Thermal Racemization of Benzyl *p*-Tolyl Sulfoxide and Thermal Rearrangement of Benzyl *p*-Toluenesulfenate[1,2]

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Abstract: Benzyl *p*-tolyl sulfoxide (**1**) was found to racemize some 1000 times faster on heating than comparable diaryl, alkyl aryl, or dialkyl sulfoxides. The mechanism for racemization involves homolysis of the benzylic carbon–sulfur bond. Competition by a pyramidal inversion mechanism has been rigorously excluded. The radical pair formed in the first step of the bond cleavage is not involved in the thermal rearrangement of benzyl *p*-toluenesulfenate (**2**) to benzyl *p*-tolyl sulfoxide, a reaction which appears to proceed by an intramolecular, concerted mechanism.

In the preceding paper,[4] it was shown that diverse diaryl, alkyl aryl, and dialkyl sulfoxides racemize by a pyramidal inversion mechanism. As part of this study we investigated the racemization of benzyl *p*-tolyl sulfoxide (**1**), a compound devoid of β-hydrogen atoms and thus incapable of decomposition by a five-center pyrolytic *cis*-elimination mechanism.[5] Henbest and Khan had previously reported[6] that **1** racemizes "at convenient first-order rates at 162° in various solvents, *e.g.*, decalin, mesitylene, and diglyme" and that the compound is "more thermolabile" (*i.e.*, stereomutates more readily) than the stereoisomeric 4-*t*-butylthiane 1-oxides, which undergo *cis–trans* interconversion at 190°. No explanation of this observation was given other than the comment that in **1** "conjugation between the tolyl and sulfoxide groups is possible," in contrast to the thiane 1-oxides. However, since the racemization of sulfoxides by the pyramidal inversion mechanism requires temperatures in the range of 180–250°, regardless of whether aromatic or aliphatic groups are attached to the sulfur atom,[4] the above interpretation of the enhanced racemization rate of **1** is untenable. The present work was initiated with the aim of elucidating the mechanistic origins of this effect.

Mechanism of Thermal Racemization of Benzyl *p*-Tolyl Sulfoxide. In preliminary experiments, **1** was thermally racemized in *p*-xylene at 135–165°, confirming the report of Henbest and Khan[6] that **1** is abnormally "thermolabile." However, examination by vpc of the product of racemization revealed that the loss of optical activity was accompanied by considerable decomposition, the rate of racemization being four to five times the rate of pyrolysis, and that the variety of decomposition products and the extent of pyrolysis could be reduced by employing benzene as a solvent. It was found that after 4.5 hr in *p*-xylene at 165°, **1** racemizes to the extent of *ca.* 100% and concurrently decomposes to the extent of *ca.* 62%, with the generation of at least four pyrolysis products, whereas in benzene at 165°, only *ca.* 39% decomposition occurs over a period of 4.5 hr and fewer pyrolysis products are generated.

Rates of racemization were measured at three temperatures (duplicate runs) and the results are collected in Table I. The entropy of activation, so much more positive than that of any comparable sulfoxide,[4] accounts for the 10^3–10^4-fold enhancement in the rate of racemization of **1** relative to phenyl *p*-tolyl sulfoxide ($k_{benzyl}/k_{phenyl} = 2.8 \times 10^3$ at 210°)[7] and methyl *p*-tolyl sulfoxide ($k_{benzyl}/k_{methyl} = 4.1 \times 10^4$ at 210°).[7] This large rate enhancement is not compatible with a pyramidal inversion mechanism on any steric or electronic grounds,[4] and points to the operation of a different mechanism.

Table I. Rate Constants and Activation Parameters for the Racemization of Benzyl *p*-Tolyl Sulfoxide (**1**)[a]

T, °C	$k \times 10^5$,[c] sec^{-1}	Period of observn[d]	Activation parameters
135	2.09 ± 0.04	1	$\Delta H^{\ddagger}$, 43.0 kcal/mol
135	2.07 ± 0.02	1	$\Delta S^{\ddagger}$, 24.6 eu
145	7.18 ± 0.05	2	E_a, 43.8 kcal/mol
145	6.99 ± 0.08	2	Log A,[e] 18.8
155	24.4 ± 0.5	2	
155	27.5 ± 0.2	2	
145	2.84 ± 0.04[b]	1	

[a] Solvent benzene unless otherwise specified. [b] Solvent pyridine. [c] First-order rate constants, tabulated with probable errors and corrected for decomposition. [d] Half-lives. [e] A has the unit sec^{-1}.

Four of the decomposition products formed during the course of the racemization were collected and identified (vpc retention times, ir, nmr) as bibenzyl (minor product), *p*-tolyl *p*-toluenethiolsulfonate, benzyl *p*-tolyl sulfide, and benzaldehyde (major products). The first two products clearly arise from radical coupling of benzyl and *p*-toluenesulfinyl radicals, respectively,[8]

(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) U. S. Public Health Service Postdoctoral Fellow, 1965–1966; (b) Procter and Gamble Fellow, 1965–1966; U. S. Public Health Service Predoctoral Fellow, 1966–1967; (c) National Science Foundation Trainee, 1966–1967; National Aeronautics and Space Administration Fellow, 1967–1968.

(4) D. R. Rayner, A. J. Gordon, and K. Mislow, *J. Amer. Chem. Soc.*, **90**, 4854 (1968).

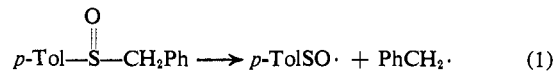
(5) C. A. Kingsbury and D. J. Cram, *ibid.*, **82**, 1810, (1960).

(6) H. B. Henbest and S. A. Khan, *Proc. Chem. Soc.*, 56 (1965).

(7) By extrapolation from the Arrhenius equation, using the parameters in Table I, k of 1 equals 0.089 sec^{-1} at 210°.

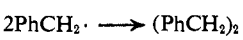
(8) It is well established [D. Barnard, *J. Chem. Soc.*, 4673 (1957); D. Barnard and E. J. Percy, *Chem. Ind.*, (London), 1332 (1960); R. M.

demonstrating homolytic cleavage of the benzylic carbon–sulfur bond in **1** (eq 1).



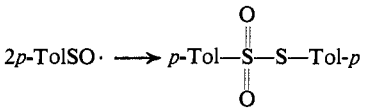
$$p\text{-Tol}\overset{\overset{O}{\|}}{\underset{}{S}}\text{—}CH_2Ph \longrightarrow p\text{-TolSO}\cdot + PhCH_2\cdot \qquad (1)$$

followed by



$$2PhCH_2\cdot \longrightarrow (PhCH_2)_2$$

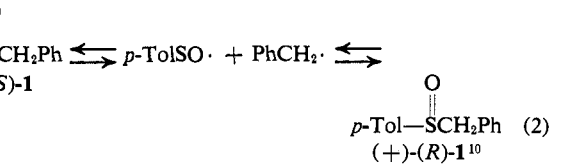
and



$$2p\text{-TolSO}\cdot \longrightarrow p\text{-Tol}\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}\text{—}S\text{—Tol-}p$$

Before commenting on the mechanism of formation of the other two decomposition products, we draw attention once more to the large positive value of the entropy of activation for racemization and the correspondingly large value for the preexponential Arrhenius factor, $A = 10^{18.8}$ sec^{-1}. This value, completely outside the range (10^{12}–10^{14} sec^{-1}) observed[4] for the A factors in processes involving pyramidal inversion of sulfoxides, suggests that the primary step (eq 1) is intimately associated with the racemization process, since "the splitting of single bonds into two large radicals always seems to be accompanied by "abnormally" large A factors, *e.g.*, 10^{15}–10^{18} sec^{-1}",[9] presumably because of an increase in degrees of freedom of rotation accompanying bond stretching and fragmentation.

These considerations suggest that the racemization of **1** may simply involve homolytic scission and cage recombination *via* an achiral radical pair (eq 2).



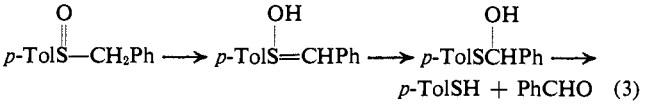
$$p\text{-Tol}\overset{\overset{O}{\|}}{\underset{}{S}}CH_2Ph \rightleftharpoons p\text{-TolSO}\cdot + PhCH_2\cdot \rightleftharpoons p\text{-Tol}\overset{\overset{O}{\|}}{\underset{}{S}}CH_2Ph \qquad (2)$$

(−)-(*S*)-**1** (+)-(*R*)-**1**[10]

Granted this supposition, the energy of activation for racemization (44 kcal/mol) may be equated with the upper limit of the dissociation energy of the benzylic carbon–sulfur bond in **1**, $D(p\text{-TolS(O)–CH}_2\text{Ph})$. This value, which is low even compared with the carbon–sulfur bond dissociation energies[11] of benzylthiol (53 ± 2 kcal/mol), benzyl methyl sulfide (51.5 ± 2 kcal/mol), and benzyl methyl sulfone (49.5 ± 2.5 kcal/mol), may be attributed to the stability of the two radical fragments, the one because it is a benzyl radical,[12] and the other because it is an arenesulfinyl radical.[3,13] That the $ArCH_2$–S bond in sulfoxides of type **1** is notably weak had previously been suggested by the observation[14] that α-naphthylmethyl *p*-tolyl sulfoxide is exceedingly photolabile under conditions where α-naphthyl *p*-tolyl sulfoxide and 2-(α-naphthyl)ethyl *p*-tolyl sulfoxide are completely stable. Homolytic cleavage of a benzylic carbon–sulfur bond was also postulated by Kingsbury and Cram[5] for the high-temperature pyrolysis of *erythro*-1,2-diphenyl-1-propyl phenyl sulfoxide on the basis of a decrease in stereospecificity and a trend toward positive values of $\Delta S^{\pm}$.

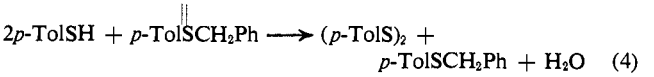
The radical pair intermediate, to the extent that it does not give rise to coupling (eq 1) or racemization (eq 2) products, may undergo further transformations, such as hydrogen abstraction from the solvent. This accounts for the observation that racemization in benzene gives fewer decomposition products than racemization in *p*-xylene: abstraction of a hydrogen atom from *p*-xylene, to give the stable *p*-methylbenzyl radical,[12] would be expected to require a lower activation energy than abstraction of a hydrogen atom from benzene, to give the less stable phenyl radical.[12]

To return to the question of the formation of the decomposition products benzaldehyde and benzyl *p*-tolyl sulfide, a "thermal Pummerer rearrangement," as proposed by Barnard-Smith and Ford for the pyrolytic cleavage of di-*n*-butyl sulfoxide,[15] would suffice to account for the former (eq 3). *p*-Toluenethiol could



$$p\text{-Tol}\overset{\overset{O}{\|}}{\underset{}{S}}\text{—}CH_2Ph \longrightarrow p\text{-TolS}\overset{\overset{OH}{|}}{=}CHPh \longrightarrow p\text{-TolS}\overset{\overset{OH}{|}}{C}HPh \longrightarrow p\text{-TolSH} + PhCHO \qquad (3)$$

then act to reduce **1** to benzyl *p*-tolyl sulfide[16] (eq 4), in an over-all sequence suggested to account for similar decomposition products in neopentyl *p*-tolyl and 1-adamantyl methyl sulfoxides.[17]



$$2p\text{-TolSH} + p\text{-Tol}\overset{\overset{O}{\|}}{\underset{}{S}}CH_2Ph \longrightarrow (p\text{-TolS})_2 + p\text{-TolSCH}_2Ph + H_2O \qquad (4)$$

The heart of the arguments presented above in support of the mechanism of racemization of **1** is that a special, low-energy pathway is available to this system (*i.e.*, homolytic carbon–sulfur bond cleavage) by virtue of the stability of the radical cleavage products, a stability which is to a large degree shared by the transition state of homolysis. By the same token, this pathway is inaccessible to those sulfoxides which do not yield stable radicals upon bond cleavage, and such sulfoxides must consequently overcome the higher energy barrier associated with pyramidal inversion in order to experience stereomutation.[4] In order to remove all doubts attaching to this thesis, it was necessary to adduce incontrovertible evidence ruling out the possibility of a pyramidal inversion mechanism for the racemization of **1**. The required evidence was provided by the following experiment.

(+)-Benzyl-α-*d* *p*-tolyl sulfoxide (**3**) was prepared

Topping and N. Kharasch, *J. Org. Chem.*, 27, 4353 (1962); S. Oae and K. Ikura, *Bull. Chem. Soc. Jap.*, 38, 58 (1965)] that arenesulfinyl radicals couple and rearrange to thiolsulfonates.

$$2ArSO\cdot \longrightarrow [ArS(O)OSAr] \longrightarrow ArSO_2SAr$$

(9) S. W. Benson and W. B. DeMore, *Ann. Rev. Phys. Chem.*, 16, 397 (1965). A recent example is the *meso–dl* isomerization of 2,3-dimethyl-2,3-diphenylsuccinonitrile, which proceeds by a homolytic dissociation–recombination mechanism (*via* 1-phenyl-1-cyanoethyl radical) and has a $\Delta S^{\pm}$ of 17 eu (L. I. Peterson, *J. Amer. Chem. Soc.*, 89, 2677 (1967)).

(10) C. J. M. Stirling, *J. Chem. Soc.*, 5741 (1963).

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

(12) T. L. Cottrell, "The Strengths of Chemical Bonds," 2nd ed, Butterworth and Co., Ltd., London, 1958, p 183 ff.

(13) J. L. Kice and N. E. Pawlowski, *J. Amer. Chem. Soc.*, 86, 4898 (1964).

(14) K. Mislow, M. Axelrod, D. R. Rayner, H. Gotthardt, L. M. Coyne, and G. S. Hammond, *ibid.*, 87, 4958 (1965).

(15) D. G. Barnard-Smith and J. F. Ford, *Chem. Commun.*, 120 (1965).

(16) C. N. Yiannios and J. V. Karabinos, *J. Org. Chem.*, 28, 3246 (1963); T. J. Wallace, *J. Amer. Chem. Soc.*, 86, 2018 (1964); T. J. Wallace and J. J. Mahon, *ibid.*, 86, 4099 (1964).

(17) Possibly in these sulfoxides homolytic processes also accompany the pyramidal inversion process, if only to a minor extent.

from (+)-(*S*)-benzyl-α-*d* alcohol,[18] $[\alpha]^{27}D$ +1.53° (neat), by the reaction sequence shown in eq 5.[19]

$$\text{PhCHDOH} \xrightarrow[2.\text{heat}]{1.\text{COCl}_2} \text{PhCHDCl} \xrightarrow[\text{DMF}]{p\text{-TolSNa}} p\text{-TolSCHDPh} \xrightarrow{\text{NaIO}_4} p\text{-TolS(O)CHDPh} \quad (5)$$

3

Oxidation of (*R*)-benzyl-α-*d* *p*-tolyl sulfide with sodium metaperiodate[20] afforded **3**, $[\alpha]^{27}D$ +1.97° (ethanol), which proved to be an equimolar mixture[21] of the two diastereomers, $(R_C,R_S)/(S_C,S_S)$-**3**[22] and $(R_C,S_S)/(S_C,R_S)$-**3**,[22] as shown by the observation that exchange of the α-deuterium for an α-hydrogen atom[23] yielded racemic **1**.[24] When **3** was heated at 145°, it was found that the rate of loss of optical activity was equal to that of optically active **1** and optically active benzyl-α-d_2 *p*-tolyl sulfoxide (**4**), taking into account a small secondary deuterium isotope effect. The salient data are collected in Table II. *This result rigorously excludes the possibility that* **1** *racemizes by the pyramidal inversion mechanism*, since such a process could not significantly affect the composition of the mixture of stereoisomers which constitutes **3**: this mixture is, in effect, a racemic modification with regard to the chiral sulfoxide center. The equality in the rates of racemization of **1** and **3** (after correction for the isotope effect) eliminates any significant competition by the pyramidal inversion mechanism and is in complete harmony with the mechanism of eq 2: the rate of loss of configuration at the methylene carbon adjacent to sulfur equals the rate of loss of configuration at sulfur, *i.e.*, racemization occurs through homolysis of the benzylic carbon–sulfur bond and *each act of homolysis leads to racemization at both chiral centers simultaneously* (eq 6).

$$\underset{(R_C,R_S)\text{-}\mathbf{3}}{p\text{-Tol}\overset{\overset{O}{\|}}{\text{S}}{}^{*}\text{—}{}^{*}\text{CHDPh}} \longrightarrow \underset{\text{achiral}}{p\text{-TolSO}\cdot} + \underset{\text{achiral}}{\text{PhCHD}\cdot} \longrightarrow \underset{\begin{array}{c}(R_C,R_S)\text{-}\mathbf{3}\\ +\,(R_C,S_S)\text{-}\mathbf{3}\\ +\,(S_C,R_S)\text{-}\mathbf{3}\\ +\,(S_C,S_S)\text{-}\mathbf{3}\end{array}}{p\text{-Tol}\overset{\overset{O}{\|}}{\text{S}}{}^{*}\text{—}{}^{*}\text{CHDPh}} \quad (6)$$

Table II. Comparison of Rate Constants for Racemization of *p*-TolS(O)CHDPh (**3**), *p*-TolS(O)CD_2Ph (**4**), and *p*-TolS(O)CH_2Ph (**1**)[a]

Run no.	Compd[b]	$k \times 10^5$, [c] sec^{-1}	k_H/k_D (per D atom)
1[d]	**1**	6.19 ± 0.20	1.04 ± 0.02
	4	5.69 ± 0.14	
2	**1**	7.15 ± 0.15	1.03 ± 0.12
	3	6.97 ± 0.86	
3	**1**	6.91 ± 0.19	1.07 ± 0.03
	4	6.02 ± 0.27	

[a] In solvent benzene at 145°. [b] Ampoules for both comparison compounds were simultaneously heated in the same bath (Experimental Section). [c] First-order rate constants, corrected for decomposition. [d] Temperature control was poor on the first run, but k_H/k_D should not be significantly affected.

The α-deuterium isotope effect of *ca.* 5% per D atom (Table II) is also in accord with the proposed homolytic scission mechanism. Secondary deuterium isotope effects of about 10% per D atom are in order for unimolecular bond scissions at 145°,[25] and values of k_H/k_D of 1.10–1.15, corrected to 145°, have been observed for homolytic bond dissociation reactions of azobis-α-phenylethane,[25] *t*-butyl phenylperacetate,[26] and *t*-butyl α-phenylperpropionate.[26]

The pyramidal inversion mechanism for the racemization of **1** is thus ruled out. An alternative mechanism is conceivable, in which intramolecular S → O migration of the benzyl group of **1** in the rate-determining step affords achiral benzyl *p*-toluenesulfenate (**2**), an intermediate which may then suffer a reverse intramolecular O → S shift of the benzyl group to give racemic **1**. However, this mechanism cannot account for the major part of the racemization of **1**, since it would require that configuration be lost at sulfur much faster than at the adjacent methylene carbon in **3**. This consideration, coupled with the large positive entropy of activation for racemization, indicates that at most only a minor portion of the reaction can proceed by this path. For the same reason the mechanism shown in eq 7 can be ruled out as an important pathway, for the equilibrium between **1** and the methylenecyclohexadienyl *p*-toluenesulfenate would not result in the loss of identity of the diastereotopic protons, so that, again, configuration would be lost at sulfur much faster than at the adjacent methylene carbon; furthermore, the large positive value of $\Delta S^{\ddagger}$ could not be reconciled with an intramolecular, concerted 1,2 shift.

While we cannot lay claim to having excluded all other conceivable alternatives to the proposed homo-

(18) V. E. Althouse, D. M. Feigl, W. A. Sanderson, and H. S. Mosher, *J. Amer. Chem. Soc.*, 88, 3595 (1966).

(19) (a) Since the reaction sequence from (*S*)-benzyl-α-*d* alcohol to the sulfide presumably involves only one inversion step (displacement of chloride by *p*-toluenethiolate), the absolute configuration of the produced benzyl-α-*d* *p*-tolyl sulfide is *R*. (b) This scheme is patterned after the procedure described by J. L. Kice, R. H. Engebrecht, and W. E. Pawlowski, *J. Amer. Chem. Soc.*, 87, 4131 (1965), for the preparation of optically active benzyl-α-*d* phenyl sulfide.

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

(21) This result provides evidence that a secondary deuterium isotope effect is of negligible importance in the oxidation of benzyl-α-*d* *p*-tolyl sulfide. In other words, while introduction of a second chiral center into a molecule containing one such center by reaction with an achiral reagent commonly produces perceptibly unequal amounts of the two diastereomers, the stereoselectivity in the present case is very close to *nil*.

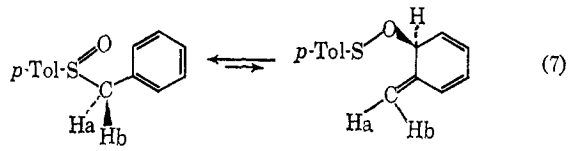
(22) Since the *R* enantiomer predominates in the starting sulfide,[19a] it follows that R_C,R_S and R_C,S_S enantiomers predominate in the respective diastereomers of **3**. The optical purities of the two diastereomers of **3** are the same and equal to the optical purity of the starting sulfide. The values of the optical purities are unknown but probably quite high, barring extensive racemization in the sequence of reactions (eq 5) leading to sulfide from presumably optically pure[18] benzyl-α-*d* alcohol.

(23) Under basic conditions (aqueous sodium hydroxide in DMSO). The completeness of exchange was monitored by nmr (A. Rauk, E. Buncel, R. Y. Moir, and S. Wolfe, *J. Amer. Chem. Soc.*, 87, 5498 (1965); S. Wolfe and A. Rauk, *Chem. Commun.*, 775 (1966)). The exchange of α-hydrogens under these conditions does not affect the configurational integrity of the neighboring chiral sulfoxide center (*cf.* D. J. Cram and S. H. Pine, *J. Amer. Chem. Soc.*, 85, 1096 (1963); Y. H. Khim, W. Tagaki, M. Kise, N. Furnkawa, and S. Oae, *Bull. Chem. Soc. Jap.*, 39, 2556 (1966); D. N. Jones and M. J. Green, *J. Chem. Soc., Sect. C*, 532 (1967)). This was independently demonstrated by exchanging optically active **1** with sodium deuterioxide in DMSO-d_6, and back-exchanging the resulting benzyl-α-d_2 *p*-tolyl sulfoxide (**4**) with sodium hydroxide in DMSO to regenerate **1**, whose optical rotation was the same as that of starting **1**.

(24) An optical purity of ≥0.1% of **1** would have been detectable.

(25) S. Seltzer, *J. Amer. Chem. Soc.*, 83, 2625 (1961), and references cited therein.

(26) T. W. Koenig and W. D. Brewer, *Tetrahedron Lett.*, 2773 (1965).



(7)

lytic scission–recombination as the *major* pathway for the racemization of **1**, this simple interpretation serves to account satisfactorily for all of our observations, and thus represents the most economic rationalization of the facts.[27]

A brief attempt to extend our study of the thermal racemization of **1** to another optically active benzylic sulfoxide, benzyl methyl sulfoxide (**5**), was only partly successful. Under conditions employed in thermal racemization of **1**, *i.e.*, heating in benzene at 135°, **5** racemized at a rate conveniently followed by polarimetry, suffering relatively little decomposition.[28] The low temperature required for the racemization of **5** excludes a pyramidal inversion mechanism[4] and again suggests the operation of a homolytic scission–recombination mechanism; if this be the case, the methanesulfinyl radical must have a stability comparable to that of the *p*-toluenesulfinyl radical, indicating that the primary stability of the arenesulfinyl radical is not associated with electron delocalization into the aromatic ring but is almost entirely due to delocalization of the odd electron over sulfur and oxygen. However, further investigation was handicapped by difficulties experienced with the interpretation of the kinetics of racemization: in marked contrast to the related sulfoxide **1**, the racemization of **5** exhibited an inhibition period of about 3 hr and the rate of racemization was not of any simple order. Only two decomposition products were discerned by vpc analysis, one of which was identified as benzaldehyde. The formation of this compound in the pyrolysis of benzyl methyl sulfoxide has been previously reported and discussed.[29]

Mechanism of Thermal Rearrangement of Benzyl *p*-Toluenesulfenate to Benzyl *p*-Tolyl Sulfoxide. In the previous section we noted the possibility that benzyl *p*-toluenesulfenate (**2**) might to a minor extent function as an intermediate in the racemization of **1**. To test whether **2**, once formed, would revert to **1**, **2** was prepared (by reaction of *p*-toluenesulfenyl chloride either with lithium benzyl alcoholate in glyme or with benzyl alcohol in carbon tetrachloride in the presence of pyridine) and heated in benzene at 140° for 2 hr. This treatment afforded **1** in 83% yield, demonstrating that the thermal O → S rearrangement of **2** to **1** occurs under conditions comparable to those employed in the thermal racemization of **1**. The material balance from this rearrangement reaction consisted of unchanged **2** and decomposition products (see below). Further work revealed that the rearrangement of **2** to **1** is much more facile than the thermal racemization of **1**. Thus, while **1** is optically stable at temperatures below 100°, it was noted that samples of **2** which had been allowed to stand at room temperature or even at 0° for several weeks had deposited crystals of **1**. The rate of rearrangement in benzene was conveniently measured by nmr, either by following the rate of decrease of the methylene nmr signal of **2** (singlet at τ 5.38 in benzene) or the rate of increase of the methylene signal of **1** (singlet at τ 6.35 in benzene[30]). Measurements were taken over the initial period of rearrangement (0.5–1.0 half-lives); after *ca.* 10 half-lives less than 5% of **2** remains[33] and the reverse rearrangement (**1** → **2**) is therefore negligible during the period of measurement. Values determined by following the rate of decrease of **2** (method A) gave more satisfactory first-order rate plots than those determined by following the rate of increase of **1** (method B). First-order rate constants calculated by the two methods were in rough agreement (Table III); the discrepancy may be due to some decomposition of **1** which accompanied the rearrangement.[34] From the more reliable rate constants obtained by method A, the following activation parameters were calculated: E_a = 30.5 kcal/mol, log A 12.9, $\Delta H^{\pm}$ = 29.7 kcal/mol, $\Delta S^{\pm}$ = −2 eu.

Table III. First-Order Rate Constants[a] for the Rearrangement of Benzyl *p*-Toluenesulfenate (**2**) to Benzyl *p*-Tolyl Sulfoxide (**1**)

T, °C	$k \times 10^5$, sec^{-1} Method A[b,c]	$k \times 10^5$, sec^{-1} Method B[d]
110	3.28 ± 0.14	7.7
120	8.75 ± 0.47	10.7
130	24.0 ± 1.2	20.4

[a] In benzene. [b] Rate of decrease of the methylene nmr signal of **2**. [c] Rate constants are listed with probable errors. [d] Rate of increase of the methylene signal of **1**.

The reversibility of the process **1** ⇄ **2** thus having been established, we now turn to a discussion of the mechanism of the rearrangement. Among the alternatives considered, dissociation of **2** into a radical pair, followed by recombination to give either **1** or **2**, would seem to be a likely possibility and one which would appear to be supported by the observation that a strong esr signal is developed by **2** in naphthalene at 160° which in time decays to a steady-state signal,[35]

(27) Although no systematic solvent study was attempted, the observation (Table I) that the rates of racemization of **1** in two solvents of widely differing polarities, benzene and pyridine, are of the same order of magnitude ($k_{C_6H_6}/k_{C_5H_5N}$ = 2.50 at 145°) argues against a heterolytic mechanism.

(28) After 6 hr, the time required for the rotation to drop to one-half of its original value, the sulfoxide was found to have decomposed to the extent of 1% in one run, and to the extent of 7% in a repeat run.

(29) W. Carruthers, I. D. Entwhistle, R. A. W. Johnstone, and B. J. Millard, *Chem. Ind.* (London), 342 (1966). By analogy with the suggestion of these authors that the decomposition products, a thiol and benzaldehyde, arise through the intermediacy of benzyl methanesulfenate, the decomposition of **1** to give benzaldehyde and, in conjunction with the subsequent reduction of **1** (eq 4), benzyl *p*-tolyl sulfide, might be thought to proceed through the intermediacy of **2**. However, this seems unlikely since so little of the racemization reaction could proceed through this intermediate.

(30) The diastereotopic[31] methylene protons in **1** are expected to exhibit chemical shift nonequivalence. However, in benzene (τ 6.35) and carbon tetrachloride (τ 6.15) accidental degeneracy is observed and the AB system appears as a singlet at 60 MHz, with $\Delta\nu_{1/2}$ 1–2 Hz. On the other hand, the expected AB quartet is displayed in the nmr spectra of **1** (60 MHz) in deuteriochloroform (τ 5.93 and 6.07, J = 12 Hz) and DMSO-d_6 (τ 5.78 and 5.94, J = 12 Hz). The solvent dependence of the separation of signals in similar cases has been noted earlier.[32]

(31) K. Mislow and M. Raban in "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.

(32) K. Mislow, M. A. W. Glass, H. B. Hopps, E. Simon, and G. H. Wahl, Jr., *J. Amer. Chem. Soc.*, **86**, 1710 (1964); G. M. Whitesides, D. Holtz, and J. D. Roberts, *ibid.*, **86**, 2638 (1964); G. M. Whitesides, J. J. Grocki, D. Holtz, H. Steinbey, and J. D. Roberts, *ibid.*, 87, 1058 (1965).

(33) The equilibrium mixture of **1** and **2** can be approached from either side. For K_{eq} (1/2) of *ca.* 100, $\Delta G°$ at 130° is *ca.* 4 kcal/mol, the minimum thermodynamic driving force of the rearrangement.

(34) Rearrangement of **2** is much faster than decomposition.

and also by the generation of the same decomposition products (*p*-tolyl *p*-toluenethiolsulfonate, benzyl *p*-tolyl sulfide, and benzaldehyde) which are formed in the racemization of **1**. However, dissociation of **2** into a radical pair as the rate-determining step of the rearrangement is difficult to reconcile with the slightly negative entropy of activation, which is in marked contrast to the highly positive entropy of activation accompanying the dissociation of **1** into the same radicals. The entropy term would appear to militate against the intermediacy of a common radical pair for the racemization of **1** and the rearrangement of **2** and instead suggests an intramolecular rearrangement. This possibility was investigated by a study of the rearrangement of (−)-(*R*)-benzyl-α-*d* *p*-toluenesulfenate (**6**):[36] if the primary step of the rearrangement involves homolytic cleavage into a radical pair, the mixture of diastereomeric benzyl-α-*d* *p*-tolyl sulfoxides should be completely racemic, whereas if conversion of **2** to **1** proceeds by an intramolecular pathway, configuration should be retained at the chiral α-carbon center.

Rearrangement of samples of (*R*)-**6** by heating for 2.00 hr at 140° in benzene solution in sealed, degassed tubes gave samples of (+)-benzyl-α-*d* *p*-tolyl sulfoxide (**3**).[39] Removal of the α-deuterium atom by exchange with DMSO and aqueous NaOH[23] gave samples of benzyl *p*-tolyl sulfoxide which were less than 0.03% optically pure, as determined by examination of their ORD spectra in the region 600–360 mμ (*c* 1, ethanol, *l* 1). Since it had been shown (see previous section) that an equimolar mixture of diastereomers of **3** containing a preponderance of enantiomers derived from (*R*)-benzyl-α-*d* *p*-tolyl sulfide is dextrorotatory, and since an equimolar mixture is demonstrated in the present case by the exchange experiment, it follows that the dextrorotatory rearrangement product (**3**) contains a preponderance of diastereomers R_C, R_S and R_C,S_S over their enantiomers. *Consequently, the rearrangement proceeds with predominant retention of configuration at carbon, and with no detectable asymmetric induction at sulfur.*

In order to determine the extent of retention of configuration at carbon, the relay compound, (−)-**3**, was prepared as before (eq 5),[19,20] starting with an aliquot of the same sample of (−)-(*R*)-benzyl-α-*d* alcohol which had been used in the preparation of (−)-(*R*)-**6**. Removal of the α-deuterium atom by basic exchange[23] showed less than 0.05% preponderance of one enantiomer of **1** over the other, indicating again that the product was an equimolar mixture of diastereomers. The magnitudes of rotation of sulfoxide samples obtained by rearrangement, (+)-**3**, were directly compared to the magnitude of rotation of the relay sample, (−)-**3**, thus giving a measure of the extent of retention of configuration in the rearrangement. The results are given in Table IV.

Table IV. Ratios of Rotations[a] of Rearrangement Products to Relay Compounds in the Rearrangement of (−)-(*R*)-Benzyl-α-*d* *p*-Toluenesulfenate (**6**) to (+)-Benzyl-α-*d* *p*-Tolyl Sulfoxide (**3**)

	Run no.				
	1	2	3	4	Average
$[\alpha]_\lambda$ of **3** rearr	0.33	0.21	0.25	0.31	0.28
$[\alpha]_\lambda$ of **3** relay	±0.02	±0.04	±0.03	±0.03	±0.06
$[\alpha]_\lambda$ of **7** rearr	0.43	0.24	0.30	0.25	0.30
$[\alpha]_\lambda$ of **7** relay	±0.05	±0.07	±0.09	±0.02	±0.09

[a] Solvent was ethanol in all cases. All ratios of $[\alpha]_\lambda$ were determined at 20-mμ intervals from 600 to 360 mμ and averaged.

As an independent check, each sulfoxide sample obtained by rearrangement was also oxidized to benzyl-α-*d* *p*-tolyl sulfone (**7**) with potassium permanganate[40] and the magnitude of the rotation of the resulting sample[41] was directly compared to that of the corresponding relay compound, (+)-(*S*)-**7**, obtained by permanganate oxidation of (+)-(*S*)-benzyl-α-*d* *p*-tolyl sulfide,[19] the precursor to (−)-**3**. The results are given in Table IV.

The extent of retention given by the figures in Table IV must however be corrected for the loss of optical activity in the product **3** which is due to racemization subsequent to rearrangement, for the rate of racemization of **3** is not negligible under the conditions of formation by rearrangement of **6**.[42] Treating the rearrangement of **6** and the subsequent racemization of **3** at carbon as consecutive irreversible first-order reactions,[43] it was calculated that the sulfoxide isolated after 2 hr at 140° had lost 20% of its optical purity through racemization after rearrangement. Correcting for this effect, the data in Table IV indicate that the rearrangement occurred with 35 ± 8% retention of configuration at carbon as determined by comparison of sulfoxides (**3**) and 37 ± 11% as determined by comparison of sulfones (**7**). Taken together, these data indicate 36 ± 9% retention of configuration at carbon.[44,45]

This degree of retention of configuration, taken together with the slightly negative entropy of activation, indicates that the major course of the rearrangement of **2** to **1** proceeds by a benzyl O → S shift of an intramolec-

(35) Since the signal was complex and not well resolved, we cannot comment on the structure of the radical or radicals giving rise to this signal. We thank Drs. E. Wasserman, M. Gueron, and J. Turkevich for helpful discussions in this connection.

(36) Prepared from (−)-(*R*)-benzyl-α-*d* alcohol,[18,37] $[\alpha]^{27}D$ −0.89° (neat), of 56% optical purity,[38] and *p*-toluenesulfenyl chloride.

(37) A. Streitwieser, Jr., J. R. Wolfe, Jr., and W. D. Schaeffer, *Tetrahedron Lett.*, 6, 338 (1959).

(38) After correction for one deuterium atom per molecule and based on $[\alpha]^{24}D$ +1.58° (neat) reported[18] for the absolute rotation of benzyl-α-*d* alcohol.

(39) The samples of sulfoxide obtained from the rearrangement reaction were purified by repeated chromatography on Florisil, retaining the total amount of sulfoxide in each step to avoid optical fractionation, until no impurities could be detected by nmr and until the ORD in the region 600–360 mμ remained unchanged. A sample of optically pure (+)-**1** was shown to be chemically and optically stable to chromatography on Florisil.

(40) Oxidation of benzyl-α-d_2 *p*-tolyl sulfoxide (**4**) to sulfone by permanganate occurred with 6% exchange of methylene deuterium atoms for hydrogen atoms.

(41) That the rotations of the samples of **7** obtained by oxidation of the product of rearrangement were not due to impurities was shown by exchange with sodium ethoxide in ethanol which gave samples of zero rotation in the range 600–360 mμ.

(42) The rate constants, $k_{rearr} = 6.3 \times 10^{-4}$ sec^{-1} and $k_{rac} = 4.0 \times 10^{-5}$ sec^{-1} at 140°, were calculated from the data in Tables I and III, neglecting isotope effects.

(43) W. J. Moore, "Physical Chemistry," 3rd ed, Prentice Hall, Inc., Englewood Cliffs, N. J., 1962, p 266.

(44) It must be pointed out that this value represents a maximum degree of retention of configuration since the degree of stereospecificity in the synthesis of the relay sulfoxide and sulfone is unknown. To correct for this effect the value here reported for degree of retention would have to be multiplied by a factor equal to the optical purity of the relay sulfoxide or sulfone divided by the optical purity of the starting benzyl-α-*d* alcohol.

(45) Assuming that the value of 36% retention is correct, the extent of asymmetric induction at sulfur in the rearrangement must be less than 0.16%.

ular type. The decomposition products formed in the course of the rearrangement most likely arise from decomposition of **1** *subsequent* to rearrangement,[34] and the esr signal either from leakage of the rearrangement by radical pathways, or from some (unknown) impurity.[35] The present O → S rearrangement is in some respects analogous to the benzyl N → O shift in the Meisenheimer rearrangement of dimethylbenzyl-α-*d*-amine oxide to O-benzyl-α-*d*-N,N-dimethylhydroxylamine[46-48] in which 23–38% retention of configuration is also observed,[46] and for which a transition state with radical character was proposed.[46,49] However, the more negative value of $\Delta S^{\pm}$ (−2 *vs.* +7.9 eu) and the lower value of $\Delta H^{\pm}$ (29.7 *vs.* 34.2 kcal/mol) found for the rearrangement of **2** to **1** argue for a transition state possessing less radical character and rather more concertedness.

It was demonstrated in the preceding section that **1** cannot racemize to an appreciable extent by way of an intramolecular reversible rearrangement to **2**. Consequently, assuming that no more than *ca.* 10% of the racemization proceeds by the rearrangement mechanism, the transition state for the latter must lie at least *ca.* 2 kcal/mol (at 140°) above the transition state invoked for the racemization, *i.e.*, the radical pair. Since $\Delta G_{rac}^{\pm}$ = 32.8 kcal/mol at 140°, $\Delta G_{rearr}^{\pm}$ of **1** → **2** ≥ *ca.* 35 kcal/mol at 140°. Since $\Delta G_{rearr}^{\pm}$ of **2** → **1** = 30.5 kcal/mol at 140°, it follows by the principle of microscopic reversibility that $\Delta G_{140°} \geq$ 4–5 kcal/mol, the thermodynamic driving force of the rearrangement.

When the radical stability of the migrating group is increased, the homolytic scission–recombination mechanism may become the pathway of lowest energy. This may possibly explain the ease of rearrangement of benzhydryl *p*-toluenesulfenate, which was found to have rearranged to the isomeric sulfoxide to the extent of 13% upon standing for 2 months at 5°; heating in refluxing benzene for a short period of time merely led to gross decomposition. All attempts to prepare triphenylmethyl *p*-toluenesulfenate by the reaction of sodium or lithium triphenylmethoxide with *p*-toluenesulfenyl chloride in dimethylformamide or glyme were unsuccessful, leading only to complex mixtures which exhibited no ir absorption bands in the sulfoxide region, near 1050 cm^{-1}. Evidently the product has available to it a low-energy pathway for decomposition into the extremely stable trityl and *p*-toluenesulfinyl radicals. This observation would also account for the repeated failures to prepare trityl aryl sulfoxides.[50]

In connection with the work dealing with the rearrangement of **2** to **1** and the racemization of **5**, we briefly investigated the rearrangement of benzyl methanesulfenate (**8**) to **5**. As previously reported,[2] **8** decomposes at *ca.* 150° to give benzaldehyde and methyl mercaptan. We also found that **8** suffers partial decomposition even on standing for several weeks at room temperature into a mixture of at least ten decomposition products. Among these, the following major components were identified by ir, nmr, and vpc: benzaldehyde, benzyl methyl sulfide, benzyl alcohol, benzyl methanesulfinate, and dibenzyl ether. In addition, **5** was found to be produced in the course of vpc analysis; absent in the decomposition mixture (by ir and nmr), its appearance under these conditions was dependent on the temperature of the injection block. The formation of these products from **8** contrasts with the behavior of **2** under the same conditions, and suggests extensive homolytic cleavage of the benzylic C–O bond of **8** to give benzyl and methanesulfinyl radicals, followed by attack of these radicals on unreacted **8** (eq 8)

$$CH_3SOCH_2C_6H_5 \longrightarrow CH_3SO\cdot + C_6H_5CH_2\cdot \qquad (8)$$

followed by

$$C_6H_5CH_2\cdot + CH_3SOCH_2C_6H_5 \longrightarrow C_6H_5CH_2SCH_3 + C_6H_5CH_2O\cdot$$

$$CH_3SO\cdot + C_6H_5CH_2O\cdot \longrightarrow CH_3S(O)OCH_2C_6H_5$$

$$C_6H_5CH_2O\cdot + R\cdot \longrightarrow C_6H_5CHO + RH$$

$$C_6H_5CH_2O\cdot + RH \longrightarrow C_6H_5CH_2OH + R\cdot$$

$$C_6H_5CH_2O\cdot + C_6H_5CH_2\cdot \longrightarrow (C_6H_5CH_2)_2O$$

Further work is required to clarify the nature of the difference in behavior exhibited by **2** and **8** upon pyrolysis.

Experimental Section[51]

Kinetic measurements and calculation of the activation parameters for the racemization of **1** were carried out by the general technique described in the preceding paper.[4] Kinetic measurements on the racemization of (+)-**3** and of **4** were carried out at 145° simultaneously with measurements on **1**. The rotations of **1** and **4** were determined at 589 mμ. ORD measurements at 11 wavelengths in the range 600–400 mμ were used to follow loss of optical activity in **3**. All rotations were corrected for decomposition as previously described.[4]

Preparation of Sulfoxides. **(+)-Benzyl *p*-tolyl sulfoxide (1)** was prepared according to the procedure of Stirling.[10] The compound had a mp of 164–165° and $[\alpha]^{25}D$ +244° (*c* 1.6, acetone); lit.[10] mp 169–170°, $[\alpha]D$ +252° (*c* 0.9, acetone). The nmr spectrum (CCl_4) showed signals at τ 7.63 (3 H, s), 6.15 (2 H, s), and 2.6–3.2 (9 H, m).

(−)-Benzyl methyl sulfoxide (5) was prepared as described before.[52]

(+)-Benzyl-α-*d* *p*-Tolyl Sulfoxide (3). (+)-(*S*)-Benzyl-α-*d* alcohol was prepared by the method of Mosher, *et al.*[18] The crude material, bp 83° (6 mm), was purified by preparative vpc (20 ft × 3/8 in. column, 30% SE-30 on Chromosorb W at 180–190°) and decolorized with activated charcoal. The resulting material, $\alpha^{27}D$ +0.149 ± 0.001° (*l* 0.1, neat), was 99+% pure by vpc, and contained 0.93 atom of deuterium per molecule as determined by nmr. Corrected to one deuterium atom per molecule, the sample had $[\alpha]^{27}D$ +1.53 ± 0.01° (lit.[18] $[\alpha]^{24}D$ +1.58 ± 0.01° (neat)). This material was converted to (+)-(*S*)-benzyl-α-*d* chloride as described by Kice, *et al.*,[19b] except that the product was purified by preparative vpc (20 ft × 3/8 in. column packed with SE-30 on Chromosorb W at 180°). This method of purification appears to lead to some loss of optical activity, to judge by the rotation of the product, $\alpha^{23}D$ +2.0 ± 0.1° (*l* 2, neat), which should have been $\alpha^{23}D$ +2.7° by extrapolation from the results of Kice, *et al.*[19b] The mate-

(46) U. Schöllkopf, M. Patsch, and H. Schäfer, *Tetrahedron Lett.*, 2515 (1964).

(47) The direction and driving force of these and related rearrangements will be discussed in the following paper.[48]

(48) P. Bickart, F. W. Carson, J. Jacobus, E. G. Miller, and K. Mislow, *J. Amer. Chem. Soc.*, **90**, 4869 (1968).

(49) G. P. Shulman, P. Ellgen, and M. Connor, *Can. J. Chem.*, **43**, 3459 (1965).

(50) D. C. Gregg, K. Hazelton, and T. F. McKeon, Jr., *J. Org. Chem.*, 18, 36 (1953); K. C. Schreiber and V. P. Fernandez, *ibid.*, **26**, 2478 (1961).

(51) Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y. Nmr measurements were taken on a Varian A-60A spectrometer with tetramethylsilane as internal standard; ORD measurements were obtained with a Cary 60 recording spectropolarimeter. Deuterium analyses were performed on AEI MS-9 mass spectrometer. We thank the National Science Foundation for providing the funds for the purchase of this instrument under Grant No. GP-5200.

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

rial was 98% pure by vpc. By a procedure exactly analogous to that described by Kice, *et al.*,[19b] in the preparation of (+)-benzyl-α-*d* phenyl sulfide from (−)-benzyl-α-*d* chloride, (−)-benzyl-α-*d* *p*-tolyl sulfide (mp 41.5–42.5°) was prepared from (+)-benzyl-α-*d* chloride. This material was oxidized with sodium metaperiodate[20] to (+)-benzyl-α-*d* *p*-tolyl sulfoxide (**3**) which, after two recrystallizations from ethanol, had mp 138–139°, exhibited the characteristic sulfoxide bands near 1050 cm^{-1} in the ir, and gave nmr signals ($CDCl_3$) at τ 2.27–3.12 (9 H, m), 5.92 and 6.03 (1.06 H, two poorly resolved triplets), and 7.63 (3 H, s). Deuterium analysis by nmr gave 0.94 ± 0.10 atom of deuterium per molecule. Mass spectral analysis gave 0.92 ± 0.01 atom of deuterium per molecule. The rotation was $[\alpha]^{27}D$ +1.97 ± 0.08° (*c* 1.32, ethanol).

(+)-Benzyl-α-d_2 *p*-Tolyl Sulfoxide (4). A mixture of 1.02 g of (+)-benzyl *p*-tolyl sulfoxide, $[\alpha]^{24}D$ +243 ± 2° (*c* 0.4, acetone), and 21 g of DMSO-d_6 (Merck Sharpe and Dohme, Ltd.) was warmed gently until solution was effected, and 30 drops of 0.76% NaOD in D_2O were then added. A yellow color immediately developed. The solution was stirred for 5 min and the reaction was quenched by addition of 500 ml of H_2O, which caused precipitation of the exchanged sulfoxide, 0.98 g of colorless needles, mp 164–165°, $[\alpha]^{24}D$ +238 ± 2° (*c* 0.4, acetone). No methylene protons were detectable by nmr. An aliquot of this material, 0.30 g, was exchanged back to benzyl *p*-tolyl sulfoxide; the product (0.27 g, mp 164–165°, nmr spectrum identical with authentic material) possessed the same specific rotation, $[\alpha]^{24}D$ +243 ± 2° (*c* 0.4, acetone), as the starting material.

(−)-Benzyl-α-*d* *p*-Tolyl Sulfoxide (3). (−)-(*R*)-Benzyl-α-*d* alcohol was prepared by the method of Streitwieser, *et al.*,[37] with the modification that the benzaldehyde-α-*d* utilized was prepared according to Wiberg's procedure.[53] The alcohol thus obtained had $\alpha^{27}D$ −0.090 ± 0.001° (*l* 0.1, neat), and a deuterium content of 0.964 atom of D per molecule.[54] Corrected for deuterium content, the product has $[\alpha]^{27}D$ −0.89 ± 0.01° (neat) (lit.[18] $[\alpha]^{24}D$ +1.58° (neat)), corresponding to an optical purity of 56.3 ± 0.6%. Conversion of this alcohol to **(−)-(*R*)-benzyl-α-*d* chloride**, $[\alpha]^{22}D$ −0.70 ± 0.04° (neat), according to the procedure previously described,[19b] was followed by conversion to **(+)-(*S*)-benzyl-α-*d* *p*-tolyl sulfide**, mp 43–44°, $[\alpha]^{27}D$ +0.92 ± 0.09° (*c* 1.2, ethanol), nmr signals ($CDCl_3$) at τ 2.74–3.10 (9 H, m), 6.02 (1 H, t, J_{HD} = 1.8 Hz), and 7.78 (3 H, s), by reaction with potassium *p*-toluenethiolate in ethanol, in an adaptation of the procedure described[19b] for the preparation of (+)-benzyl-α-*d* phenyl sulfide. Oxidation with sodium metaperiodate[20] gave the desired sulfoxide in 88.4% yield after elution from Florisil with chloroform. The product had mp 138–139° and $[\alpha]^{27}D$ −1.22 ± 0.08° (*c* 1.3, ethanol).

Benzhydryl *p*-tolyl sulfoxide was prepared by the sodium metaperiodate oxidation[20] of benzhydryl *p*-tolyl sulfide,[55] mp 65–66° (lit.[55] mp 66–67°), using a modified procedure in order to avoid acid cleavage[50] of the sulfide. Pyridine was added to a slurry of 1.4 g (0.0048 mol) of the sulfide in 20 ml of ethanol until solution was complete. A solution of 1.1 g (0.0051 mol) of sodium metaperiodate in 20 ml of water was added and the mixture was stirred at room temperature overnight. The insoluble material was filtered and washed with chloroform; the washings were combined with the filtrate and the chloroform layer was washed with water and 1.25 *M* sulfuric acid, dried over $MgSO_4$, and concentrated to give 1.3 g of crude sulfoxide (mp 120–127°), contaminated with unchanged sulfide. Chromatography on silica gel gave 0.36 g of sulfide on elution with benzene and 0.85 g (57%) of sulfoxide on elution with 10% ethyl acetate in benzene. Recrystallization of the sulfoxide from benzene gave product with mp (N_2, sealed tube) 137–138° (lit.[55] mp 143–144°), ir absorption (Nujol mull) at 1050 cm^{-1}, and nmr peaks ($CDCl_3$) at τ 7.67 (3 H, s), 5.22 (1 H, s), 2.89 (4 H, s), and 2.70 (10 H, m).

Anal. Calcd for $C_{20}H_{18}OS$: C, 78.39; H, 5.92; S, 10.47. Found: C, 78.53; H, 5.99; S, 10.29.

Preparation of the Sulfenates. Benzyl *p*-toluenesulfenate (2) was prepared by the dropwise addition (1 hr) of a solution of 3.18 g (0.020 mol) of *p*-toluenesulfenyl chloride[56] in 50 ml of CCl_4 to a stirred solution containing 2.16 g (0.020 mol) of benzyl alcohol and 1.6 g (0.02 mol) of pyridine (dried over KOH) in 100 ml of CCl_4. The reactants were stirred an additional 5 min before being extracted with 500 ml of water. The organic layer was dried over $MgSO_4$, filtered, and evaporated. The lemon-yellow residue was distilled (kugelrohr). After a small forerun of benzyl alcohol, the sulfenate distilled as a light yellow liquid, bp 105° (0.07 mm), 2.7 g (59%). The ir spectrum (neat) showed the absence of a 1050-cm^{-1} absorption characteristic of sulfoxides but did show a broad band at 975–950 cm^{-1} which appears to be characteristic of sulfenates. The nmr (CCl_4) showed singlets at τ 7.74 (3 H) and 5.37 (2 H).

Anal. Calcd for $C_{14}H_{14}OS$: C, 73.00; H, 6.13; S, 13.92. Found: C, 72.97; H, 6.25; S, 14.18.

Alternatively, **2** could be prepared as follows. To a solution of 1.0 g (0.01 mol) of benzyl alcohol in 20 ml of cyclohexane under nitrogen was added 5 ml of 1.6 *M* *n*-butyllithium. After the addition of 30 ml of glyme, a solution of 0.79 g (0.005 mol) of *p*-toluenesulfenyl chloride[56] in 10 ml of glyme was added dropwise to the stirred solution of the lithium benzyl alcoholate. The reaction mixture was diluted with ether and washed with water. The ethereal layer was dried over $MgSO_4$ and evaporated under reduced pressure, giving 2.0 g of crude product which was distilled (kugelrohr) to give 0.58 g (50%) of **2**, bp 100–110° (0.05 mm). This sample was identical (ir and nmr) with that prepared as described above.

(−)-(*R*)-Benzyl-α-*d* *p*-toluenesulfenate (6) was prepared from (−)-(*R*)-benzyl-α-*d* alcohol (see above) and *p*-toluenesulfenyl chloride[56] as described for **2**. After kugelrohr distillation, bp *ca.* 100° (0.025 mm), the compound had $[\alpha]^{26}D$ −0.3 ± 0.1° (*c* 8.2, ethanol) and was *ca.* 90% pure by nmr. The nmr spectrum ($CDCl_3$) had signals at τ 2.60–3.04 (9 H, m), 5.40 (1 H, poorly resolved triplet), and 7.75 (3 H, s), and a singlet at τ 7.81 (impurity, amounting to 10% of the sum of the signals at τ 7.75 and 7.81, estimated on the basis of peak heights).

Benzhydryl *p*-Toluenesulfenate. Benzhydrol (2.76 g, 0.015 mol) was added to 40 ml of cyclohexane under nitrogen and under the rigorous exclusion of moisture. Sufficient ether (*ca.* 20 ml) was added to effect solution. Addition of 8.4 ml of 1.6 *M* *n*-butyllithium resulted in precipitation of the lithium salt of the alcohol. The solvent and excess alcohol were removed by filtration using positive N_2 pressure and the precipitate was washed with two 10-ml portions of benzene. After the addition of 75 ml of glyme (freshly distilled from $LiAlH_4$), the stirred suspension was treated dropwise with 2.07 g (0.013 mol) of *p*-toluenesulfenyl chloride in 25 ml of glyme. The color of the sulfenyl chloride was discharged rapidly; toward the end of the addition, a colorless, clear solution was obtained. The solution was drained into a flask and concentrated on a rotary evaporator (bath <35°). The residue was taken up in CH_2Cl_2 and filtered to remove lithium chloride. Removal of the solvent left 4.1 g of crude solid sulfenate. Infrared absorption (Nujol mull) showed a band at 975 cm^{-1} and no 1050-cm^{-1} absorption characteristic of sulfoxides. The nmr spectrum ($CDCl_3$) showed signals at τ 7.70 (3 H, s), 4.44 (1 H, s), and near 2.72 (14 H, m). Low-temperature recrystallization from ether yielded the analytical sample.

Anal. Calcd for $C_{20}H_{18}OS$: C, 78.39; H, 5.92; S, 10.47. Found: C, 78.56; H, 6.02; S, 10.62.

Benzyl Methanesulfenate (8). Methanesulfenyl chloride was prepared by passing 7.0 g (0.10 mol) of Cl_2 gas over the surface of 10.3 g (0.110 mol) of dimethyl disulfide at −15 ± 5°. The produced orange-red liquid was added at 0° to a solution of lithium benzyloxide, prepared by addition of 63 ml of *n*-butyllithium (Foote, 1.6 *M* in hexane) to a stirred solution of 10.8 g (0.10 mol) of benzyl alcohol in 100 ml of glyme (distilled from $LiAlH_4$) at 0°, until the color of the sulfenyl chloride persisted. After stirring an additional 10 min the reaction mixture was hydrolyzed by addition of 100 ml of a saturated solution of ammonium chloride. The organic layer was separated and the aqueous layer was extracted with 100 ml of ether. The combined organic layers were washed with water, dried over magnesium sulfate, and evaporated under reduced pressure. The light yellow residue was distilled (kugelrohr), bp 60–65° (0.05 mm). An ir spectrum (neat) showed the absence of sulfoxide bands at 1050 cm^{-1} and exhibited a strong band at 975 cm^{-1}, characteristic of a sulfenate (see above). The nmr spectrum ($CDCl_3$) showed three signals at τ 7.32 (3 H, s), 5.27 (2 H, s), and 2.65 (5 H, s).

Anal. Calcd for $C_8H_{10}OS$: C, 62.30; H, 6.54; S, 20.79. Found: C, 62.17; H, 6.76; S, 21.04.

Rearrangements of Sulfenates to Sulfoxides. Rearrangement of Benzyl *p*-Toluenesulfenate (2). A solution of 0.6182 g of **2** in 2 ml of benzene was heated in a sealed tube under N_2 for 2.0 hr at

(53) K. B. Wiberg, *J. Amer. Chem. Soc.*, 76, 5371 (1954).

(54) Deuterium combustion analysis, performed by J. Németh, Urbana, Ill. Analysis by electronic integration of nmr signals gave 1.01 ± 0.03 atoms of D per molecule.

(55) D. C. Gregg, F. Vartuli, and J. W. Wisner, Jr., *J. Amer. Chem. Soc.*, 77, 6660 (1955).

(56) F. Kurzer and J. R. Powell, "Organic Syntheses," Coll. Vol. IV, John Wiley and Sons, Inc., New York, N. Y., 1963, p 934.

140°. On cooling, white crystals deposited. The contents of this tube were washed into a flask with acetone. Evaporation under reduced pressure left a semicrystalline residue which was triturated with petroleum ether (bp 30–60°) and filtered. The crystals were thoroughly washed with petroleum ether and dried to give benzyl *p*-tolyl sulfoxide (**1**), 0.5137 g (83%), mp 136–138°, identical (ir spectrum, Nujol mull) with authentic racemic benzyl *p*-tolyl sulfoxide, mp 137–139°. The mixture melting point was undepressed. The filtrate and washings were evaporated, leaving a yellow oil, 0.0953 g, accounting for a total of 98.5% of the material balance. This oil, which partially solidified on standing, was shown to be a complex mixture by vpc. Four of the components were identified by their retention times as bibenzyl, benzyl *p*-tolyl sulfide, *p*-tolyl *p*-toluenethiolsulfonate, and a peak which corresponded to sulfoxide-sulfenate.

Rearrangement of Benzyl-α-*d* *p*-Toluenesulfenate (6). The rearrangement of **6** was carried out four times at 140° for 2.00 hr as described for the rearrangement of **2**. The total product (unrecrystallized) was repeatedly chromatographed on Florisil and eluted with chloroform until the nmr spectrum indicated no detectable impurities and the ORD was unchanged. Electronic integration of the nmr signals indicated 1.02 ± 0.05 atoms of deuterium per molecule. The samples obtained had $[\alpha]^{27}D$ +0.25° to +0.45° (*c* 1, ethanol). Rotations at 20-mμ intervals between 600 and 360 mμ were compared with the corresponding values of $[\alpha]_\lambda$ of the relay compound, (−)-**3**, $[\alpha]^{27}D$ −1.22 ± 0.08° (see above). The results are tabulated in Table IV. Oxidation of the samples with potassium permanganate in glacial acetic acid and water following the procedure described[19b] for the oxidation of benzyl-α-*d* ethyl sulfide gave, after recrystallization from ethanol, (−)-**benzyl-α-*d* *p*-tolyl sulfone** (**7**), mp 145–146°, $[\alpha]^{27}D$ −0.35 to −0.65° (*c* 0.5, ethanol), in 80–90% yields. The relay compound (+)-**7** was similarly prepared by permanganate oxidation of (+)-(*S*)-benzyl-α-*d* *p*-tolyl sulfide, $[\alpha]^{27}D$ +0.92 ± 0.09° (ethanol), described above, and had mp 145–146° (lit.[57] mp 144°), $[\alpha]^{27}D$ +1.7 ± 0.2° (*c* 0.52, ethanol), after recrystallization from ethanol, chromatography on Florisil, and recrystallization from benzene–petroleum ether (bp 30–60°). The nmr spectrum ($CDCl_3$) showed signals at τ 7.61 (3 H, s), 5.73 (1 H, poorly resolved triplet), and 2.40–3.04 (9 H, m), and the deuterium content was 0.97 ± 0.05 and 0.97 ± 0.01 atoms of deuterium per molecule by nmr and by mass spectral analysis, respectively. Comparison of the rotations of the oxidized samples with $[\alpha]_\lambda$ of the relay compound (**7**) at 20-mμ intervals between 600 and 360 mμ yielded the ratios tabulated in Table IV. To test whether the oxidation of **3** to **7** was complete under the above conditions, *i.e.*, to ascertain whether the rotation of **7** was not in part diminished due to the presence of unoxidized **3** as a contaminant, a sample of **1**, $[\alpha]^{24}D$ +243 ± 3° (*c* 0.42, acetone), was oxidized to sulfone with potassium permanganate as described above. After one recrystallization from ethanol (yield 78.5%), the nmr spectrum ($CDCl_3$) showed no discernible sulfoxide methylene proton absorption at τ 5.97–6.03, and the ORD spectrum showed $\alpha^{27}D$ 0.000 ± 0.001° over the range 600–350 mμ (*c* 0.55, ethanol, *l* 1). At this concentration, 0.04% of unoxidized (+)-sulfoxide would have been detectable. It follows that the oxidation is sufficiently complete to deny the presence of significant amounts of unoxidized **3**.

Rearrangement of Benzhydryl *p*-Toluenesulfenate. A sample of this ester was refluxed in benzene for 1 hr. Examination of recovered material showed that the ester had undergone gross decomposition. The infrared absorption at 975 cm^{-1} and the nmr signal of the benzhydryl methine proton of the sulfenate at τ 4.44 had disappeared but the presence of sulfoxide could not be ascertained among the many decomposition products. A sample of the sulfenate which had been stored for 2 months at 5° indicated that the sulfenate had undergone partial rearrangement (13%) to the sulfoxide since the ir spectrum (Nujol mull) showed an absorption band at 1050 cm^{-1} characteristic of sulfoxides. Trituration of the partially decomposed and rearranged sulfenate with ether, followed by filtration, left the insoluble sulfoxide which was identified by comparison of its ir spectrum with that of an authentic sample of benzhydryl *p*-tolyl sulfoxide.

Rearrangement of Benzyl Methanesulfenate (8). On standing for 2.5 weeks at room temperature, the analytical sample of this sulfenate was found to have undergone extensive decomposition, as shown by ir, nmr, and vpc analysis. The ir spectrum (neat) showed several new absorption bands, among them one at 1703 cm^{-1} (conjugated carbonyl) and a broad band at 3600–3200 cm^{-1}, indicative of the presence of an alcohol. The 975-cm^{-1} band of the sulfenate was still present, although of diminished intensity. The 1050-cm^{-1} band characteristic of a sulfoxide was absent. Similarly, the nmr spectrum showed several new signals which were not present in the pure sulfenate. Examination of this partially decomposed sulfenate sample by vpc analysis on a 2-ft 10% Carbowax 20M on 60–80 W Chromosorb column showed that it contained no fewer than ten compounds. Six of the major decomposition products were collected and identified, as shown in Table V. The presence of **5** demonstrates that this sulfenate can also rearrange to the corresponding sulfoxide under the proper conditions. The absence of a band near 1050 cm^{-1} in the ir spectrum and a methylene signal at τ 6.15 in the nmr spectrum of the partially decomposed sulfenate prior to vpc analysis indicate that **5** was formed on vpc analysis. Since the peaks on the chromatogram were sharp and well formed, **5** appears not to have been formed in the column, and we conclude that it probably formed in the injection block. In order to test this hypothesis, the temperature of the injection block was lowered from 235 to 200°. This procedure reduced the amount of **5** by nearly half, while the amount of benzyl alcohol increased. The amounts of the other components remained unchanged.

Table V

Compound	Method of identification[a]	Ratio (vpc)[d]
Benzaldehyde	Ir, rt[b]	0.7
Benzyl methyl sulfide	Ir, nmr, rt	1.0
Benzyl alcohol	Ir, rt	2.0
Benzyl methanesulfinate	Ir, nmr[c]	0.7
Dibenzyl ether	Rt	0.2
Benzyl methyl sulfoxide (**5**)	Nmr, rt	1.0

[a] These identifications were made by comparisons with authentic materials unless otherwise specified. [b] Rt = vpc retention time. [c] Without reference to an authentic sample. The ir spectrum (neat) showed strong absorption at 1130 cm^{-1}, characteristic of the S=O band of a sulfinate. Its nmr spectrum ($CDCl_3$) featured three signals at τ 7.34 (3 H, s) assigned to the methyl protons, 4.94 (2 H, s) assigned to the methylene protons, and 2.62 (5 H, s) assigned to the phenyl protons. [d] Without correction for differences in thermal conductivity.

(57) For the undeuterated compound, see H. J. Backer, J. Strating, and J. F. A. Hazenberg, *Rec. Trav. Chim.*, 72, 813 (1953).