The Thermal Decomposition of Thiolsulfonates. IV. The Stereochemistry of the Reaction[1]

John L. Kice, Ronald H. Engebrecht, and Norman E. Pawlowski

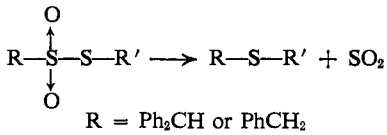
Contribution from the Department of Chemistry, Oregon State University, Corvallis, Oregon. *Received March 10, 1965*

The stereochemistry of the thermal decomposition of thiolsulfonates (eq. 2) has been investigated by synthesis of optically active phenyl α-toluenethiolsulfonate-α-d and study of the stereochemistry of its decomposition. In contrast to other internal substitution reactions, such as the decomposition of chlorocarbonates, the reaction seems to be remarkably nonstereospecific, the product, phenyl benzyl-α-d sulfide, being almost completely racemic. Other experiments have demonstrated that this is not due either to racemization of the thiolsulfonate prior to its decomposition or to racemization of the sulfide under the reaction conditions used for the decomposition. The mechanistic implications of this observed lack of stereospecificity are discussed.

There are a considerable number of internal substitution reactions whose over-all course may be formulated as shown in eq. 1. In these reactions the

$$RYZ \longrightarrow RZ + Y \qquad (1)$$

liberated fragment Y is usually some simple stable molecule, such as carbon dioxide, sulfur dioxide, nitrogen, etc. Naturally, there is a broad spectrum of mechanistic possibilities for the reactions lying in this general class. In recent years in this laboratory we have been particularly interested in one such internal substitution, the thermal decomposition of thiolsulfonates.[2] Diphenylmethanethiolsulfonates (Ph_2CHSO_2SR') and α-toluenethiolsulfonates ($PhCH_2SO_2SR'$) decompose on heating in inert solvents with predominant formation of the corresponding sulfide and quantitative evolution of sulfur dioxide (eq. 2).



$$R\text{—}\overset{\overset{O}{\uparrow}}{\underset{\underset{O}{\downarrow}}{S}}\text{—}S\text{—}R' \longrightarrow R\text{—}S\text{—}R' + SO_2 \qquad (2)$$

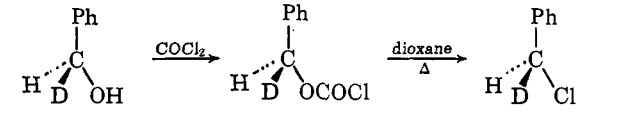
R = Ph_2CH or $PhCH_2$

Previous investigations[2] of the mechanism of this reaction have been concerned entirely with its kinetic aspects, such as the response of rate to variations in thiolsulfonate structure and solvent ionizing power. However, it is clear from studies of other internal substitutions, such as the decompositions of chlorocarbonates[3] and chlorosulfites,[4-7] that knowledge of reaction stereochemistry is often of as great, or greater, value in elucidating details of mechanism in systems of this type. Study of the stereochemistry of the thiolsulfonate decomposition has therefore, from the start, seemed an important objective whose realization was necessary before any definitive conclusions could be drawn concerning the mechanistic relationship of the thiolsulfonate decomposition to other internal substitutions. The present paper describes the attainment of this goal through the synthesis of a suitable optically active aralkanethiolsulfonate and the study of the stereochemistry of its decomposition.

Results

Synthesis of Optically Active Phenyl α-Toluenethiolsulfonate-α-d (I). The principal experimental problem in the present work was the synthesis of an optically active aralkanethiolsulfonate of known stereochemistry. A number of routes which, it was hoped, might lead to an optically active *para*-substituted diphenylmethanethiolsulfonate ($PhArCHSO_2SR'$) proved unpromising. However, the elegant studies of Streitwieser and his collaborators[8] have shown that one can also profitably employ an optically active primary center (RCHX)D to investigate reaction stereochemistry. In the present instance synthesis of an optically active α-toluenethiolsulfonate-α-*d* ($PhCHDSO_2SR'$), whose stereochemistry could be unequivocally related to that of the sulfide ($PhCHDSR'$) resulting from its decomposition, both appeared and has proved possible. Because previous work with the undeuterated analog had shown its decomposition to be quite clean-cut,[2c] the phenyl ester (R′ = Ph) was selected for synthesis and study.

Starting point for the synthesis was optically active D-(−)-benzyl-α-*d* chloride, prepared from the optically active alcohol[8a] by the reaction sequence shown below.



$[\alpha]^{25}D$ −0.694° $\alpha^{25}D$ −0.661° (*l* 1, neat)

The magnitude and sign of rotation of the chloride[8a] show that the reaction must proceed with a very high degree of retention, in agreement with the observations of Wiberg and Shryne[3a] on the stereochemistry of the decomposition of 1-phenylethyl chlorocarbonate.

The conversion of the chloride to the desired thiolsulfonate was carried out as shown in Chart I. The first step of the thiolsulfonate synthesis, an S_N2 displacement of chloride by sulfite, should proceed with

(1) This research supported by the National Science Foundation.

(2) (a) J. L. Kice, F. M. Parham, and R. M. Simmons, *J. Am. Chem. Soc.*, 82, 834 (1960); (b) J. L. Kice and F. M. Parham, *ibid.*, 82, 6168 (1960); (c) J. L. Kice and R. H. Engebrecht, *J. Org. Chem.*, 27, 4654 (1962).

(3) (a) K. B. Wiberg and T. M. Shryne, *J. Am. Chem. Soc.*, 77, 2774 (1955); (b) K. L. Olivier and W. G. Young, *ibid.*, 81, 5811 (1959).

(4) (a) E. S. Lewis and C. E. Boozer, *ibid.*, 74, 308 (1952); 75, 3182 (1953); (b) S. H. Sharman, F. F. Caserio, R. F. Nystrom, J. C. Leak, and W. G. Young, *ibid.*, 80, 5965 (1958).

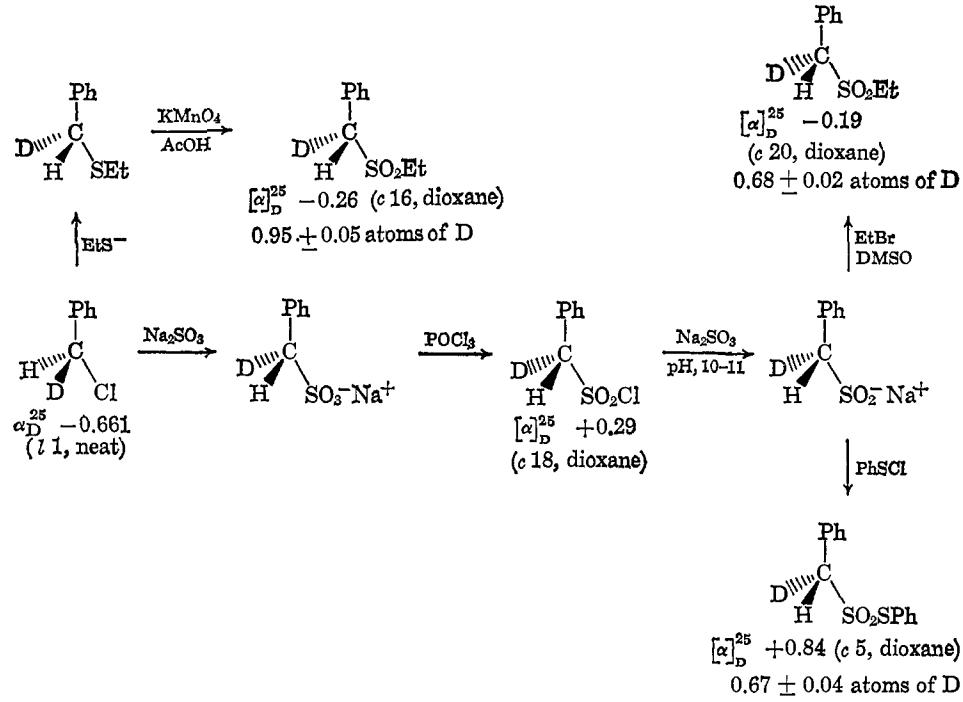
(5) D. J. Cram, *ibid.*, 75, 332 (1953).

(6) H. L. Goering, T. D. Nevitt, and E. F. Silversmith, *ibid.*, 77, 4042 (1955).

(7) W. G. Young, *et al.*, *ibid.*, 77, 4182 (1955).

(8) (a) A. Streitwieser, Jr., and J. R. Wolfe, *ibid.*, 79, 903 (1957); (b) A. Streitwieser, Jr., J. R. Wolfe, and W. D. Schaeffer, *Tetrahedron*, 6, 338 (1959); (c) A. Streitwieser, Jr., and W. D. Schaeffer, *J. Am. Chem. Soc.*, 79, 379 (1957); 78, 5597 (1956); (d) A. Streitwieser, Jr., *ibid.*, 77, 1117 (1955).

Chart I. Synthesis of Optically Active Thiolsulfonate



inversion of configuration. The next two steps, conversion of the sulfonate to the sulfonyl chloride and reduction of the latter to the α-toluenesulfinate, should not alter the configuration of the asymmetric center. The essential stereochemical integrity of these three steps was checked in the following manner. A portion of the α-toluenesulfinate-α-*d* was converted to ethyl benzyl-α-*d* sulfone by reaction with ethyl bromide at room temperature in dimethyl sulfoxide. A sample of the same sulfone was also prepared from the starting benzyl-α-*d* chloride by (1) reaction of the chloride with sodium ethanethiolate (SN2 reaction, inversion of configuration) and (2) oxidation of the resulting ethyl benzyl-α-*d* sulfide to the sulfone with potassium permanganate in glacial acetic acid. If the stereochemistry of the first three steps of the thiolsulfonate synthesis has been exactly as outlined above, the two samples should have the same specific rotation. As the data in Chart I show, although the sign of rotation is the same, the absolute magnitude of the rotation of the sulfone from the α-toluenesulfinate is only 72% of that from oxidation of the sulfide. This is indicative of the loss of a certain amount of optical activity during the first three steps of the synthesis. Deuterium analyses by n.m.r. on the two sulfones show that the one prepared from the sulfinate has only 72% of the deuterium content of that prepared by oxidation of the sulfide. A deuterium exchange reaction is therefore apparently responsible for all of the loss of optical activity observed.[9]

(9) Just how, or at what stage, this occurs is not certain. However, the fact that the degree of racemization does not exceed the degree of exchange shows that the exchange process must occur with a very high degree of retention of configuration. Otherwise the concurrent exchange of an α-hydrogen by hydrogen would lead to additional racemization. Originally we felt that exchange was occurring at the sulfonyl chloride stage in the mildly basic medium used for its reduction to the sulfinate. However, King and Durst[10] have recently shown that in basic media α-toluenesulfonyl chloride undergoes elimination to the sulfene PhCH=SO_2 in preference to exchange of its α-hydrogens. For this reason we now suspect that the observed exchange involves the α-toluenesulfinate-α-*d* ion, which is actually exposed to the basic reaction medium for some time after being formed by reduction of the sulfonyl chloride. The propensity of sulfones to undergo exchange with a very high degree of retention of configuration is well established.[11] That a sulfinate anion should behave similarly is consistent with the requirements recently outlined[12] as being necessary if a second-row element functional group is to preserve asymmetry in a carbanion.

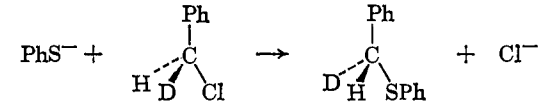
(10) J. F. King and T. Durst, *J. Am. Chem. Soc.*, 86, 287 (1964).

(11) D. J. Cram, D. A. Scott, and W. D. Nielsen, *ibid.*, 83, 3696 (1961); E. J. Corey and E. T. Kaiser, *ibid.*, 83, 490 (1961); D. J. Cram and A. S. Wingrove, *ibid.*, 85, 1100 (1963).

(12) D. J. Cram, R. D. Trepka, and P. St. Janiak, *ibid.*, 86, 2731 (1964).

The final step in the thiolsulfonate synthesis involves reaction of the α-toluenesulfinate-α-*d* (as the sulfinic acid) with benzenesulfenyl chloride under extremely mild and faintly acidic conditions. The likelihood of any racemization of the active center during this reaction seems very remote. Suitable deuterium analyses established that there was not loss of deuterium during this step.

Optically Active Phenyl Benzyl-α-d Sulfide. Another sample of optically active benzyl-α-*d* chloride, $\alpha^{25}D$ −0.631° (*l* 1, neat), was converted to phenyl benzyl-α-*d* sulfide by reaction with sodium thiophenolate in ethanol (SN2 reaction, inversion of configuration). The product, $[\alpha]^{25}D$ +0.38°, is of the same stereochemical series as the thiolsulfonate. A series of control experiments showed that the sulfide was optically stable under the various conditions used for the decomposition of the thiolsulfonate.



$\alpha^{25}D$ −0.631° (*l* 1, neat) $[\alpha]^{25}D$ +0.384° (*c* 15, dioxane)
0.88 ± 0.06 atom of D

Stereochemistry of the Thiolsulfonate Decomposition. Optically active phenyl α-toluenethiolsulfonate-α-*d* ($[\alpha]^{25}D$ +0.84°) was subjected to thermal decomposition in dilute solution in bromobenzene, methyl benzoate, and benzonitrile. In each case the product phenyl benzyl-α-*d* sulfide was isolated by procedures shown by

Table I. Stereochemistry of the Decomposition of Phenyl α-Toluenethiolsulfonate-α-*d*

Reaction conditions Solvent	Temp., °C.	[α]^{25}D of PhCHDSPh,[a] deg.	Reaction stereochemistry
PhBr	Reflux	−0.022 ± 0.006	8 ± 3% net inv.
PhCOOMe	172	−0.013 ± 0.006	5 ± 3% net inv.
PhCN	165–170	−0.048 ± 0.006	16 ± 3% net inv.

[a] Rotations in dioxane (*c* 12–20). On the basis of 72% optical purity for the starting thiolsulfonate [α]D for the sulfide for complete retention would be +0.29°.

control experiments not to lead to its racemization, and its rotation was determined. The results are shown in Table I. Based on the optical purity of the thiolsulfonate being only 72% that of the starting benzyl-α-*d* chloride of αD equal to −0.66, decomposition with complete retention of configuration would lead to sulfide with a specific rotation of +0.29°. Clearly the decomposition of the thiolsulfonate occurs in all three solvents with a very high degree of racemization.

In order to be sure that the observed results represent the actual stereochemistry of the decomposition itself one must demonstrate that the thiolsulfonate does not undergo significant racemization prior to decomposition. This was done in the present case by heating samples of the optically active thiolsulfonate in methyl benzoate until sulfur dioxide evolution measurements showed that 20, 40, or 70% decomposition had occurred. The reaction was then stopped, and the undecomposed thiolsulfonate was recovered. Measurement of its specific rotation showed that in no case had loss of optical activity occurred. That loss of optical activity also does not arise as a result of loss of deuterium during the course of the decomposition was established by comparison of the deuterium contents of the starting thiolsulfonate and the product sulfide. Within the experimental error of the n.m.r. method used for the measurement these were the same.

Decomposition of Phenyl Diphenylmethanethiolsulfonate in the Presence of Galvinoxyl. Our earlier conclusion[2a,b] that radical intermediates were not involved in the thiolsulfonate decomposition to any significant extent was based entirely on the observation that thiolsulfonates were ineffective as initiators of styrene polymerization. In view of the present stereochemical results it seemed important to reinvestigate this point using a more dependable probe. A trial experiment showed that a bromobenzene solution of the stable free radical galvinoxyl,[13] thought to be one of the more reliable reagents for counting radicals, underwent no decrease in optical density on being heated for 10 hr. at 115°. Since phenyl diphenylmethanethiolsulfonate (Ph_2CHSO_2SPh) decomposes in bromobenzene at this temperature at a quite reasonable rate ($k_1 = 2.1 \times 10^{-5}$ sec.$^{-1}$),[2b] measurement of the rate of disappearance of galvinoxyl during the decomposition of dilute bromobenzene solutions of this thiolsulfonate hopefully should provide a suitable method of determining whether or not the thiolsulfonate decomposition is a radical reaction.

(13) P. D. Bartlett and T. Funahashi, *J. Am. Chem. Soc.*, 84, 2596 (1962); P. D. Bartlett and C. Ruchardt, *ibid.*, 82, 1756 (1960); D. L. Tuleen, W. G. Bentrude, and J. C. Martin, *ibid.*, 85, 1938 (1963); W. G. Bentrude and J. C. Martin, *ibid.*, 84, 1561 (1962).

A series of experiments of this type was carried out; the results are shown in Table II. One complicating factor in their interpretation is the fact that galvinoxyl can be destroyed by the sulfur dioxide liberated in the thiolsulfonate decomposition. This is evident from the much faster rate of fading observed when the flow rate of the nitrogen used to remove the sulfur dioxide from the solution is reduced. That a similar reaction is also responsible for at least part of the galvinoxyl consumed even in those experiments where a fast nitrogen flow rate was employed is suggested by the fact that the rate of consumption of galvinoxyl is not proportional to thiolsulfonate concentration; instead $k_0/(RSO_2SR')$ becomes larger at low thiolsulfonate concentrations.

Table II. Decomposition of Phenyl Diphenylmethanethiolsulfonate in Presence of Galvinoxyl

(Galvinoxyl)$_0$ × 10^3, *M*	(RSO_2SR') × 10^3, *M*	Rate of N_2 flow	k_0 × 10^7, M^{-1} sec.$^{-1}$[a]	$[k_0/2k_1 \cdot (RSO_2SR')]$
1.1	10.2	Rapid	0.35	0.08
1.1	5.1	Rapid	0.27	0.13
1.1	5.3	Slow	0.88	0.39
1.1	2.7	Rapid	0.19	0.17

[a] Zero-order rate of disappearance of galvinoxyl: solvent, bromobenzene; temp., 115° in all runs.

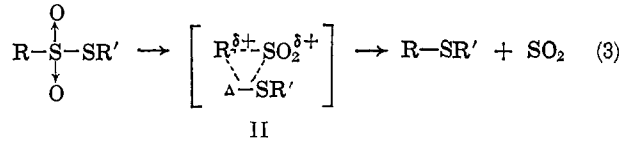
The values of $k_0/2k_1(RSO_2SR')$ in Table II show that in all the experiments employing rapid nitrogen flow the rate of consumption of galvinoxyl is only a small fraction of that expected if decomposition of the thiolsulfonate involved a radical mechanism. Furthermore, the decrease in this ratio with increasing thiolsulfonate concentration argues that the actual fraction of the decomposition which yields trappable free radicals is, at the most, 0.08. Although the thiolsulfonate decomposition could conceivably be a homolytic reaction and yet still have this low an efficiency of production of detectable radical intermediates, it seems much more plausible to conclude that it is not, and that almost all of the consumption of galvinoxyl in the present system is probably due to other causes.

The weight of the evidence from the galvinoxyl experiments thus only tends to affirm the verdict reached earlier from initiation studies, namely, that radical intermediates play at best a minor role in the thiolsulfonate decomposition.

Discussion

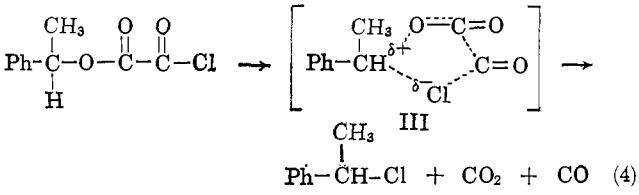
Previous study[2] of the thiolsulfonate decomposition has shown that the rate of decomposition of RSO_2SR' depends markedly on both R and R'. The dependence on R' parallels the acidity of the corresponding mercaptans, R'SH. Changing R from benzhydryl to benzyl brings about a 150–200-fold decrease in rate. Rates are also sensitive to solvent, being more rapid in better ionizing solvents, although in no case does the effect seem as large as normally observed for reactions, such as the chlorocarbonate decomposition,[3] involving rate-determining ionization to well-defined, ion-pair intermediates. On the other hand, both the galvinoxyl experiments and the failure of thiolsulfonates as polymerization initiators[2a,b] argue against a radical mech-

anism. In sum these results suggest that the rate-determining transition state for the thiolsulfonate decomposition possesses some ionic character, with partial negative charge on the sulfide sulfur and partial positive charge on R. Because of this a mechanism such as the one shown in eq. 3 has previously been advocated.[2]



II (3)

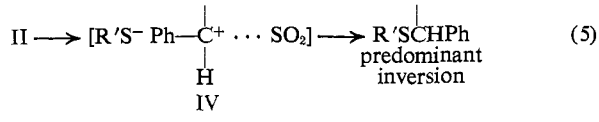
Internal substitution reactions such as the chlorocarbonate or chlorosulfite decompositions are generally characterized by considerable stereospecificity. With chlorocarbonates degrees of retention ranging from 15 to 99% have been observed.[3] With chlorosulfites both predominant inversion[4a] and predominant retention[3a,4a] have been reported, but in no case was more than 80–85% racemization observed. Recently, Rhoads and Michel[14] studied the thermal decomposition of 1-phenylethyl chloroglyoxalate (eq. 4). This particular internal substitution, like the thiolsulfonate



III (4)

decomposition, is characterized by notably less sensitivity to solvent ionizing power than the chlorocarbonate or chlorosulfite decompositions. Because of this Rhoads and Michel[14] proposed a mechanism involving a transition state or intermediate (III) which while definitely less ionic than a true ion pair is nonetheless more polar than the intermediates proposed for cyclic covalent rearrangements.[15,16] Significantly, optically active 1-phenylethyl chloroglyoxalate gave optically active chloride with a high degree of retention.

It is thus quite clear that the decomposition of phenyl α-toluenethiolsulfonate-α-*d* is markedly less stereospecific than any of the internal substitutions discussed above, even including the chloroglyoxalate reaction, which shows a similar dependence of rate on solvent ionizing power. In view of the high degree of stereospecificity observed by Rhoads and Michel[14] in the chloroglyoxalate reaction, it now seems difficult to defend a mechanism for the thiolsulfonate decomposition, such as eq. 3, in which II serves as the *immediate* precursor of the sulfide. Instead one might propose that, rather than collapsing directly to sulfide, II undergoes dissociation to a mercaptide ion and a sulfur dioxide solvated carbonium ion (eq. 5). Because solvation by sulfur dioxide should hinder approach to



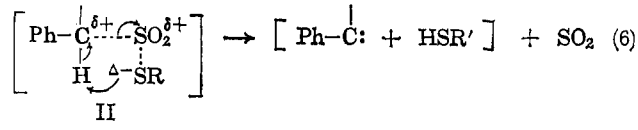
IV (5)

the front side of the carbonium ion, collapse of IV to product should yield sulfide of predominantly inverted configuration.

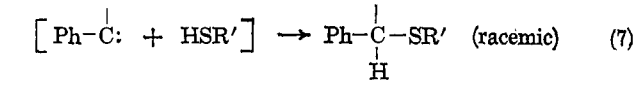
While this is consistent with the configuration of the small portion of the product which is optically active, one can question whether the mechanism in eq. 5 would lead to such a low degree of net inversion, particularly since ion-pair recombination in such internal substitutions as the chlorocarbonate and chlorosulfite decompositions appears to be significantly more stereospecific. One can, of course, argue that the reaction conditions of the thiolsulfonate decomposition are more conducive to racemization of the ion pair than those involved in the other reactions in question. Thus the temperature is 70–100° higher. Moreover, racemization of an ion pair involving the primary benzyl-α-*d* cation might well occur more rapidly than racemization of those ion pairs containing secondary alkyl carbonium ions which have been involved in the other previously studied systems.[17]

However, at this stage one can hardly be certain whether these differences alone could be sufficient to account for the results, and we would therefore like to suggest another possibility which we believe could be responsible at least in part for the extensive racemization observed. This particular suggestion, while admittedly speculative, has the merit of being able to explain the origin of certain minor products isolated in previous thiolsulfonate decompositions.[2a,b]

All of the thiolsulfonates (RSO_2SR') whose decompositions have been studied so far have had as R an aralkyl group with at least one α-hydrogen. In such cases it seems conceivable that an alternate path to eq. 5 for the disappearance of II (or IV) could be as shown in eq. 6. Before they have a chance to diffuse apart



II (6)



(racemic) (7)

the carbene and mercaptan formed in eq. 6 could then react rapidly to give principally the sulfide (eq. 7).[19] Any sulfide formed by this path would almost certainly be racemic.

The postulate of reaction 6 can also explain the formation of certain minor products isolated in diphenylmethanethiolsulfonate decompositions[2a,b] without the necessity of suggesting, as was done earlier,[2b] that in solvents such as bromobenzene a small amount of

(14) S. J. Rhoads and R. E. Michel, *J. Am. Chem. Soc.*, **85**, 585 (1963).
(15) S. Winstein, A. Gagneux, and W. G. Young, *ibid.*, **82**, 5956 (1960).
(16) S. G. Smith, *ibid.*, **83**, 4285 (1961).

(17) The decomposition of nitrosamides is believed to involve formation of a carbonium–carboxylate ion pair as a key intermediate.[18a] The ester isolated as one of the products is formed by collapse of this ion pair to covalency. White and Stuber[18b] have shown that this ion pair exhibits a greater tendency toward racemization (as evidenced by a lower per cent retention of configuration in the ester product) when the carbonium ion is a secondary aralkyl cation (1-phenylethyl cation) than when it is a tertiary aralkyl cation (2-phenyl-2-butyl cation). By extension one might therefore expect significantly more rapid racemization for an ion pair involving a benzyl-α-*d* cation than for secondary alkyl or aralkyl cations.
(18) (a) E. H. White and C. A. Aufdermarsh, Jr., *J. Am. Chem. Soc.*, **83**, 1179 (1961); (b) E. H. White and J. E. Stuber, *ibid.*, **85**, 2168 (1963).
(19) Rapid reaction of a mercaptan and an aryl carbene, although never specifically investigated or reported, seems eminently reasonable, particularly since Kirmse[20] has observed rapid reaction of diphenylcarbene with an alcohol, methanol.

radical decomposition occurs in competition with the usual nonradical decomposition path. Thus in the decomposition of Ph_2CHSO_2SR' in such solvents there is always formed a small amount of tetraphenylethane.[2a,b] This is a product which is formed rather generally from diphenylcarbene in the presence of a variety of hydrogen donors.[20,21] Should a small fraction of the diphenylcarbene formed by eq. 6 in the decomposition of a diphenylmethanethiolsulfonate escape reaction with mercaptan it could yield tetraphenylethane *via* the general route

$$Ph_2C: + RH \longrightarrow R\cdot + Ph_2CH\cdot \quad (8)$$

$$2Ph_2CH\cdot \longrightarrow Ph_2CHCHPh_2 \quad (9)$$

Some recently reported results[22] seem to provide additional support for our suggestion that a reaction such as eq. 6 might play an important role in the thiolsulfonate decomposition. Okamoto, Matsui, and Shingu[22] have found that the reaction of benzhydryl halides with certain hindered nucleophiles such as 2,6-di-*t*-butyl-4-methylphenoxide in acetonitrile leads to large amounts of tetraphenylethane, even though other evidence indicates that the initial step of the reaction is the ionization of the aralkyl halide to a carbonium–halide ion pair. Okamoto, *et al.*,[22] have explained this result as being due to an electron-transfer reaction between the hindered nucleophile and the benzhydryl cation which leads to the formation of a pair of free radicals (eq. 10). It appears, however, that their

$$Ph_2CH^+ + Nu:^- \longrightarrow Nu\cdot + Ph_2CH\cdot \longrightarrow Ph_2CHCHPh_2 \quad (10)$$

results could be equally well explained by the intervention of a reaction akin to eq. 6 followed by formation of tetraphenylethane from diphenylcarbene *via* eq. 8 and 9. We have avoided postulating a reaction akin to eq. 10 as an important contributor to the thiolsulfonate decomposition because of our negative evidence for significant involvement of radical intermediates in the reaction.

$$Ph_2CH^+ + Nu:^- \longrightarrow NuH + Ph_2C \xrightarrow{\text{eq. 8 and 9}} Ph_2CHCHPh_2$$

We would emphasize that eq. 6 and 7 represent but one speculation as to how the extensive racemization observed in the thiolsulfonate decomposition can be reconciled with the rate and product data previously obtained.[2] Others, who take a more sanguine view of the plausibility of certain assumptions than we do, may prefer any of several alternatives. Clearly, no definitive decision can be reached at present. However, there would seem considerable reason to believe that the thiolsulfonate decomposition may differ significantly in several important mechanistic respects from other previously studied internal substitution reactions. That being the case, the earlier suggestion[2b] of a possible fairly close mechanistic relation between the thiolsulfonate decomposition and the chlorocarbonate and chlorosulfite decompositions now seems open to question and the observation that both the R–SO_2 and SO_2–S bonds are cleaved in the rate-determining step of the thiolsulfonate reaction cannot be taken as any indication that multiple bond scission is likely in the rate-determining steps of these other classic SNi reactions.[23]

(20) W. Kirmse, *Ann.*, **666**, 9 (1963).
(21) W. Kirmse, L. Horner, and H. Hoffman, *ibid.*, **614**, 19 (1958).
(22) K. Okamoto, Y. Matsui, and H. Shingu, *Bull. Chem. Soc. Japan*, **38**, 153 (1965).

Experimental[25]

Preparation of (−)-Benzyl-α-d Alcohol. The original procedure for the preparation of this alcohol[8a] has subsequently been improved by minor modifications.[8b] The modified procedure was used in the present work. Two separate batches of the alcohol were prepared: batch 1, b.p. 89–90° (8 mm.), α^{25}_{546} −1.830 ± 0.003° (*l* 2); batch 2, b.p. 74–75° (4 mm.), $\alpha^{25}D$ −0.728 ± 0.002° (*l* 1). The reported rotations for the alcohol[8b] are: α^{30}_{5463} −3.669 ± 0.004° (*l* 4) and $\alpha^{30}D$ −3.006 ± 0.004° (*l* 4).

(−)-Benzyl-α-d Chloride. Optically active benzyl-*α-d* alcohol (11.8 g., 108 mmoles) was allowed to react with 12.6 g. of phosgene in toluene solution using the procedure described[26] for the conversion of the undeuterated alcohol to carbobenzoxy chloride.

The crude benzyl-*α-d* chlorocarbonate obtained after removal of the toluene solvent and excess phosgene under reduced pressure was not purified further but was instead dissolved in 50 ml. of purified dioxane, and the resulting solution was refluxed for 36 hr. The dioxane was then removed by fractional distillation under reduced pressure, and the crude benzyl-*α-d* chloride was purified by fractional distillation through an 18-in., vacuum-jacketed, Vigreux column to give 11.6 g. (85%) of the pure chloride, b.p. 68–69° (15 mm.). The rotations of the various samples of the chloride are tabulated in Table III.

Table III

Run	Rotation of starting benzyl-*α-d* alcohol, deg.	Rotation of benzyl-*α-d* chloride, deg.
1	α^{25}_{546} −1.830 (*l* 2)	α^{25}_{546} −0.821 ± 0.005 (*l* 1)
2	α^{25}_{546} −1.830 (*l* 2)	$\alpha^{25}D$ −0.631 ± 0.003 (*l* 1)
3	$\alpha^{25}D$ −0.728 (*l* 1)	$\alpha^{25}D$ −0.661 ± 0.003 (*l* 1)

α-Toluenesulfonyl-α-d Chloride. Optically active benzyl-*α-d* chloride was converted to *α*-toluenesulfonyl-*α-d* chloride using the same procedure described[27] for the synthesis of *α*-toluenesulfonyl chloride from the undeuterated alkyl halide. The average yield was 75%. Samples of the sulfonyl chloride, m.p. 93–94°, had the rotations indicated.

(23) See, however, a recent demonstration[24] using a more closely related reaction which does suggest that scission of more than one bond is involved in the rate-determining step of the chlorocarbonate decomposition.
(24) J. L. Kice, R. A. Bartsch, M. A. Dankleff, and S. L. Schwartz, *J. Am. Chem. Soc.*, **87**, 1734 (1965).
(25) Optical rotations of the various deuterated compounds were determined using a Rudolph photoelectric precision polarimeter (0.001°). Recorded readings are the mean of at least ten readings for the polarimeter tube containing the optically active compound minus the mean of at least ten readings for the empty or solvent-filled tube. Rotations of liquids were determined neat. Rotations of solids were determined as solutions in the solvent indicated. All rotations were taken using center-filled tubes of 4-mm. bore.
(26) H. E. Carter, R. L. Frank, and H. W. Johnston, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 167.
(27) M. A. Belous and I. Ya. Postovsky, *J. Gen. Chem. USSR*, **20**, 1761 (1950).

Rotation of starting benzyl-α-*d* chloride	Rotation of α-toluenesulfonyl-α-*d* chloride
α^{25}_{546} −0.821 (*l* 1)	$[\alpha]^{25}D$ +0.288 ± 0.006 (*l* 2; *c* 18, dioxane)
$\alpha^{25}D$ −0.631 (*l* 1)	$[\alpha]^{25}D$ +0.268 ± 0.006 (*l* 2; *c* 20, dioxane)

α-Toluenesulfinic-α-d Acid. Optically active α-toluenesulfonyl-α-*d* chloride was converted to the sulfinic acid by a modification of the method previously described[2c] for the undeuterated compounds. In the modified method a solution of the sulfonyl chloride in ether, rather than the solid sulfonyl chloride, was shaken with the alkaline solution of sodium sulfite. Under such conditions the reaction is much faster, and it is desirable to cool the separatory funnel containing the mixture periodically in an ice bath. The second point of difference was that no attempt was made to crystallize the sulfinic acid at the end of the work-up, but rather the crude oily material was used directly in subsequent steps. Over-all yields were much higher by this modified method, and no difficulties were encountered in the purification of the products of subsequent steps.

Phenyl α-Toluenethiolsulfonate-α-d. The α-toluenesulfinic-α-*d* acid obtained from 10 g. of α-toluenesulfonyl-α-*d* chloride was diluted with 10 ml. of water. A 5% solution of benzenesulfenyl chloride[28] in benzene was added slowly with shaking until the orange color persisted on standing. The layers were then separated, and the benzene layer was washed with two 10-ml. portions of water. After the solution was dried over anhydrous sodium sulfate, the benzene was partially removed under reduced pressure, and the thiolsulfonate was crystallized from 1:1 benzene–hexane. After recrystallization from the same solvent it melted at 110–110.5° (lit.[2c] m.p. 110–111°). The over-all yield from the sulfonyl chloride was 70–75%. All the material used in the studies of the stereochemistry of the decomposition was prepared starting from benzyl-α-*d* chloride of $\alpha^{25}D$ −0.66°. This thiolsulfonate showed $[\alpha]^{25}D$ +0.837 ± 0.020° (*l* 2; *c* 5, dioxane). An n.m.r. analysis on an acetone solution of the thiolsulfonate gave the relative areas of the peaks due to aromatic and benzylic hydrogens as 10:1.33, indicating a deuterium content of 0.67 ± 0.04 atom of D per molecule. The validity of this analytical method was confirmed by comparison with the results of a standard deuterium analysis.[29]

Benzyl-α-d Ethyl Sulfone from α-Toluenesulfinic-α-d Acid. A sample of α-toluenesulfinic-α-*d* acid prepared from 10.5 mmoles of the same batch of optically active sulfonyl chloride used to synthesize the optically active thiolsulfonate was dissolved in 2 ml. of water and 30 ml. of dimethyl sulfoxide. The acid was then neutralized by the addition of 0.88 g. (10.5 mmoles) of solid sodium bicarbonate. To the resulting solution of the sulfinate was then added 2.0 g. (17 mmoles) of ethyl bromide, and the solution was allowed to stand at room temperature for 36 hr. At the end of this time the solvent was removed by vacuum distillation at 1 mm. The residue was diluted with 40 ml. of water, and the precipitated sulfone was filtered off. After recrystallization from 75% methanol–water there was obtained 0.57 g. (30%) of benzyl-α-*d* ethyl sulfone, m.p. 82–83°, $[\alpha]^{25}D$ −0.189 ± 0.013° (*l* 2; *c* 20, dioxane). An n.m.r. analysis on an acetone solution of the sulfone, again using the relative areas of the peaks due to aromatic and benzylic hydrogens, showed these to be in the ratio of 5:1.32, which corresponds to a deuterium content of 0.68 ± 0.02 atom of D per molecule.

Benzyl-α-d Ethyl Sulfone from Benzyl-α-d Chloride. Under nitrogen, to a mixture of 1.5 g. of ethyl mercaptan dissolved in 5 ml. of absolute ethanol was first added 1.35 g. of potassium hydroxide in 15 ml. of 95% ethanol. Then 3.06 g. of benzyl-α-*d* chloride, $\alpha^{25}D$ −0.66° (*l* 1), dissolved in 10 ml. of ethanol was added with good stirring. Potassium chloride precipitated immediately, but to ensure complete reaction the mixture was heated at 50° for 1 hr. The precipitated salt was removed by filtration. The ethanol was evaporated from the filtrate, and the residue was vacuum distilled, giving 1.9 g. (52%) of benzyl-α-*d* ethyl sulfide, b.p. 96–99° (13 mm.).

The sulfide, 1.9 g., was dissolved in 10 ml. of glacial acetic acid. To this solution was added in small portions 2.36 g. of potassium permanganate dissolved in the minimum amount of water, the mixture being shaken vigorously during the addition. The excess permanganate and manganese dioxide were destroyed by addition of some aqueous 5% sodium bisulfite solution. The resulting mixture was added to three times its volume of cold water, and the sulfone which precipitated was filtered off. Recrystallization from ethanol gave 0.8 g. (35%) of benzyl-α-*d* ethyl sulfone, m.p. 79–80°, $[\alpha]^{25}D$ −0.264 ± 0.007° (*l* 2, *c* 17, dioxane). The deuterium content of the sulfone, determined by the method described above, was 0.95 ± 0.05 atom of D per molecule.

Phenyl Benzyl-α-d Sulfide. Under nitrogen, 0.56 g. of potassium hydroxide in 10 ml. of 95% ethanol was added to 1.1 g. of thiophenol in 5 ml. of the same solvent. To this solution was then added 1.27 g. of benzyl-α-*d* chloride, $\alpha^{25}D$ −0.63° (*l* 1), in 10 ml. of ethanol. The mixture was stirred for 3 hr. at 60°, and the precipitated potassium chloride was filtered off while the solution was still hot. The filtrate was cooled, and the sulfide which crystallized was filtered off and recrystallized from 95% ethanol, giving 1.6 g. (80%) of phenyl benzyl-α-*d* sulfide, m.p. 43–45° (lit.[30] 43–44°), $[\alpha]^{25}D$ +0.384 ± 0.007° (*l* 2; *c* 15, dioxane). Comparison of the areas of the aromatic proton signals with those for the benzylic protons indicated a deuterium content of 0.88 ± 0.06 atom of D per molecule. A combustion analysis using the falling-drop method[29] also indicated 0.88 atom of D per molecule.

Stereochemistry of the Decomposition of Phenyl α-Toluenethiolsulfonate-α-d. In each case the decomposition was carried out using the same apparatus and procedure previously employed for studying the decomposition of the undeuterated phenyl ester,[2c] and described in detail in earlier publications.[2a,b] Once the decomposition was complete the solvent was removed as completely as possible by distillation at pressures of about 1 mm. and the residue was treated

(28) H. Lecher and F. Holschneider, *Ber.*, **57**, 755 (1924).
(29) Analysis by Josef Nemeth, University of Illinois.
(30) R. Pummerer, *Ber.*, **43**, 1406 (1910).

with a small amount of 80% ethanol and cooled to induce crystallization of the majority of the phenyl benzyl-α-*d* sulfide. This was then filtered off and recrystallized again from aqueous ethanol. The filtrates from the crystallizations were evaporated, and the residue was chromatographed on acid-washed alumina. Elution with hexane and hexane–benzene mixtures permitted the separation of the remainder of the sulfide. This was recrystallized and added to the material obtained by direct crystallization. In the case of the run in benzonitrile all the sulfide was isolated by initial chromatography followed by recrystallization of the appropriate chromatographic fractions. The rotations of the samples of the sulfide obtained from the various runs are shown in Table IV. The deuterium contents of these same sulfide samples were also determined, using the n.m.r. technique described above, and the results are shown in Table IV. In all of the runs 7.5 mmoles of optically active thiolsulfonate was decomposed and in no case was less than 4.0 mmoles of phenyl benzyl-α-*d* sulfide isolated, even after purification. Crude yields of the sulfide were, of course, considerably higher, but rotations were measured only on samples having a melting point of at least 42–43°.

Table IV. Optical Rotation and Deuterium Content of Phenyl Benzyl-α-*d* Sulfide from the Decomposition of Optically Active Thiolsulfonate[a]

Solvent	Temp. of decompn., °C.	Phenyl benzyl-α-*d* sulfide — $[\alpha]^{25}D$, deg.	D content[b]
C_6H_5Br	Reflux	−0.022 ± 0.006 (*l* 2; *c* 18, dioxane)	0.66 ± 0.03
$C_6H_5COOCH_3$	172–175	−0.013 ± 0.006 (*l* 2; *c* 16, dioxane)	0.66 ± 0.03
C_6H_5CN	165–170	−0.048 ± 0.006 (*l* 2; *c* 16, dioxane)	0.67 ± 0.03

[a] In each run the starting phenyl α-toluenethiolsulfonate-α-*d* had $[\alpha]^{25}D$ +0.84 ± 0.02° and a deuterium content of 0.67 ± 0.04 atoms of D per molecule. [b] Atoms of D per molecule.

Optical Stability of Phenyl Benzyl-α-d Sulfide under the Conditions of the Thiolsulfonate Decomposition. Solutions of optically active sulfide in the solvents used for the thiolsulfonate decomposition were heated under nitrogen for the lengths of time indicated in Table V. The solvent was then removed by vacuum distillation and the residual sulfide was crystallized from aqueous ethanol. The rotations of the recovered samples are compared with those of the starting samples in Table V. In each case there was no significant change in rotation. The heating periods in every case equalled or exceeded those involved in the decomposition of the thiolsulfonate in that solvent.

Optical Stability of Phenyl Benzyl-α-d Sulfide to Chromatography on Alumina. A sample of phenyl benzyl-α-*d* sulfide, $[\alpha]^{25}D$ +0.362 ± 0.015° (*l* 2; *c* 17, dioxane), was chromatographed on acid-washed alumina. The main fraction of the recovered sulfide was recrystallized from aqueous ethanol and its rotation was determined: $[\alpha]^{25}D$ +0.334 ± 0.009° (*l* 2; *c* 17, dioxane). Although this result may be indicative of the occurrence of a slight amount of racemization during chromatography, it certainly is not extensive enough to be responsible for the extensive racemization of the sulfide observed in Table IV, particularly when one recalls that except for the benzonitrile run the majority of the sulfide was always isolated without recourse to chromatography.

Table V. Optical Stability of Phenyl Benzyl-α-*d* Sulfide

Solvent	Temp., °C.	Time, hr.	$[\alpha]^{25}D$ of phenyl benzyl-α-*d* sulfide (*l* 2; *c* 15, dioxane), deg. Before heating	After heating
C_6H_5Br	Reflux	90	+0.384 ± 0.006	+0.388 ± 0.009
$C_6H_5COOCH_3$	170	60	+0.384 ± 0.006	+0.376 ± 0.009
C_6H_5CN	171	78	+0.394 ± 0.007	+0.403 ± 0.007

Lack of Racemization of Phenyl α-Toluenethiolsulfonate-α-d prior to Decomposition. A sample of optically active thiolsulfonate of $[\alpha]^{25}D$ +0.44 ± 0.02° (*l* 1; *c* 9, dioxane) was prepared by diluting the optically active material of $[\alpha]^{25}D$ +0.84° with an approximately equal weight of undeuterated thiolsulfonate. Portions of this material were then partially decomposed in methyl benzoate at 172° in the usual manner until measurements of sulfur dioxide evolution indicated that the desired fraction of thiolsulfonate had decomposed. The reaction was then stopped, and the undecomposed thiolsulfonate was recovered by first removing the solvent at 1 mm. and then extracting the residue with three 25-ml. portions of hexane. Recrystallization of the hexane-insoluble residue from benzene–hexane gave thiolsulfonate, m.p. 108–109°, whose specific rotation was then determined. The following results were obtained: (per cent of original thiolsulfonate decomposed), $[\alpha]^{25}D$ of recovered thiolsulfonate (*l* 1; *c* 8–10, dioxane); (20%), $[\alpha]^{25}D$ +0.45 ± 0.02°; (40%), $[\alpha]^{25}D$ +0.46 ± 0.02°; (70%), $[\alpha]^{25}D$ +0.46 ± 0.02°. Clearly there is no racemization of the thiolsulfonate prior to decomposition. Actually there seems to be a slight increase in specific rotation, although its magnitude is small enough to be within experimental error. If the increase is actually real, the fact that it occurs only during the first 40% of decomposition suggests that it is due to the presence in the starting thiolsulfonate of a small amount of a thermally less stable substance which decomposes more rapidly than the thiolsulfonate. In particular, if this substance were optically active and significantly levorotatory there would need be only a very small amount present in the original optically active thiolsulfonate to account for the observed results. Although the thiolsulfonate was purified by recrystallization and appeared pure, a small amount of impurity could easily have gone undetected. The fact that no further significant increase in [α] occurs after 40% decomposition rules out the possibility that the majority of the change is due to an isotope effect which causes the α-deuteriothiolsulfonate to decompose slightly more slowly than the undeuterated and inactive thiolsulfonate.