2.61 g (0.045 mol) of allyl alcohol in 120 ml of anhydrous ether, blanketed under a nitrogen atmosphere. A gelatinous precipitate formed. A solution of *p*-toluenesulfenyl chloride[52] (4.77 g, 0.030 mol) in 40 ml of ether was added. The intense yellow-orange color of the sulfenyl chloride was discharged instantly upon addition. The reaction mixture was washed with 50-ml portions of saturated sodium chloride solution and dried (magnesium sulfate), and the solvent was removed at room temperature. The crude product was shown to be (±)-allyl *p*-tolyl sulfoxide by comparison of its ir and nmr spectra with those of (+)-**2**; after kugelrohr distillation the water-white oil was identical with (+)-**2** in all spectral properties.

(±)-Allyl-γ-*d*$_2$ *p*-Tolyl Sulfoxide. Allyl-α-*d*$_2$ alcohol was prepared by lithium aluminum deuteride reduction of acrylyl chloride[53] and purified by glpc (4 ft × 0.25 in. column, Carbowax 4000, 70°); ir and nmr spectra were in accord with those reported.[54] The reaction of the lithium salt of the alcohol with *p*-toluenesulfenyl chloride in ether–hexane was carried out as described above for the undeuterated counterpart. The nmr spectrum of the product displayed an aromatic AA′BB′ quartet (4 H) at τ 2.60, a broadened triplet (1 H) at τ 4.34 (CD$_2$=C*H*CH$_2$–), a doublet (*J* = *ca.* 7 Hz, 2 H) at τ 6.50 (CD$_2$=CHC*H*$_2$–), and a sharp singlet (3 H) at τ 7.62 (aromatic methyl). There was no measurable signal between τ 4.6 and τ 6.3. Unrearranged sulfenate or sulfoxide should display a three-proton signal in the vinyl region and no doublet. The nmr spectrum of the compound was not changed in any respect after kugelrohr distillation at 110–115° (0.05 mm), after heating 45 min in benzene at 75°, or after heating 10 min in chlorobenzene at 100°.

(±)-Allyl-γ-*d*$_2$ Trichloromethyl Sulfoxide. The lithium salt of allyl-α-*d*$_2$ alcohol was prepared as above and allowed to react with trichloromethanesulfenyl chloride. The product, after the usual work-up, displayed an unusually simple ir spectrum: practically no

(50) K. Mislow, M. M. Green, and M. Raban, *J. Amer. Chem. Soc.*, **87**, 2761 (1965).

(51) Elemental analyses were performed by Schwarzkopf Microanalytical Laboratories, Woodside, N. Y. Optical rotatory dispersions were measured on a Cary 60 recording spectropolarimeter. Unless otherwise indicated, nmr spectra were measured on a Varian A-60A spectrometer and refer to approximately 10% solutions in deuteriochloroform, with tetramethylsilane as internal standard. Signs of coupling constants are unknown, unless explicitly specified.

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

(53) R. D. Schuetz and F. W. Millard, *J. Org. Chem.*, **24**, 297 (1959).

(54) K. D. McMichael, *J. Amer. Chem. Soc.*, **89**, 2943 (1967).

absorption at *ca.* 3000 cm^{-1} and the only strong absorptions at 1110 and 800 cm^{-1}; the characteristic 1050-cm^{-1} S=O stretching frequency has apparently been shifted to shorter wavelengths. That the compound is the rearranged sulfoxide (title compound) and not unrearranged allyl-α-d_2 trichloromethanesulfenate is unequivocally proven by the 100-MHz nmr spectrum in deuteriochloroform, the details of which are given in the text. The relative signs of the coupling constants were assigned on the basis of decoupling experiments, and the absolute signs, as given in the text, were assigned on the basis of the finding,[55] applicable to J_{AB}, that geminal coupling in sp^3-hybridized systems are of the order of *ca.* −13 Hz.

(±)-Allyl-α-d_2 2,4-Dinitrobenzenesulfenate. The lithium salt of allyl-α-d_2 alcohol was prepared as above and allowed to react with 2,4-dinitrobenzenesulfenyl chloride. The reaction mixture was worked up by leaching the crude product, a brown oil, with boiling hexane and crystallizing the product from the concentrated hexane extracts. The material thus obtained had mp 81–85°, and, after recrystallization from petroleum ether (bp 60–70°), had mp 83–86° (lit.[21] mp 86–87° for undeuterated material). The nmr spectrum is discussed in the text and is consistent with the assigned structure.

Reaction of Lithium Crotyl Alcoholate with Trichloromethanesulfenyl Chloride. The lithium salt of crotyl alcohol was prepared by reaction of crotyl alcohol with *n*-butyllithium, as described for allyl alcohol, and the reaction of the salt with trichloromethanesulfenyl chloride in ether–hexane was carried out as described for the reaction of lithium allyl alcoholate with *p*-toluenesulfenyl chloride. A liquid mixture of products was obtained which we were unable to separate by chromatography or distillation. The nmr spectrum (CCl_4) is attributable to a mixture of α-methylallyl trichloromethyl sulfoxide (32 ± 1%), itself a mixture of diastereomers, and crotyl trichloromethanesulfenate (68 ± 1%); the weighted relative integration of the sulfenate methylene proton ($CH_3CH{=}CHCH_2$–) signal at τ 5.28 (d, J = *ca.* 5.5 Hz) *vs.* the sulfoxide methine proton ($CH_2{=}CHCH(CH_3)$–) signal at τ 6.09 (apparent quintet) is in agreement with the relative integration of the sulfoxide methyl proton ($CH_2{=}CHCH(CH_3)$–) signals at τ 8.43 (d, J = 7 Hz) and 8.57 (d, J = 7 Hz) *vs.* the sulfenate methyl proton ($CH_3CH{=}CH$–) signal at τ 8.22 (d, J = 5 Hz). The ir spectrum of the neat liquid shows a strong band at 1110 cm^{-1}, presumably S=O stretch, and one of equal intensity at *ca.* 930 cm^{-1}, presumably due to sulfenate, with a shoulder at 910 cm^{-1} (vinyl C–H out-of-plane bending).

Preparation, Reduction, and Oxidation of α-Methylallyl *p*-Tolyl Sulfoxide. Lithium crotyl alcoholate was allowed to react with *p*-toluenesulfenyl chloride as described for lithium allyl alcoholate in the preparation of (±)-**2**. After work-up, a sulfoxide (ir absorption at 1050 cm^{-1}) was obtained which decomposed on kugelrohr distillation at 115° (0.05 mm) but which, undistilled, after chromatography on silica gel (elution with ethyl acetate) and removal of solvent, displayed an nmr spectrum with an aromatic AA′BB′ quartet at τ 2.64 (4 H), a vinyl multiplet at τ 4.71 (3 H), a methine multiplet at τ 6.65 (1 H), a sharp aromatic methyl singlet at τ 7.65 (3 H), and a doublet at τ 8.74 (J = 7 Hz, 3 H), assigned to $CH_2{=}CHCH(CH_3)$–. These data are consistent with the identity of the product as a mixture of diastereomers of (±)-**α-methylallyl *p*-tolyl sulfoxide.** There was no signal at τ 8.34, where the allylic methyl protons ($CH_3CH{=}CH$–) of crotyl *p*-tolyl sulfoxide (**6**) appear (*vide infra*). Reduction with diimide was carried out as described for the reduction of (+)-**2**, except that the reaction was carried out at room temperature and recycling was necessary to complete the reduction. The nmr spectrum of the product was consistent with a mixture of diastereomers of (±)-**2-butyl *p*-tolyl sulfoxide** and was not significantly different (a) from a diastereomeric mixture of (±)-2-butyl *p*-tolyl sulfoxides prepared by sodium metaperiodate oxidation[56] of the sulfide obtained by reaction of 2-bromobutane with sodium *p*-thiocresolate; (b) from the diastereomeric mixture of (+)-2-butyl *p*-tolyl sulfoxides,[57] $[\alpha]^{26}D$ +192° (*c* 2.0, ethanol), prepared by reaction of 2-butylmagnesium bromide with (−)-**3**. (+)-**2-Butyl *p*-tolyl sulfoxide**[57] was purified by kugelrohr distillation at 95° (0.04 mm).

Anal. Calcd for $C_{11}H_{16}OS$: C, 67.30; H, 8.22; S, 16.34. Found: C, 67.25; H, 8.35; S, 16.17.

A solution of (−)-**3** (4.0 g, 15.5 mmol) in 70 ml of anhydrous ether was added at −70° to the Grignard reagent prepared from 1.81 g (20 mmol) of crotyl chloride and 0.48 g (20 mmol) of magnesium metal in 200 ml of ether. The solution was warmed to 20° and 25 ml of a saturated aqueous solution of ammonium chloride was added. The ether layer was separated, washed with 200 ml of water, dried over anhydrous magnesium sulfate and filtered, and the solvent was removed under reduced pressure to give a light yellow oil. Chromatography over Florisil (10% methanol in ethyl acetate eluent) gave a product which exhibited an nmr spectrum identical with that of authentic α-methylallyl *p*-tolyl sulfoxide (diastereomeric mixture as above).

A solution of sodium periodate (2.2 g) in 20 ml of water was added to a cooled solution of 0.97 g of (±)-α-methylallyl *p*-tolyl sulfoxide in 5 ml of pyridine and 15 ml of ethanol, and the mixture was stirred for 3 days at room temperature. The precipitated solids were filtered, the residue was washed with chloroform, and the combined filtrate and washings were washed with cold water. The organic layer was dried, solvent was removed under reduced pressure, and the viscous crude product, which crystallized on standing, was chromatographed on silica gel (elution with benzene). The ir spectrum of the eluate showed the characteristic sulfone absorptions at 1150 and 1300 cm^{-1}. The nmr spectrum (carbon tetrachloride) displayed an aromatic AA′BB′ quartet (4 H) centered at τ 2.57, a vinyl proton multiplet (3 H) at τ 3.9–5.2, a methine multiplet (1 H) at τ 6.4, an aromatic methyl singlet (3 H) at τ 7.62, and a doublet (3 H) at τ 8.66 (J = 7 Hz) assigned to the aliphatic methyl protons. The spectral data are consistent with the identity of the product as (±)-**α-methylallyl *p*-tolyl sulfone.** The compound was unchanged after glpc purification (2 ft 10% SE-30 on Chromosorb 60–80, 187°) and was free of crotyl *p*-tolyl sulfone (see below) both by glpc and by nmr analysis.

Preparation and Oxidation of (±)-Crotyl *p*-Tolyl Sulfoxide ((±)-6). Lithium α-methylallyl alcoholate was allowed to react with *p*-toluenesulfenyl chloride as described for lithium crotyl alcoholate above. After work-up, including chromatography on Florisil or silica gel (using ethyl acetate as eluent), the product, obtained in better than 90% yield, had an ir spectrum consistent with the structure of **6**: absorptions at 1050 (S=O stretch), 1665 (C=C stretch), and 970 (*trans* CH=CH). The nmr spectrum was also consistent with the structure of **6**, featuring an aromatic AA′BB′ quartet (4 H) centered at τ 2.67, a vinyl multiplet (2 H) centered at τ 4.60, a broadened methylene doublet (2 H) at τ 6.68 (J = 6.5 Hz) for the *trans* isomer and at τ 6.43 (J = *ca.* 5 Hz) for the *cis* isomer, an aromatic methyl singlet (3 H) at τ 7.62, and an allylic methyl signal at τ 8.34 (broadened doublet, J = 5.5 Hz) for the *trans* isomer and at τ 8.53 (doublet, J = 7 Hz) for the *cis* isomer. Reduction with diimide as described above for α-methylallyl *p*-tolyl sulfoxide yielded *n*-butyl *p*-tolyl sulfoxide, spectrally identical with (+)-*n*-butyl *p*-tolyl sulfoxide prepared by the Grignard reaction from (−)-**3**.[42]

Oxidation of (±)-**6** as described above for (±)-α-methylallyl *p*-tolyl sulfoxide afforded (±)-**crotyl *p*-tolyl sulfone**: ν_{max}^{neat} 1150 and 1300 cm^{-1} (sulfone stretch) and 970 cm^{-1} (*trans* –CH=CH–). The nmr spectrum featured an aromatic AA′BB′ quartet centered at τ 2.55 (4 H), a vinyl multiplet at τ 4.1–4.9 (2 H), a pair of overlapping doublets (total, 2 H) at τ 6.28 and 6.38, corresponding to the methylene protons in the *cis* and *trans* forms of the sulfone, an aromatic methyl singlet at τ 7.62 (3 H), and a pair of broadened doublets (total, 3 H) at τ 8.35 and τ 8.63, corresponding to the allylic methyl protons in the *cis* and *trans* forms of the sulfone.

Anal. Calcd for $C_{11}H_{14}O_2S$: C, 62.82; H, 6.71; S, 15.25. Found: C, 62.79; H, 7.03; S, 15.00.

Isomerization of α-Methylallyl *p*-Tolyl Sulfone. Crotyl *p*-tolyl and α-methylallyl *p*-tolyl sulfones were separable by glpc on a 4-ft column of 10% silicone gum rubber on Chromosorb at 200°; with a carrier gas flow of 75 cc/min, crotyl *p*-tolyl sulfone and α-methylallyl *p*-tolyl sulfone had retention times of 20.9 and 14.7 min, respectively. Both compounds could be collected without change, as shown by the nmr spectra before injection and after collection. However, upon standing *neat* for 9 days at room temperature α-methylallyl *p*-tolyl sulfone isomerized to a mixture containing (by glpc) 40% of α-methylallyl *p*-tolyl sulfone and 60% of crotyl *p*-tolyl sulfone. After 3 more days the respective percentages were 22 and 78%.[58]

(55) R. C. Cookson, T. A. Crabb, J. J. Frankel, and J. Hudek, *Tetrahedron Suppl.*, **7**, 355 (1966).

(56) N. J. Leonard and C. R. Johnson, *J. Org. Chem.*, **27**, 282 (1962).

(57) This product is a mixture of diastereomers which are epimeric at carbon and which have the *R* configuration at sulfur, by analogy with the product of the reaction of (−)-**3** with 2-octylmagnesium bromide.[42]

(58) The rearrangement of α-methylallyl *p*-tolyl sulfone (in the neat state) into the crotyl isomer, which is in contrast to the *constitutional* (though not stereochemical) stability of the corresponding sulfoxides, may explain the observation[24] that crotyl phenyl sulfide and α-methylallyl phenyl sulfide each gave the *same* mixture of 90% crotyl phenyl sulfone and 10% α-methylallyl phenyl sulfone on oxidation with hydrogen peroxide in acetic acid–acetic anhydride at 0–5°.

α-Methylallyl *p*-Toluenesulfenate (5). A suspension of 20 mmol of lithium α-methylallyl alcoholate was prepared under nitrogen in 40 ml of dimethyl ether (dried by passing the gas through anhydrous calcium sulfate) by addition of 24 mmol of methyllithium (stripped of diethyl ether) in 20 ml of dimethyl ether to a solution of 1.44 g (20 mmol) of α-methylallyl alcohol in 20 ml of dimethyl ether maintained at −60 to −70°. A solution of 3.17 g (20 mmol) of *p*-toluenesulfenyl chloride in 20 ml of dimethyl ether was added to the alkoxide over a period of 30 min. The temperature was maintained below −60° during the addition. At the end of the addition the orange color of the sulfenyl chloride had been completely discharged and a portion of the resulting solution was forced through a fritted glass disk into an nmr tube immersed in a Dry Ice–acetone bath. The nmr spectrum of the product was determined at −60°. No TMS was present in the sample and consequently τ values were determined relative to the *p*-methyl singlet, assumed to be located near τ 7.62, the value found for crotyl *p*-tolyl sulfoxide at ambient temperature in deuteriochloroform. The spectrum of the product displayed a singlet at τ 2.65 (4 H, aromatic protons), a complex multiplet (1 H) of at least eight lines at τ 3.70–4.35 (vinylic proton at C-2 of the allyl group), a quartet (2 H) centered at τ 4.58 (terminal methylene protons), an unsymmetrical quartet (1 H) at τ 4.85 (methine proton at C-1), a singlet (3 H) at τ 7.60 (*p*-tolyl methyl protons), and a multiplet (3 H) at τ 8.50–8.90 (CH_2=CHCH(CH_3)–), in addition to the dimethyl ether signal and trace absorption due to unreacted alcohol. The above sample, which had been maintained at −60° or below up to this time, was allowed to warm to room temperature and the dimethyl ether was allowed to evaporate. Carbon tetrachloride was added as solvent and the nmr spectrum was redetermined. The spectrum was identical with that of crotyl *p*-tolyl sulfoxide except for trace absorption from dimethyl ether and unreacted alcohol. No *cis*-crotyl *p*-tolyl sulfoxide could be detected.

(−)-Crotyl *p*-Tolyl Sulfoxide ((−)-6). A solution of 8.75 ml of 1.6 *M* methyllithium (14 mmol, Foote Chemical Co.) in ether was added dropwise to the two-phase system of 1.01 g (14 mmol) of α-methylallyl alcohol, $[\alpha]^{24}D$ +17.15° (neat),[59] in 50 ml of freshly distilled toluene at *ca.* −70°, under nitrogen. To the stirred mixture was added 2.22 g (14 mmol) of *p*-toluenesulfenyl chloride by way of an injection through a septum cap. A light yellow, homogeneous solution resulted. When the solution was allowed to warm to 0° (ice bath), a white precipitate formed and the solution became colorless. The solution was centrifuged and the clear supernate was separated and held at 0° for racemization studies. An aliquot was worked up to yield 13 mmol of **6** for the total sample, indicative of a nearly quantitative yield. The nmr spectrum was identical with that of authentic **6** prepared from (±)-2-α-methylallyl alcohol and *p*-toluenesulfenyl chloride except for trace absorption probably arising from 2-butyl *p*-toluenesulfenate and ethyl *p*-toluenesulfenate. Initial rotations under the conditions of measurement (*l* 0.1, *c* 4.3) were α_{500} −0.278, −0.280, and −0.272° at 49.3, 41.0, and 28.9°, respectively. The residual infinity rotation of +0.014° may be due to unrearranged (and unrearrangeable, under the present reaction conditions) (+)-2-butyl *p*-toluenesulfenate which results from reaction of the contaminant, (+)-2-butanol, and *p*-toluenesulfenyl chloride. The infrared spectrum (neat) had a strong absorption band at 970 cm^{-1} (*trans* -CH=CH-). Although the initially isolated **6** and even racemized **6** isolated from the kinetic runs appeared to be devoid of *cis* isomer, slow isomerization occurred at room temperature, as judged by nmr;[45] after *ca.* 20 days the composition of **6** had become constant at 77% *trans*, 23% *cis*.

(59) Prepared by resolution *via* the brucine salt of the half-ester as previously described,[60] except that lithium aluminum hydride reduction was employed to cleave the phthalate ester. The product was shown by glpc (2 ft 10% Carbowax 20M on Chromosorb W) to contain 2.1% ethanol and 5.1% 2-butanol. The absolute rotation reported[60] for α-methylallyl alcohol is $[\alpha]^{24}D$ 32.8° (neat) and, were the sample uncontaminated, this would lead to a calculated optical purity of 52.3%. Since ethanol is inactive, since the absolute rotation of 2-butanol ($[\alpha]^{27}D$ 13.5° (neat)[61]) is less than that of α-methylallyl alcohol, and since configurationally related α-methylallyl alcohol and 2-butanol have the same sign of rotation,[35] it follows that the calculated value of the optical purity is a *minimum* value, the maximum value being 52.3/0.928 = 56.3%.

(60) J. Kenyon and D. R. Snellgrove, *J. Chem. Soc.*, 1174 (1925).

(61) R. H. Pickard and J. Kenyon, *ibid.*, 45 (1911).