and Sims[4] have shown that 3 refluxed in 60% aqueous acetone for 36 hr produced a large amount of *trans*-9,10-dihydroxy-9,10-dihydrophenanthrene. This is consistent with SN2 attack by water on the epoxides. Unfortunately, because of its symmetry the question of the importance of the NIH shift on 3 cannot be detected. Thus, 3 most certainly hydrolyzes in an analogous manner to simple epoxides.

A Novel Route to Racemization of Sulfoxides

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Abstract: Optically active *sec*- and *tert*-alkyl phenyl sulfoxides undergo racemization together with fragmentation in aqueous perchloric acid. A detailed investigation of *tert*-butyl phenyl sulfoxide (**1**) showed that the racemization is neither due to nucleophilic substitution at sulfur nor to pyramidal inversion. The rates of racemization (k_r) and fragmentation (k_d) reactions follow the same kinetic law, both depending on the concentration of the protonated sulfoxide, and they are similarly affected by the acidity of the medium. Similar rates (k_d/k_r = 2–3) and similar energies of activation were found for the two reactions. Experiments with ^{18}O-labeled **1** and with (R_S,R_C)-α-phenylethyl phenyl sulfoxide showed that racemization at sulfur does not occur *via* oxygen exchange and it is accompanied by partial racemization of carbon chiral center ($k_{SO}/k_{alkyl} \sim 3.5$). The results are discussed on the basis of two alternative mechanisms, one involving a reversible S → O shift of the alkyl group, the other an alkyl cation sulfenic acid ion–molecule pair.

The rates of reduction and of racemization of sulfoxides are very sensitive to the steric requirements of the groups attached to the sulfur atom.[1–3]

Mislow, *et al.*,[1] reported that methyl *p*-tolyl sulfoxide racemizes in a 2:1 v/v mixture of dioxane and 12 *M* aqueous HCl more than 10^5 times faster than the tertiary butyl derivative.

Andersen, *et al.*,[2] found a ratio $k_{Me}/k_{tert\text{-}Bu}$ greater than 10^3 for the reduction with sodium iodide in aqueous perchloric acid of phenyl alkyl sulfoxides.

We studied[3,4] the reduction with sodium iodide and the racemization with sodium chloride and sodium bromide in aqueous perchloric acid of phenyl alkyl sulfoxides, and found[3] a decrease in reactivity from the methyl to the isopropyl derivative ($k_{Me}/k_{i\text{-}Pr}$ about 60) similar to that observed by Mislow[1] and Andersen.[2]

However, we have not been able to make any direct comparison with the tertiary butyl derivative, since, in our conditions, the rate of loss of optical activity of (+)-*tert*-butyl phenyl sulfoxide appears to be independent of halide ion concentration. This reaction, in fact, occurs in the absence of any added salt. It suggests a peculiar behavior of this substrate and we observed as reaction products large amounts of diphenyl disulfide and phenyl benzenethiolsulfonate, together with racemized sulfoxide.

Diphenyl disulfide and phenyl benzenethiolsulfonate often appear as decomposition products of organosulfur compounds.[5] The most intriguing fact, however, is the observed racemization of the sulfoxide in the absence of any nucleophile.[6] We now report a detailed study of this reaction. Some preliminary results have been published elsewhere.[7]

Results

The reactions were run in aqueous perchloric acid solutions at 25°.

Product Analysis. *tert*-Butyl phenyl sulfoxide (**1**) (250 mg) was allowed to react for 35 days in aqueous perchloric acid, 6 *M*. After work-up the following products were isolated: diphenyl disulfide (**2**) (55 mg), phenyl benzenethiolsulfonate (**3**) (34 mg), and **1** (29 mg). When **1** was kept for 64 hr in 8.9 *M* perchloric acid, only **1** and **2** were found as major reaction products; **3** was present only in trace amounts as evidenced by thin-layer chromatography.

The stoichiometric eq 1 requires a 1:1 ratio of **2** and **3**.

$$\underset{\mathbf{1}}{4\text{PhSO-}tert\text{-Bu}} + 2\text{H}_2\text{O} \longrightarrow \underset{\mathbf{2}}{\text{Ph}_2\text{S}_2} + \underset{\mathbf{3}}{\text{PhSSO}_2\text{Ph}} + tert\text{-BuOH} \quad (1)$$

Even in the less concentrated solution we used, we found **2** in a greater amount than **3**. This is not surprising since it is reported that phenyl benzenethiolsulfonate suffers hydrolysis in acid media[5] to give diphenyl disulfide and sulfinic or sulfonic acids. We did not succeed in isolating any amount of the above acids from the strongly acidic reaction mixture.

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[1] K. Mislow, T. Simmons, J. T. Melillo, and A. L. Ternay, Jr., *J. Amer. Chem. Soc.*, **86**, 1452 (1964).

[2] R. A. Strecker and K. K. Andersen, *J. Org. Chem.*, **33**, 2234 (1968).

[3] D. Landini, F. Montanari, H. Hogeveen, and G. Maccagnani, *Tetrahedron Lett.*, 2691 (1964); D. Landini, F, Montanari, G. Modena, and G. Scorrano, *Chem. Commun.*, 3 (1969).

[4] D. Landini, G. Modena, F. Montanari, and G. Scorrano, *J. Amer. Chem. Soc.*, **92**, 7163 (1970).

[5] A. Schoberl and A. Wagner in "Methoden der Organischen Chemie," Vol. IX, E. Muller, Ed., G. Thieme Verlag, Stuttgart, 1955.

[6] C. R. Johnson and J. C. Sharp, *Quart. Rep. Sulfur Chem.*, **4**, 1 (1969).

[7] G. Scorrano, U. Quintily, and G. Modena, *Chim. Ind. (Milano)*, **53**, 155 (1971).

Table I. Specific Rotation of *tert*-Butyl Phenyl Sulfoxide Recovered after Reaction in Aqueous Perchloric Acid 8.9 *M* at 25°

	t, min			
	0	3	1593	4308
$[\alpha]^{25}\mathrm{Hg}$	222.7	217.4	204.4	162.4

The fate of the alkyl moiety was not investigated in detail; however, nmr analysis of the reaction solution showed the same absorption at δ 1.5 (s) as that of a solution of *tert*-butyl alcohol in perchloric acid of the same concentration.

Table II. Rate Coefficients for Decomposition (k_d), Racemization (k_r), and Overall (k_α) Reactions of Substituted Phenyl Alkyl Sulfoxides (ArSOR)[a]

Ar	R	[H$^+$], *M*	*t*, °C	$-H_0$	$-H_A$	$k_\alpha \times 10^7$, sec^{-1}	$k_d \times 10^7$, sec^{-1}	$k_r \times 10^7$, sec^{-1}	7 + log k_d',[b] sec^{-1}	7+ log k_r',[b] sec^{-1}
C_6H_5	*tert*-C_4H_9	5.11	25	2.34	1.99	3.26	1.86	0.96	0.68	0.40
		8.30	25	4.48	3.20	30.6	22.8	7.8[c]	1.40	0.93
		8.97	25	5.15	3.44	36.3	23.2	11.5	1.39	1.08
		10.4	25	6.47	3.93	78.0	55.0	17.6	1.75	1.25
		11.9	25	7.88	4.57	133.0	105.0	27.4	2.02	1.44
		8.97	35	*d*	*d*	241.0	175.0[c]	65.6		
		8.97	45	*d*	*d*	1000.0	734.0[c]	266.0		
p-$CH_3C_6H_4$	*tert*-C_4H_9	8.98	25	5.15	3.44	15.0	10.6	4.8		
C_6H_5	*i*-C_3H_7	10.4	25	6.47	3.93	1.6				

[a] In aqueous perchloric acid. [b] The pK_a value used is −2.19. [c] Estimated from the relationship $k_\alpha = k_d + k_r$. [d] Not measured.

From the reaction of optically active **1**, we recovered a sulfoxide with specific rotation lower than that of the starting material. A typical example is reported in Table I.

The two reactions of *tert*-butyl phenyl sulfoxide, decomposition and racemization, occur at convenient rates at acid concentration above 5 *M*. Therefore, the pK_a of the sulfoxide was needed for the analysis of the kinetic data.

pK_a Measurements. The ionization ratio[8] [SOH$^+$]/[SO] may be evaluated by analyzing the uv spectra of *tert*-butyl phenyl sulfoxide in acid solutions,[9] with the methods described by Davis and Geissman[10] and Hammett, *et al.*[11] Plots of log [SOH$^+$]/[SO] *vs.* $-H_A$, the acidity function obeyed by sulfoxides,[4,9] allowed us to evaluate a pK_a value of −2.19.

Recently,[12] we found that pK_a values may be obtained by the circular dichroism (CD) spectra of optically active sulfoxides in acid solutions. In particular, by plotting the molecular ellipticities of the negative extremum, centered for (+)-*tert*-butyl phenyl sulfoxide at about 210 nm, *vs.* $-H_A$, we obtained a good sigmoid curve. From such a curve we evaluated, with the usual formula,[13] a pK_a value of −2.3.

This value is in good agreement with that found with the uv technique (−2.19). Moreover, the CD measurements were made at room temperature (about 18°), whereas the uv spectra were taken at 25°; it is known that the acidity function H_0 decreases with increasing temperature.[14]

Since measurements of temperature effect on H_A have not been reported, we used throughout this paper the value −2.19 as the pK_a value of the *tert*-butyl phenyl sulfoxide.

Dependence of Reaction Rates on Acidity. We measured the rates of the two reactions in aqueous perchloric acid at 25°. The rate of decomposition (k_d) was measured by following the disappearance with time of the ir band at 1090 cm^{-1} characteristic of the SO absorption of the *tert*-butyl phenyl sulfoxide.[15] The rate of racemization (k_r) was measured by recovering the residual sulfoxide at various times and measuring its specific activity. The overall reaction rate ($k_\alpha = k_d + k_r$) was measured by following the loss of optical activity of acid solutions of (+)-**1**.

Even if the required experimental technique is quite complex (see Experimental Section), the data collected in Table II are internally consistent.

The experimental rate coefficients were evaluated from the expression

$$\text{rate} = k_{\text{obsd}}[\text{SO}]_{\text{st}} \tag{2}$$

Since the sulfoxide is substantially protonated in the range of acid concentration used in this research, the rate coefficients of interest are those evaluated on the basis of the actual amount of protonated substrate

$$\text{rate} = k'[\text{SOH}^+] \tag{3}$$

The fraction of protonated sulfoxide may be evaluated from the following relationships

$$K_a = \frac{[\text{SO}][\text{H}^+]}{[\text{SOH}^+]} = \frac{[\text{SO}]h_A}{[\text{SOH}^+]} \tag{4}$$

$$[\text{SO}]_{\text{st}} = [\text{SOH}^+] + [\text{SO}] \tag{5}$$

and therefore

$$[\text{SOH}^+] = \frac{h_A}{h_A + K_a}[\text{SO}]_{\text{st}} \tag{6}$$

By combining eq 2, 3, and 6 we obtain

$$k' = \frac{h_A + K_a}{h_A}k_{\text{obsd}} \tag{7}$$

---

(8) The symbols [SOH$^+$] and [SO] represent the concentrations of protonated and free sulfoxide, respectively, whereas [SO]$_{\text{st}}$ stands for the stoichiometric concentration of the sulfoxide.

(9) D. Landini, G. Modena, G. Scorrano, and F. Taddei, *J. Amer. Chem. Soc.*, **91**, 6703 (1969).

(10) C. T. Davis and T. A. Geissman, *ibid.*, **76**, 3507 (1954).

(11) L. A. Flexser, L. P. Hammett, and A. Dingwall, *ibid.*, **57**, 2103 (1935).

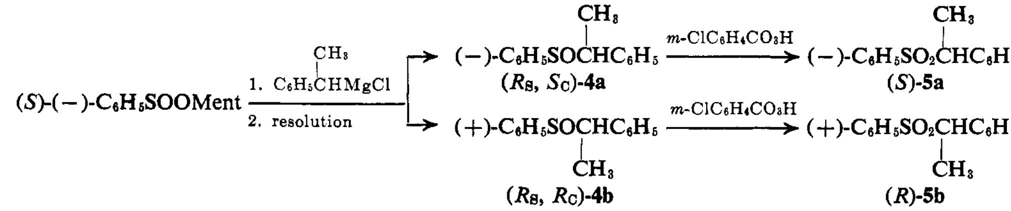
(12) U. Quintily and G. Scorrano, *Chem. Commun.*, 260 (1971).

(13) M. A. Paul and F. A. Long, *Chem. Rev.*, **57**, 1 (1957).

(14) P. Tickle, A. G. Briggs, and J. M. Wilson, *J. Chem. Soc. B*, 65 (1970); C. D. Johnson, A. R. Katritzky, and S. A. Shapiro, *J. Amer. Chem. Soc.*, **91**, 6654 (1969).

(15) L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," Wiley, New York, N. Y., 1966.

Chart I



Rate coefficients taking into account the protonation of the substrate have been evaluated for the decomposition (k_d') and for the racemization (k_r') reactions, and are collected in Table II. In Table III we reported the slopes of plots of log k' *vs.* various acidity functions, for both reactions.

Table III. Correlation of Rate Coefficients with Acidity Functions for the Decomposition and Racemization Reactions of *tert*-Butyl Phenyl Sulfoxide[a]

	log k' *vs.*		
Reaction	$-H_0$ s^b	$-H_A$ s^b	H_0 + log [H$^+$] s^b
Decomposition	0.24	0.52	−0.25
Racemization	0.17	0.41	−0.20

[a] In aqueous perchloric acid at 25°. [b] The slopes (s) of the plots log k' *vs.* acidity functions were evaluated by least-squares analysis.

Oxygen Exchange. We synthesized the *tert*-butyl phenyl sulfoxide ^{18}O labeled by oxidation of the corresponding sulfide with iodobenzene dichloride and labeled water in pyridine.[16] The ^{18}O content was evaluated by mass spectroscopic analysis.

The labeled sulfoxide (^{18}O content 8.2 ± 0.3 %) was allowed to react for 71 hr in 8.9 *M* perchloric acid. The recovered sulfoxide had an ^{18}O content of 8.6 ± 0.4 %. Under the same conditions, optically active **1** suffers 25% racemization; hence racemization is not accompanied by oxygen exchange.

Reaction of α-Phenylethyl Phenyl Sulfoxide (4). During the racemization of the sulfoxide, the alkyl moiety may also suffer changes in its chirality. Therefore, we prepared the sulfoxide **4** which has been resolved and characterized as shown in Chart I, and studied its behavior in acid solutions.

The configurations at carbon and sulfur centers have been rigorously assigned (see Experimental Section) on the basis of the known stereochemistry of Grignard reactions with sulfinates[17] and of the configuration of **5b** already assigned by Corey, *et al.*[18] Moreover, Nishio and Nishihata[19] recently reported configurational assignments for compounds related to **4a** and **4b**, in agreement with those given above. The specific rotations of the sulfoxides and sulfones of Chart I are reported in Table IV.

The contribution to the specific rotation by each of the two chiral centers has been evaluated as follows. Let us call x and y the contributions of the SO and the alkyl group, respectively. Then we have

$$x + y = 204.2 \tag{8}$$

$$x - y = -9.45 \tag{9}$$

Solutions of this system give the values reported in Table IV. From these data we may conclude that optically pure sulfone **5** derives from a sulfoxide **4** in which the alkyl group contributes to the specific rotation by ±106.8°, depending on the sign of rotation of **5**. The extimated error is within ±2%.

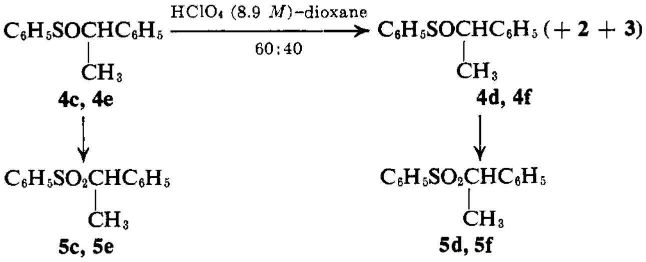
Table IV. Specific Rotation of α-Phenylethyl Phenyl Sulfoxides and Sulfones[a]

Compd	[α]D, deg	Contribution to the specific rotation by SO	Alkyl
4a	−9.45	97.4	−106.8
4b	204.2	97.4	+106.8
5a	−100.8		
5b	+98.5[b]		

[a] In acetone at 25°. [b] +103.0° in methanol.

Two samples of **4** (R_S and R_C) of different optical purity were allowed to react in a mixture (60:40) of 8.9 *M* perchloric acid–dioxane, since they are sparingly soluble in aqueous acid (see Chart II).

Chart II



The specific activities of starting and recovered sulfoxides are collected in Table V. From the per cent of

Table V. Specific Rotations of α-Phenylethyl Phenyl Sulfoxides before (**4c**, **4e**) and after (**4d**, **4f**) Reaction in Perchloric Acid (8.9 *M*)-Dioxane, 60:40

Compd	[α]^{25}D	Reaction time, hr	Contribution[a] to [α] by SO	Alkyl	Racemization % at SO	Alkyl
4c	197.2	0	93.6	103.6		
4d	130.1	42	45.6	84.5	51.3	19.4
4e	168.0	0	80.2	87.8		
4f	101.4	47	32.8	68.6	59.1	21.9

[a] Evaluated from the specific rotations ([α]^{25}D) of the corresponding sulfones. They are: **5c**, 96.8; **5d**, 79.0; **5e**, 82.1; **5f**, 64.1.

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(16) G. Barbieri, M. Cinquini, S. Colonna, and F. Montanari, *J. Chem. Soc. C*, 659 (1968).

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

(18) E. J. Corey and T. H. Lowry, *Tetrahedron Lett.*, 803 (1965).

(19) M. Nishio and K. Nishihata, *Chem. Commun.*, 1485 (1970).

racemization at the SO and at the alkyl group, we evaluated a reactivity ratio k_{SO}/k_{alk} of about 3.5.

Activation Parameters. The reactions of *tert*-butyl phenyl sulfoxide were studied at various temperatures. From the data collected in Table II we evaluated apparent values of 29.5 ± 2 and 32.5 ± 4 kcal/mol for the energy of activation of the racemization and decomposition reactions, respectively. No correction was made for the amount of protonated sulfoxide, owing to the lack of H_A values at temperatures different from 25°.

Substrate Structure Effect. The reactions of *tert*-butyl *p*-tolyl sulfoxide and of isopropyl phenyl sulfoxide were briefly examined. The results, reported in Table II, show that the overall reaction is slowed down by an electron-donating substituent in the aryl group or by changing the alkyl moiety with a less electron-donating group. The rates of decomposition and racemization are affected in about the same manner by substituents in the aryl group, as shown by the data reported for the *p*-tolyl sulfoxide.

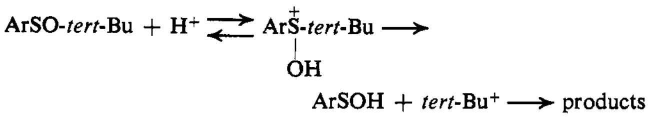
Discussion

The (+)-*tert*-butyl phenyl sulfoxides undergo in acid solutions two reactions: fragmentation, leading to diphenyl disulfide and phenyl benzenethiolsulfonate, and racemization. The rates of the two reactions follow the same kinetic law, and both depend on the concentration of the protonated sulfoxide. The rate coefficients k' (= rate/[SOH$^+$]) slightly increase with the acid concentration. The slopes of the plots of log k' *vs.* acidity functions are small, in particular much smaller than those observed for the reduction and racemization with halide ions of sulfoxides,[4] where a second proton intervenes before the rate-limiting step. They probably reflect a medium effect. Moreover, the dependence on the Bunnett and Olsen[20] acidity function, $H_0 + \log [H^+]$, shows slopes (ϕ values) in the range (−0.25 to −0.20) usually found for reactions in which the water molecule does not intervene in the transition state.[20]

The question arises as to whether the two reactions are independent or whether they represent a partition of a common intermediate.

The fragmentation reaction may be formulated in a simple way as in Scheme I.

Scheme I



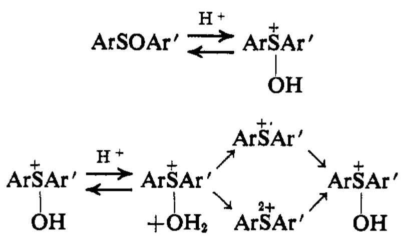
$$ArSO\text{-}tert\text{-}Bu + H^+ \rightleftharpoons Ar\overset{+}{S}(OH)\text{-}tert\text{-}Bu \longrightarrow ArSOH + tert\text{-}Bu^+ \longrightarrow \text{products}$$

The order in a_{H^+} observed and the structural effects both agree with the hypothesis of a simple unimolecular heterolysis of the protonated sulfoxide.

The racemization reactions may follow, in principle, a number of paths.[6] However, in the present case, they should satisfy two stringent requirements: absence of oxygen exchange and first-order dependence on acidity.

Oae suggested[21] that in concentrated sulfuric acid (>86%) the racemization occurs through a diprotonated sulfoxide which undergoes either homolysis to a cation radical or dehydration to a sulfide dication followed by a fast back reaction (Scheme II).

Scheme II

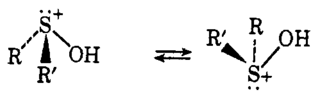


In less concentrated acid, the same author suggests[21] a nucleophilic attack by water on protonated sulfoxide (Scheme III).

Scheme III

Both schemes require oxygen exchange; Scheme II requires diprotonation of the sulfoxide, Scheme III intervention of the water molecule as nucleophile. None of these requirements are met by our experimental results.

Another possible mechanism is the pyramidal inversion of the protonated sulfoxide.

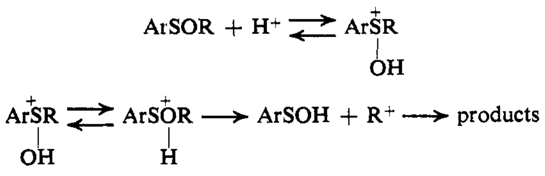


Mislow, *et al.*,[22] found that unprotonated sulfoxides undergo pyramidal inversion at 190–210°, with energies of activation of the order of 36–43 kcal/mol. It may well be that protonation would lower the energy barrier of the reaction. However, the intervention of pyramidal inversion in the system investigated seems unlikely because of the partial racemization at the alkyl chiral center, which accompanies the racemization at sulfur, and the relatively great importance of structural factors. In fact, the rates are slowed down by a factor of 50 by substituting in **1** the isopropyl group for the tertiary butyl group and by a factor of 2 by substituting the para tolyl for the phenyl group. This has to be compared with the small effects observed[22] in the thermal pyramidal inversion of sulfoxides.

In conclusion, the known mechanisms of racemization seem inadequate to explain our results. This, and the already pointed out similarity between racemization and fragmentation reactions, suggests that the route leading to racemization may be found within the framework of the path leading to fragmentation, which also means that the two reactions may in fact result from partition of a common intermediate into two reaction paths.

The two schemes reported below (Schemes IV and V)

Scheme IV



$$ArSOR + H^+ \rightleftharpoons Ar\overset{+}{S}(OH)R$$

$$Ar\overset{+}{S}(OH)R \rightleftharpoons ArS\overset{+}{O}(H)R \longrightarrow ArSOH + R^+ \longrightarrow \text{products}$$

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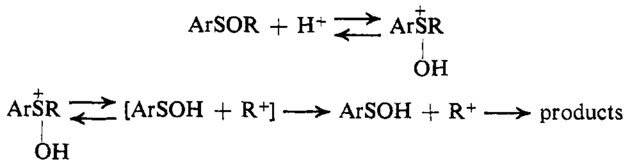
[20] J. F. Bunnett and F. P. Olsen, *Can. J. Chem.*, **44**, 1917 (1966).

[21] S. Oae, *Quart. Rep. Sulf. Chem.*, **5**, 53 (1970).

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

Scheme V



$$\mathrm{ArSOR} + \mathrm{H^+} \rightleftharpoons \mathrm{Ar}\underset{\mathrm{OH}}{\overset{+}{\mathrm{S}}}\mathrm{R}$$

$$\mathrm{Ar}\underset{\mathrm{OH}}{\overset{+}{\mathrm{S}}}\mathrm{R} \rightleftharpoons [\mathrm{ArSOH} + \mathrm{R^+}] \longrightarrow \mathrm{ArSOH} + \mathrm{R^+} \longrightarrow \text{products}$$

are in agreement with these premises and with all the other experimental results.

Scheme IV requires an intramolecular S → O migration of an alkyl group in the rate-determining step to afford an achiral protonated sulfenic ester, an intermediate which may then suffer a reverse intramolecular O → S shift of the alkyl group to give racemic sulfoxide, or decompose to sulfenic acid and alkyl cation. The sulfenic acid then disproportionates to disulfide and thiolsulfonate.[5,23,24] This mechanism would require that configuration be lost only at sulfur; however, we found significant racemization at carbon.

The rearrangement of sulfenic esters to sulfoxides has been studied by Mislow, *et al.*[25] The (−)-(*R*)-benzyl *α*-*d*-*p*-toluenesulfenate rearranges to (+)-benzyl-*α*-*d*-*p*-tolyl sulfoxide with 35% retention of configuration at carbon. This rearrangement has been thought to proceed by a benzyl O → S shift of an intramolecular type.[25]

Our findings, that the alkyl moiety of the *α*-phenylethyl phenyl sulfoxide retains 65–70% of its configuration while the sulfur center completely loses its optical activity, compare well with Mislow's results. However, intramolecular rearrangements usually occur with complete retention of configuration of the migrating group.[26]

Scheme V requires the dissociation of protonated sulfoxide in alkyl cation and sulfenic acid. Complete separation of the two fragments of the ion–molecule pair would require complete racemization of both centers before reverting to sulfoxide. However, if the alkyl cation and the sulfenic acid form an intimate ion–molecule pair, a certain degree of retention of configuration at carbon may be expected. Loss of chirality at sulfur may occur by rotation around the Ar–S bond or by formation of the sulfenate ester,[27] whereas racemization at carbon requires rotation of the cation. The latter process is known to be relatively slow in intimate pairs.[28]

Ion–molecule pairs have been suggested by Darwish, *et al.*,[29] as intermediates in the racemization of some sulfonium salts.

While Scheme IV cannot be, at this stage, completely rejected, Scheme V seems to better accommodate our results.

Recently, Baldwin, *et al.*,[30] observed chemically induced dynamic nuclear polarization (CIDNP) in the Stevens rearrangement of a sulfonium ylide. On this basis a radical pair has been proposed to explain the observed 36% retention of stereochemical integrity of the migrating site. Since Stevens and sulfenate rearrangements are of the same type,[30] a search for radical pairs in our reaction appeared worthwhile. However, the slowness of decomposition of *tert*-butyl phenyl sulfoxide in perchloric acid prevented us from observing any CIDNP effect.

Experimental Section

Solvents. The perchloric acid solutions were made up by dilution of the commercial concentrated product and titration with standard NaOH. The H_0 values were obtained by interpolation of published data.[31] The H_A values were kindly provided by Professor K. Yates.[32]

Racemic Sulfoxides. The racemic sulfoxides were synthesized by oxidation with H_2O_2 in methanol of the corresponding sulfides and carefully purified by column chromatography and by repeated crystallizations from petroleum ether. They had the following melting points: *tert*-butyl phenyl sulfoxide, mp 57–58° (lit.[33] 58–59°); *tert*-butyl *p*-tolyl sulfoxide, mp 68–69°. *Anal.* Calcd for $C_{11}H_{16}OS$: C, 67.30; H, 8.21; S, 16.33. Found: C, 68.09; H, 8.18; S, 16.30.

(+)-*tert*-Butyl Phenyl Sulfoxide (1). It was prepared in a 60% yield by Andersen's method,[34] from diasterochemically pure (−)-menthyl (−)-benzenesulfinate,[35] $[\alpha]^{25}\mathrm{D}$ −206.1 (*c* 2.0, acetone) and *tert*-butyl magnesium chloride, as described in the literature.[36] It had mp 88–89° (from hexane), $[\alpha]^{25}{}_{\mathrm{Hg}}$ +222.7 (*c* 1.5, ethanol), lit.[36] mp 88–89°, $[\alpha]^{20}\mathrm{D}$ +180.0 (*c* 2.0, ethanol).

(+)-Isopropyl Phenyl Sulfoxide. It was prepared as described for **1**. It had bp 101–102° (0.01 mm), $[\alpha]^{25}\mathrm{D}$ +170 (*c* 1.0, acetone).

(+)-*tert*-Butyl *p*-Tolyl Sulfoxide. It was synthesized in 60% yield from (−)-menthyl (−)-*p*-toluenesulfinate,[37] mp 108–109° (from acetone) $[\alpha]^{25}\mathrm{Hg}$ −239.9 (*c* 1.5, acetone), and *tert*-butyl magnesium chloride. It had mp 88–89° (petroleum ether), $[\alpha]^{25}\mathrm{Hg}$ +238.9 (*c* 1.3, ethanol), lit.[17] mp 89.5–90°, $[\alpha]\mathrm{D}$ +190.0 (ethanol).

^{18}O-Labeled *tert*-butyl phenyl sulfoxide was prepared following Montanari, *et al.*,[16] by oxidation of the corresponding sulfide (bp 44° (0.35 mm)) with iodobenzene dichloride.

Iodobenzene dichloride[38] (60 mmol), dissolved in 5 ml of anhydrous pyridine, was added under nitrogen to a cooled solution (−40°) of enriched water (60 mmol, ^{18}O content about 10 atom %) and *tert*-butyl phenyl sulfide (60 mmol) in 5 ml of anhydrous pyridine. After the addition, the solution was kept for 2 hr at −40°, then warmed at room temperature, diluted with water, and extracted with chloroform. The chloroform solution was then washed (diluted HCl and water), dried (Na_2SO_4), and concentrated under reduced pressure. The sulfoxide, purified by column chromatography (yield 45%) had an ^{18}O atom content of 8.2 ± 0.3 %, as evaluated by mass spectroscopic analysis. The conditions used for the analysis on a Hitachi Perkin-Elmer RMU-6D mass spectrometer were: electron accelerating voltage, 60 eV; temperature of ionization source, 100°; temperature of vaporization, 60°.

The enrichment was evaluated from the ratio of the $m + 2$ and m peaks, allowing for natural abundance of the $m + 2$ peak.

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(−)- and (+)-α-Phenylethyl Phenyl Sulfoxides (4a and 4b). The title compounds were synthesized from (−)-menthyl (−)-benzenesulfinate[36] and α-phenylethyl magnesium chloride. The diastereomeric sulfoxides were separated by repeated column chromatography on silica and eluent petroleum ether–ethyl ether (4:1). The separation was monitored by pmr since the two sulfoxides have different chemical shifts for the CH proton, in respect to tetramethylsilane in deuteriochloroform.

The physical constants were: **4a**, mp 71–72° (from petroleum ether (bp 30–60°)); $[\alpha]^{25}\mathrm{D}$ −9.45 (*c* 1.5, acetone); pmr τ 8.3 PCH_3, d), 6.2 (P*CH*, q), ~2.5–3.1 (aromatic, m) (*Anal.* Calcd for $C_{14}H_{14}OS$: C, 73.00; H, 6.13; S, 13.92. Found: C, 72.90; H, 6.23; S, 14.06); **4b**, mp 89–90° (from petroleum ether); $[\alpha]^{25}\mathrm{D}$ +204.2 (*c* 1.5, acetone); pmr τ 8.4 (PCH_3, d), 6.0 (P*CH*, q), 2.5–3.1 (aromatic, m) (*Anal.* Calcd for $C_{14}H_{14}OS$: C, 73.00; H, 6.13; S, 13.92. Found: C, 73.11; H, 6.18; S, 14.08).

(−)-α-Phenylethyl phenyl sulfone (5a) was obtained by oxidation with *m*-chloroperoxybenzoic acid of **4a**. It crystallizes from methanol: mp 119–120°; $[\alpha]^{25}\mathrm{D}$ −100.8 (*c* 1.8, acetone), −104.6 (*c* 1.7, methanol). *Anal.* Calcd for $C_{14}H_{14}O_2S$: C, 68.26; H, 5.73; S, 13.02. Found: C, 68.06; H, 5.83; S, 13.16.

(+)-α-Phenylethyl phenyl sulfone (5b) was synthesized by oxidation with the *m*-chloroperoxybenzoic acid of **4b**. Crystallized from methanol it had: mp 119–120°; $[\alpha]^{25}\mathrm{D}$ +98.5 (*c* 1.2, acetone), +130.0 (*c* 1.0, methanol); lit.[18] $[\alpha]^{30}\mathrm{D}$ +94.0 (*c* 1.5, methanol).

Assignment of Configuration to 4a and 4b. The levorotatory menthyl sulfinates (see Chart I) have been reported to have the *S* configuration at the sulfur atom.[17] Since the Grignard reaction with α-phenylethyl magnesium bromide occurs with inversion of configuration,[17] both **4a** and **4b** have the *R* configuration at sulfur.

The oxidation of sulfoxides **4** yields sulfones **5** without affecting the configuration at carbon. To the dextrorotatory sulfone (**5b**) Corey, *et al.*,[18] assigned the *R* configuration.

It follows that **5a** has the *S* configuration at carbon and hence **4a** has the R_S, S_C configuration and **4b** the R_S, R_C.

Product Analysis of the Reaction of *tert*-Butyl Phenyl Sulfoxide in Acid Solutions. The *tert*-butyl phenyl sulfoxide (**1**) (250 mg) was dissolved in $HClO_4$, 6 *M* (50 ml), and kept at 25°. After a few days a white precipitate (diphenyl disulfide) appeared. The reaction was continued for 35 days. Then the solution was neutralized with sodium carbonate and extracted several times with chloroform. The chloroform solution was dried (Na_2SO_4), the solvent distilled under reduced pressure, and the residue chromatographed on silica, eluent petroleum ether–ethyl ether (6:4). Three major products were isolated and characterized by comparison (ir and mixture melting point) with authentic samples. They were: diphenyl disulfide (**2**) (55 mg), mp 59–61°, lit.[39] mp 61.5°; phenyl benzenethiolsulfonate (**3**) (34 mg), mp 44–46°, lit.[40] 45–46°; and *tert*-butyl phenyl sulfoxide (**1**) (29 mg), mp 57–58°.

In a similar experiment, **1** (1.0 g) was kept for 64 hr in 8.9 *M* perchloric acid. After work-up, the chromatographic analysis yielded diphenyl disulfide **2** (0.29 g) and sulfoxide **1** (0.59 g) as major products. The thiolsulfonate **3** was present only in trace amounts.

Reactions of α-Phenylethyl Phenyl Sulfoxide. α-Phenylethyl phenyl sulfoxide (**4c**) (0.7 g) (mp 89–90°, $[\alpha]^{25}\mathrm{D}$ +197.2 (*c* 1.5, acetone)), was dissolved in 25 ml of a mixture (60:40) of $HClO_4$ (8.9 *M*) and dioxane and kept at 25° for 42 hr. The solution was neutralized (Na_2CO_3) and extracted several times with chloroform. The chloroform was distilled off at reduced pressure and the residue chromatographed on silica, eluent petroleum ether–ethyl ether (1:1). Together with some amount of diphenyl disulfide (**2**) and phenyl benzenethiolsulfonate (**3**) (not analyzed) we recovered 0.4 g of a sulfoxide **4d**, $[\alpha]^{25}\mathrm{D}$ +130.1 (*c* 1.5, acetone).

The oxidation with *m*-chloroperoxybenzoic acid of **4c** and **4d** gives the sulfones **5c**, $[\alpha]^{25}\mathrm{D}$ +96.8 (*c* 0.8, acetone), and **5d**, $[\alpha]^{25}\mathrm{D}$ +79.0 (*c* 0.73, acetone), respectively.

A similar reaction was run with 0.73 g of sulfoxide **4e**, $[\alpha]^{25}\mathrm{D}$ +168.0 (*c* 1.5, acetone). It afforded, after 47 hr, 0.275 g of a sulfoxide **4f**, $[\alpha]^{25}\mathrm{D}$ +101.4 (*c* 0.8, acetone).

The oxidation of **4e** and **4f** gives sulfones **5e**, mp 114–116°, $[\alpha]^{25}\mathrm{D}$ +82.1 (*c* 0.7, acetone), and **5f**, mp 108–110°, $[\alpha]^{25}\mathrm{D}$ 64.1 (*c* 0.6, acetone), respectively.

The contribution to the specific activities by the SO and alkyl groups was evaluated as described and reported in the Results (see Tables IV and V).

pK_a of *tert*-Butyl Phenyl Sulfoxide. The uv spectra were recorded on a Cary 15 spectrophotometer in a 1-cm thermostated cell. The data were analyzed following the methods of Davis and Geissman[10] and Hammett, *et al.*[11]

The Davis and Geissman method[10] involves using data obtained at two wavelengths, close to the points of maximal difference between the extinction coefficient of the un-ionized and ionized forms. The two wavelengths characteristic of the *tert*-butyl phenyl sulfoxide were at 220 and 236 nm. Plots of the difference of optical densities (OD) at these wavelengths against acidity functions gave sigmoids from which the protonated:free base ratio could be evaluated with the usual formula.[13]

The Hammett method[11] involves shifting absorption curves laterally until they all intersect at a common point, as they theoretically should in the absence of medium effects. Ionization ratios are then calculated from OD values based on these shifted curves. This method involves arbitrariness in deciding how to shift experimental absorption curves to produce an approximate isosbestic point. Different isosbestic points can be chosen: we used the OD values at 225 nm for the isosbestic at 218 nm and those at 235 nm for the isosbestic at 221 nm. Plots of OD values against acidity functions give sigmoid curves from which we evaluated the protonated:free base ratio.

Since the sulfoxides obey with reasonable accuracy the H_A acidity function,[4,9] we obtained the pK_a value of the *tert*-butyl phenyl sulfoxide from conventional plots of[8] log $[SOH^+]/[SO]$ *vs.* $-H_A$. The data are collected in Table VI.

Table VI. pK_a Values of *tert*-Butyl Phenyl Sulfoxide Evaluated from Uv Measurements in Aqueous Perchloric Acid at 25°

Method	pK_a	Slope[a]
Davis and Geissman	−2.18	0.88
Isosbestic point at 218 nm	−2.19	1.22
Isosbestic point at 221 nm	−2.20	0.93

[a] pK_a values and slopes were obtained by least-squares analysis of plots of log $[SOH^+]/[SO]$ *vs.* $-H_A$. We found correlation coefficients better than 0.99.

Even if corrections for medium effect on uv spectra are made on an empirical basis, both methods above described give similar results and the pK_a values obtained are well in the limit of precision of 0.2 pK_a unit usually found in such measurements.[9]

The CD spectra were taken on a Roussell-Jouan 185 Model II Dichrograph. The evaluation of the data has been reported elsewhere.[13]

The nmr technique, described for other sulfoxides,[9] cannot be used with the *tert*-butyl phenyl sulfoxide since the difference in chemical shifts of the alkyl group of the protonated and free base is too small (1–2 Hz).

Kinetic Experiments. The numerical evaluation of reaction rates required the use of the usual relationship for first-order reactions,[41] whereas different experimental techniques were used for the various rate measurements.

Overall Reaction Rate (k_α). The overall reaction rate was evaluated by following polarimetrically the loss of optical activity of the substrate. About 0.3 g of sulfoxide was dissolved in 25 ml of thermostated aqueous perchloric acid of the desired concentration. Aliquots were withdrawn at various times from the thermostated solution, filtered through Millipore BDWP (the reaction products are only sparingly soluble in aqueous acids), and transferred in a sample cell of Bendix NPL 143C automatic polarimeter. The rotations were recorded at 25°.

Rate of Decomposition (k_d). About 0.5 g of racemic sulfoxide was dissolved in 25 ml of $HClO_4$ of the desired concentration, thermostated at 25°. Aliquots of 2 ml were withdrawn at various times, poured into 70 ml of 2% KOH in water, and extracted three times with 25 ml of $CHCl_3$. In such conditions a blank test assured complete recovery of *tert*-butyl aryl sulfoxides. The chloroform solution was dried (Na_2SO_4) and the solvent was removed. The residual was dissolved in CCl_4 and quantitatively transferred to a

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5-ml flask which was then filled to the mark. The CCl_4 solution was examined in a 1-mm BaF_2 cell with a Perkin-Elmer ir spectrophotometer for the intensity of the band at 1090 cm^{-1}.

Rate of Racemization (k_r). About 1.5 g of optically active sulfoxide of known specific activity was dissolved in 25 ml of thermostated aqueous perchloric acid. Two or three aliquots were withdrawn at various times, diluted with water, neutralized, and extracted with chloroform. The residual obtained from distillation under reduced pressure of the solvent was chromatographed on silica and eluent petroleum ether–ethyl ether (1:1). The specific activity of the recovered sulfoxide was measured polarimetrically.

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Cyclic Sulfimides and Sulfoximides

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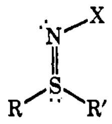
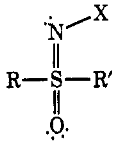
Abstract: Thian-1-imide (**3**) has been synthesized and found to have a slight excess (55/45 at −85°) of the imide functionality in the equatorial position, in contrast to the isoelectronic thiane 1-oxide (**9**), which favors an axial orientation of the oxide functionality. The *N*-tosyl- (**6**) and *N*-benzenesulfonyl (**7**) derivatives of **3**, however, favor the axial imide conformation. Configurational criteria for the imide functionality on sulfur are developed on the basis of the chemical-shift difference and the coupling constant between the α protons. The resonances of the α or γ protons in these compounds (β positions deuterated) change from one averaged AB spectrum at room temperature to two distinct AB spectra at −90°, corresponding to the axial and equatorial imide conformers. The equilibrium constants are obtained directly from the spectra. Complete line-shape analyses of the spectral changes have produced activation parameters for ring reversal in thian-1-imide (**3**), thian-1-(*N*-tosyl)imide (**6**), thian-1-imide 1-oxide (**5**), and thian-1-(*N*-tosyl)imide 1-oxide (**8**).

The sulfimide[2] functional class **1** is the isoelectronic nitrogen analog of sulfoxides. The sulfur atom is pyramidal, with two aliphatic or aromatic substituents, one nonbonding electron pair, and the imide functionality. The S–N bond probably possesses some double-bond character due to $(p\text{–}d)_\pi$ bonding, but to a lesser extent than the S–O bond in sulfoxides. The sulfoximide class **2** bears a similar relationship to sulfones. In recent years there has been considerable effort in developing new preparative methods for these functionalities and in defining the stereochemistry of their reactions at sulfur.[3] In this paper we report the fundamental conformational properties of the sulfimide and sulfoximide functionalities incorporated into a six-membered ring.



1



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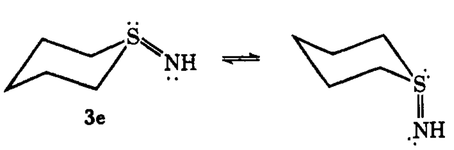
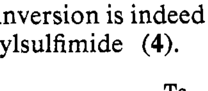
Three limiting conformational modes of interconversion are available to thian-1-imide (**3**) and its derivatives. (1) Ring reversal equilibrates the axial and equatorial forms (eq 1). The equilibrium constant is determined by the various interactions of the imide group with the rest of the molecule, and the activation energy to reversal depends on the torsional properties of the ring bonds. The nmr spectrum should be sensitive to this process,[4] with the room-temperature spectrum a weighted average for the two conformers and the low-temperature spectrum a set of discrete resonances for each. (2) Pyramidal inversion about sulfur should be slow on the nmr time scale.[3,5] This process therefore need not be considered in interpreting any temperature variation in the spectrum. To make certain that sulfur inversion is indeed slow, we examined *N*-tosylbenzylmethylsulfimide (**4**). Slow inversion is



3e **3a** (1)



$$C_6H_5CH_2\text{—}\overset{\overset{\displaystyle\ddot{N}\text{—}Ts}{\|}}{\ddot{S}}\text{—}CH_3$$

4

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[1] (a) This work was supported by the National Science Foundation (Grants GP-9257 and GP-22942), the Advanced Research Projects Agency of the Department of Defense through the Northwestern University Materials Research Center, and the Petroleum Research Fund, administered by the American Chemical Society (Grant No. 2970-AC4,5); (b) National Science Foundation Trainee, 1968–1969.

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