to 60°. The mixture was refluxed for 30 min, cooled, and made basic with aqueous sodium bicarbonate. The nonacidic fraction was extracted with ether and the ether solution washed successively with dilute hydrochloric acid and water. After drying with anhydrous sodium sulfate and filtration, the ether was evaporated to yield the crude product (2.0 g). A small sample was injected into a 6-ft silicone rubber column at 150° and a pure sample of 1-cyanonaphthalene-2,4-d_2 was obtained; crystals (mp 36–37°) formed on standing. The percentages of isotopic incorporation were: d_0, 14.3%; d_1, 5.0%; d_2, 78.0%; d_3, 2.7%.

2-Cyanonaphthalene-1,3-d_2 was prepared from 2-naphthylamine hydrochloride in a manner exactly analogous to the above. The percentages of isotopic incorporation were: d_0, 7.8%; d_1, 5.6%; d_2, 85.0%; d_3, 1.6%.

Benzothiophene-2,3-d_2. 2,3-Dibromobenzothiophene (1.46 g) in benzene (5 ml) was added dropwise with stirring into a solution of phenyllithium in ether (prepared from 430 mg of lithium and 3.2 g of phenyl bromide in 20 ml of ether at room temperature) under an atmosphere of nitrogen. The mixture was heated at 45° for 6 hr and then was kept stirring at room temperature for another 12 hr. Organic material was isolated from the reaction in the usual manner and then dissolved in petroleum ether (bp 40–60°). The solution was filtered through a column of alumina and the light yellow liquid obtained from the first two fractions was rechromatographed

in the same manner. Benzothiophene-2,3-d_2 (304 mg, d_1, 2%; d_2, 98%) was obtained as a low-melting colorless crystalline solid (mp 30–32°) from the first two fractions off the column.

Thiazole-2-d_1. Methylmagnesium bromide in ether (14 ml) was prepared from magnesium (365 mg) and methyl bromide (1.2 g). 2-Bromothiazole (820 mg) in ether (4 ml) was added dropwise with stirring. After 1 hr, deuterium oxide (1 ml) was added and the ethereal solution separated. Evaporation of the ether and distillation of the residue gave thiazole-2-d_1 (40 mg, d_0, 2%; d_1, 98%) as a colorless liquid, bp 110–114°.

Benzothiazole-2-d_1. Benzothiazole (250 mg) was added to a solution of sodium deuterioxide (80 mg) in deuterium oxide (1.0 ml), and the mixture was heated on a water bath at 60° with stirring for 12 hr. The solvent was removed and the heating repeated with a fresh sample of deuterium oxide. The organic material was isolated in the usual manner to give benzothiazole-2-d_1 (168 mg, d_0, 4%; d_1, 96%), bp 108–112° (18 mm).

The Relative Nucleophilicity of Some Common Nucleophiles toward Sulfenyl Sulfur. The Nucleophile- and Acid-Catalyzed Racemization of Optically Active Phenyl Benzenethiolsulfinate[1]

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Abstract: In acidic aqueous dioxane in the absence of added nucleophiles optically active phenyl benzenethiolsulfinate, (+)-I, racemizes only very slowly, but the addition of small amounts of alkyl sulfides, halide ions, or thiocyanate ion leads to quite rapid racemization of (+)-I. The racemization reaction is first order in both nucleophile and hydrogen ion; its solvent isotope effect indicates that it is specific H^+ catalyzed. Although only the acid- and nucleophile-catalyzed racemization of (+)-I occurs in their absence, addition of sulfinic acid or mercaptan to such aqueous dioxane solutions leads to the disappearance of I via acid- and nucleophile-catalyzed reactions with the sulfinic acid or mercaptan. The formal kinetics and the rate constants of these latter reactions are exactly the same under a given set of conditions as those for racemization, indicating that all the processes have the same rate-determining step. The only satisfactory mechanism which can accommodate these observations is the one shown in Chart I. This involves a rate-determining attack of the nucleophilic catalyst on the sulfenyl sulfur of sulfinyl-protonated I. This means that data on the relative reactivity of various nucleophiles as catalysts for the racemization (Table V) provide a quantitative measure of the relative reactivity of these species in a substitution at sulfenyl sulfur. Comparison of such data with data (Table VI) for the relative reactivity of the same nucleophiles in substitutions at sulfinyl sulfur and peroxide oxygen shows not only that sulfenyl sulfur is, as expected, a "softer" electrophilic center than sulfinyl sulfur but also that it is about as "soft" as peroxide oxygen. The latter was not expected on the basis of previous predictions.

Optically active phenyl benzenethiolsulfinate (I) can be prepared by asymmetric oxidation of phenyl disufide with an optically active peracid.[2a,b]

$$(+)\text{-PhSSPh}$$
$$\overset{\|}{O}$$
$$(+)\text{-I}$$

In aqueous dioxane this thiolsulfinate undergoes a facile nucleophile- and acid-catalyzed racemization which forms the subject of the present paper.[2c] This racemization is of interest for two reasons. First, it represents another example of cooperative electrophilic and nucleophilic catalysis of the scission of a sulfur-sulfur bond.[3] Second, and more important, the data obtained for various nucleophiles as catalysts provide a quantitative measure of the relative reactivity of these

(1) This research was supported by the National Institutes of Health under Research Grant GM-12104.

(2) (a) J. L. Kice and G. B. Large, *Tetrahedron Letters*, 3537 (1965); (b) W. E. Savige and A. Fava, *Chem. Commun.*, 417 (1965); (c) A. Fava and P. Koch (private communication) have studied the purely thermal racemization of (+)-I and also the racemization as catalyzed by nucleophiles alone in aprotic solvents. Under the reaction conditions used in the present work both of these reactions are much slower than the acid- and nucleophile-catalyzed racemization of (+)-I.

(3) (a) J. L. Kice and E. H. Morkved, *J. Am. Chem. Soc.*, **86**, 2270 (1964); (b) J. L. Kice and G. Guaraldi, *ibid.*, **88**, 5236 (1966); **89**, 4113 (1967); (c) J. L. Kice, C. G. Venier, and L. Heasley, *ibid.*, **89**, 3557 (1967). (d) For a general review see J. L. Kice, *Accounts Chem. Res.*, **1**, 58 (1968).

Table I. Racemization of (+)-I as Catalyzed by Various Anions in 60% Dioxane at 39.1° [a]

Run	Nucleophile	$(Nu^-) \times 10^2$, M	$(HClO_4)$, M	$(LiClO_4)$, M	$k_\alpha \times 10^4$, sec^{-1}	$[(k_\alpha - k_\alpha^0)/(Nu^-)]$[b]
1	I⁻	0.020	0.10	0.00	26	13
2		0.015	0.10	0.00	20	13
3		0.010	0.10	0.00	13	13
4			0.10	0.40	7.8	7.8
5			0.20	0.30	16	16
6			0.05	0.45	4.0	4.0
7	SCN⁻	0.20	0.02	0.00	28	1.4
8		0.10	0.02	0.00	14	1.4
9		0.05	0.02	0.00	7.1	1.4
10		0.10	0.02	0.48	6.3	0.63
11			0.01	0.49	3.3	0.33
12			0.005	0.495	1.7	0.17
13			0.03	0.47	9.3	0.93
14			0.05	0.45	13	1.3
15	Br⁻	3.0	0.10	0.00	10	0.034
16		2.0	0.10	0.00	6.8	0.034
17		1.5	0.10	0.00	5.5	0.036
18		1.0	0.10	0.00	3.6	0.036
19			0.10	0.40	1.9	0.019
20			0.20	0.30	3.8	0.038
21			0.30	0.20	5.7	0.057
22			0.40	0.10	7.9	0.079
23			0.50	0.00	10	0.10
24			0.00	0.00	0.04	
25	Cl⁻	10.0	0.40	0.00	2.3	0.0023
26			0.30	0.10	1.8	0.0018
27			0.20	0.20	1.3	0.0013
28			0.10	0.30	0.60	0.00056

[a] Thiolsulfinate concentration 0.05 M in all runs. [b] k_α^0 is the rate of racemization of (+)-I in the absence of added nucleophile and equals 0.04×10^{-4} sec^{-1} under these conditions.

species in a substitution at sulfenyl sulfur. Comparison of such data with data[4] for the relative reactivity of the same nucleophiles in a substitution at sulfinyl sulfur allows one to draw conclusions regarding the relative importance of the polarizability and basicity of a nucleophile in determining its reactivity in substitutions at these two different sulfur centers in a protic solvent, and thus provides a test of predictions made earlier by Edwards and Pearson[5] regarding such systems.

Results

Optically active phenyl benzenethiolsulfinate, (+)-I, was prepared by oxidation of phenyl disulfide with (+)-percamphoric acid in chloroform.[2a,b] The $[\alpha]_{436}$ in dioxane of the various samples of (+)-I used for the

$$PhSSPh \xrightarrow[\text{acid, } -5°]{\text{(+)-percamphoric}} (+)\text{-PhSSPh}$$
$$\underset{\underset{\text{(+)-I}}{O}}{\overset{\|}{}}$$
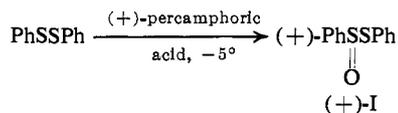
racemization studies ranged from +8.5 to +14.0°.

Racemization of (+)-I in 60% Dioxane. In 60% dioxane (v/v) containing 0.10–0.50 M perchloric acid, (+)-I (0.05 M) racemizes only very slowly at 39.1° ($k_\alpha = 4.3 \times 10^{-6}$ sec^{-1}) at a rate which seems to be independent of the concentration of perchloric acid.[6] Addition of very small amounts (10^{-2} to 10^{-4} M) of such nucleophiles as iodide, bromide, or thiocyanate ion to such acidic solutions results in a dramatic in-

(4) (a) J. L. Kice and G. Guaraldi, *Tetrahedron Letters*, 6135 (1966); (b) *J. Am. Chem. Soc.*, 90, 4076 (1968).

(5) J. O. Edwards and R. G. Pearson, *ibid.*, 84, 16 (1962).

(6) The rate of this acid-independent racemization of (+)-I is in good agreement with the rate of purely thermal racemization of (+)-I in polar solvents found by Fava and Koch.[2c]

crease in the rate of loss of optical activity. That this is due entirely to the racemization of (+)-I and not to the disappearance of the thiolsulfinate through any chemical reaction is demonstrated by the fact that loss of optical activity is *not* accompanied by any change in the ultraviolet spectrum of the solution. Were the thiolsulfinate, which absorbs much more strongly in the ultraviolet than its usual decomposition products, undergoing any chemical reaction, such as disproportionation to thiolsulfonate and disulfide,[7] loss of optical activity would be accompanied by a pronounced change in the absorption spectrum of the solution.

Kinetics of the Nucleophile- and Acid-Catalyzed Racemization of (+)-I. Two different types of nucleophiles have been studied as catalysts for the racemization. The results for the first group, which consisted of a series of common anions, are summarized in Table I. The second set of nucleophiles used as catalysts consisted of a group of alkyl sulfides. The results with these are shown in Table II. The sulfides were studied principally to provide evidence as to the exact relationship between the acid- and nucleophile-catalyzed racemization and other acid- and nucleophile-catalyzed reactions of thiolsulfinates. The latter have been studied[3c,8] using alkyl sulfides as the nucleophiles.

The following aspects of the kinetics of the racemizations catalyzed by the various nucleophilic anions (Table I) seem worth noting. Sets of runs with iodide (runs 1–3), thiocyanate (runs 7–9), and bromide (runs 15–18) in which only the concentration of the nucleophilic anion was varied show that the rate of racemization of (+)-I, k_α, depends on the first power of

(7) E. Vinkler and F. Klivenyi, *Acta Chim. Acad. Sci. Hung.*, 22, 345 (1960); D. Barnard, *J. Chem. Soc.*, 4675 (1957).

(8) J. L. Kice and G. B. Large, *J. Org. Chem.*, 33, 1940 (1968).

Table II. Alkyl Sulfide Catalyzed Racemization of (+)-I in 60% Dioxane at 39.1° [a]

Run	Sulfide	$(R_2S) \times 10^2$, M	$(HClO_4)$, M	$(LiClO_4)$, M	$k_\alpha \times 10^4$, sec⁻¹	k_8 [b]
29	n-Bu₂S	0.20	0.10	0.00	2.6	0.13
30		0.10	0.10	0.00	1.38	0.13
31					2.48 (D₂O)	0.24
32			0.20	0.00	3.9	0.39
33			0.30	0.00	7.8	0.78
34			0.40	0.00	14	1.4
35			0.50	0.00	24	2.4
36			0.10	0.40	4.5	0.45
37			0.20	0.30	8.7	0.87
38	(PhCH₂)₂S	1.0	0.10	0.00	0.81	0.0077
39	(HOOCCH₂CH₂)₂S	10.0	0.10	0.00	2.7	0.0027

[a] All runs at a thiolsulfinate concentration of 0.05 M. [b] $k_8 = [(k_\alpha - k_\alpha^0)/(R_2S)]$. k_α^0 is the rate of racemization of (+)-I in the absence of sulfide under otherwise identical conditions. See footnote b of Table I for its value.

nucleophile concentration in all cases investigated. This is proved by the constancy of $[(k_\alpha - k_\alpha^0)/(Nu^-)]$ within each set of runs. Because experiments at a fixed perchloric acid concentration with added lithium perchlorate (runs 3 and 4, 8 and 10, and 18 and 19) showed that the rates of the various anion-catalyzed racemizations were all subject to large salt effects, k_α being markedly lower at higher ionic strengths, the dependence of k_α on perchloric acid concentration was investigated for all cases in runs carried out at a fixed ionic strength of 0.5. As Figure 1 shows, under such conditions k_α responds linearly to increasing hydrogen ion concentration, demonstrating that the anion-catalyzed racemizations are also acid catalyzed.[9] Note also that the plots in Figure 1 show no detectable intercept at $(H^+) = 0.00$ M, indicating that the only important pathway for racemization of (+)-I under these conditions is one involving catalysis by both nucleophile and acid. This conclusion was verified by a run with bromide (run 24) at $(H^+) = 0.00$ M. All of the results for the various anion-catalyzed racemizations thus indicate that k_α depends on acid and nucleophile concentration in the following manner.

$$k_\alpha - k_\alpha^0 = k_{Nu}'(H^+)(Nu^-) \quad (1a)$$

The formal kinetics of the sulfide-catalyzed racemization are quite similar. The variation of k_α with sulfide concentration (runs 29 and 30, Table II) shows that the sulfide-catalyzed racemization, like that induced by anions, depends on the first power of the sulfide concentration. At a fixed hydrogen ion concentration there is a marked increase in k_α with an increase in ionic strength (runs 30 and 36). Runs carried out at a fixed ionic strength with varying (H^+) (runs 35–37) show, however, that under these conditions k_α for the sulfide-catalyzed racemization, like the rate constants for the various anion-catalyzed racemizations, varies linearly with (H^+) (curve E, Figure 1). The dependence of k_α on sulfide and acid can thus be expressed as

$$k_\alpha - k_\alpha^0 = k_S'(R_2S)(H^+) \quad (1b)$$

The solvent isotope effect, $(k_{H_2O}/k_{D_2O}) = 0.54$, associated with the sulfide-catalyzed racemization (runs 30 and 31) suggests that the acid catalysis is of the specific hydrogen ion variety. The dependence of k_S

(9) Because of the basicity of SCN⁻ the dependence of k_α on (H⁺) for that system had to be investigated at perchloric acid concentrations of 0.03 M or less in order to avoid acidities where protonation of the nucleophile would be important.
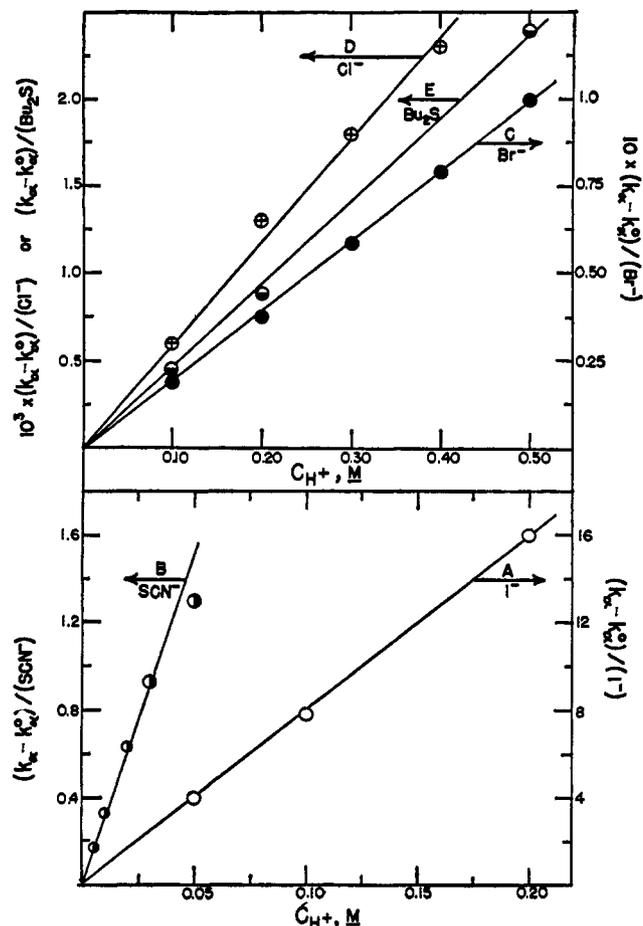

Figure 1. Variation of racemization rate with perchloric acid concentration. All runs at a constant ionic strength of 0.50: curve A, I⁻-catalyzed racemization, O; curve B, SCN⁻-catalyzed racemization, ◐; curve C, Br⁻-catalyzed racemization, ●; curve D, Cl⁻-catalyzed racemization, ⊕; curve E, n-Bu₂S-catalyzed racemization, ◓.

on sulfide structure (runs 30, 38, and 39) indicates that electron-withdrawing substituents in the R groups of R_2S decrease the reactivity of a sulfide, and it is similar to the variation of reactivity with sulfide structure which has been found previously[3c] for the sulfide-catalyzed thiolsulfinate–sulfinic acid reaction.

Sulfide Catalysis of the Reaction of I with a Sulfinic Acid. In acidic aqueous dioxane phenyl benzenethiolsulfinate reacts with arylsulfinic acids $(ArSO_2H)$,

just as it does in acetic acid–water.[3c] The disappearance of the thiolsulfinate can be followed spectrophotometrically. The significant point, as far as the present study is concerned, is that this I–sulfinic acid reaction can be catalyzed by added alkyl sulfides, just as was the case in acetic acid–water.[3c] As in acetic acid–water the rate of the sulfide-catalyzed reaction is first order in sulfide and thiolsulfinate, but *independent* of sulfinic acid concentration. Within experimental error the kinetics and rate of the sulfide-catalyzed $ArSO_2H$–I reaction in aqueous dioxane are *identical* with those for the sulfide-catalyzed racemization of (+)-I under the same conditions. This can be seen by comparison of the data in Table III (which shows rate data for the

Table III. Alkyl Sulfide Catalyzed I–Sulfinic Acid Reaction in 60% Dioxane at 39.1° [a]

Sulfide	$(R_2S) \times 10^2$, M	$(HClO_4)$, M	$k_1 \times 10^4$,[b] sec^{-1}	k_S[c]
None	0.00	0.30	3.3	
		0.50	3.4	
		0.10	3.2	
n-Bu$_2$S	0.10	0.30	11.4	0.81
	0.20	0.30	18	0.74
		0.50	46	2.1
		0.10	6.1	0.14

[a] All runs at $(I)_0 = 1.46 \times 10^{-4}$ M and $(C_6H_5SO_2H) = 1.2 \times 10^{-3}$ M. Other experiments (not shown) at different sulfinic acid concentration show that k_S is independent of sulfinic acid concentration. [b] k_1 equals experimental first-order rate for disappearance of I. [c] $k_S = [(k_1 - k_1^0)/(R_2S)]$. k_1^0 equals rate of disappearance of thiolsulfinate in the absence of sulfide under otherwise identical conditions. For values used see runs in first part of table.

sulfide-catalyzed I–$ArSO_2H$ reaction) with appropriate data in Table II for the sulfide-catalyzed racemization. The obvious conclusion is that the sulfide-catalyzed I–$ArSO_2H$ reaction and the sulfide-catalyzed racemization of (+)-I involve the same rate-determining step. Given the similar kinetics observed for the sulfide-catalyzed I–$ArSO_2H$ reaction in acetic acid–water and 60% dioxane, it also seems likely that this rate-determining step is the same one as in acetic acid–water.[3c]

Bromide Ion Catalysis of the Reaction of I with a Sulfinic Acid. Experiments with 0.01 M added bromide ion in 60% dioxane–0.3 M HClO$_4$ reveal that this species, like the sulfide, catalyzes the reaction of I with an arylsulfinic acid, and that the rate of this bromide ion catalyzed I–$ArSO_2H$ reaction is exactly the same as the rate of bromide-catalyzed racemization of (+)-I. The correspondence of the rates of the two nucleophile-catalyzed reactions is therefore not restricted to the sulfides alone but extends to the anionic catalysts of Table II as well.

Sulfide Catalysis of the Reaction of I with a Mercaptan. Aryl thiolsulfinates react with mercaptans as shown in eq 2.[10] Kinetic studies[8] of this reaction in

$$PhSSPh + 2R'SH \longrightarrow 2PhSSR' + H_2O \qquad (2)$$
$$\overset{\|}{\underset{O}{}}$$
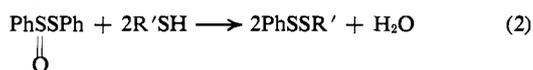
acetic acid–water have shown that it can be catalyzed by added alkyl sulfides *via* exactly the same mechanism as is involved in sulfide catalysis of the I–$ArSO_2H$ reaction[3c] in that medium.

(10) A Schöberl and H. Gräfje, *Ann.*, **617**, 71 (1958).

If in acidic aqueous dioxane the sulfide-catalyzed racemization of (+)-I and the sulfide-catalyzed I–$ArSO_2H$ reaction do indeed have the same rate-determining step, the I–mercaptan reaction should also be subject to catalysis by added sulfides in this solvent, and, more important, the rate of the sulfide-catalyzed process should be the same as the rate of racemization of (+)-I. This point was investigated by studying catalysis of the reaction of n-butyl mercaptan with I by added n-butyl sulfide. The results (Table IV)

Table IV. Alkyl Sulfide Catalyzed I–Mercaptan Reaction in 60% Dioxane at 39.1° [a]

Sulfide	$(R_2S) \times 10^2$, M	$(HClO_4)$, M	$k_1 \times 10^4$,[b] sec^{-1}	k_S[c]
None	0.00	0.30	0.13	
		0.20	0.14	
n-Bu$_2$S	0.10	0.30	7.6	0.75
	0.20	0.30	14.9	0.74
		0.20	7.5	0.37

[a] All runs at $(I)_0 = 1.56 \times 10^{-4}$ M and $(n$-BuSH$) = 3.12 \times 10^{-3}$ M. [b] k_1 equals experimental first-order rate constant for disappearance of I. [c] $k_S = [(k_1 - k_1^0)/(R_2S)]$. k_1^0 equals rate of disappearance of I in the absence of sulfide under otherwise identical conditions. For values used see runs in first section of table.

show clearly that k_S as estimated from data for the sulfide-catalyzed I–mercaptan reaction is indeed the same, within experimental error, as k_S for the sulfide-catalyzed racemization (Table II). In acidic 60% dioxane three different sulfide-catalyzed processes—racemization of (+)-I, and the reaction of I with either mercaptan or sulfinic acid—all, therefore, have the same rate-determining step.

Discussion

The Mechanism of the Acid- and Nucleophile-Catalyzed Racemization of (+)-I. Besides being consistent with the formal kinetics (eq 1) of the reaction, any acceptable mechanism for the nucleophile- and acid-catalyzed racemization of (+)-I must also be able to accommodate the following facts. Although only racemization of (+)-I occurs in their absence, in the presence of either sulfinic acid or mercaptan one observes nucleophile- and acid-catalyzed reactions of I with these additives; these result in the disappearance of I. Both the formal kinetics and the rate constants of these nucleophile- and acid-catalyzed reactions of I with $ArSO_2H$ or mercaptan are *exactly the same* as those of the nucleophile and acid-catalyzed racemization of (+)-I. Thus all of these reactions have the same rate-determining step. Since the solvent isotope effect for the n-Bu$_2$S-catalyzed racemization of (+)-I (k_{H_2O}/k_{D_2O} = 0.54) indicates that the various acid- and nuclophile-catalyzed reactions are specific H$^+$ catalyzed, this rate-determining step presumably involves attack of the nucleophilic catalyst on the protonated thiolsulfinate. This rate-determining reaction of the nucleophile with protonated I must lead to intermediates which in the absence of added $ArSO_2H$ or R'SH subsequently revert to thiolsulfinate, but with racemization; in the presence of $ArSO_2H$ or R'SH the same intermediates are captured by these reagents and prevented from returning to thiolsulfinate. These various requirements can only be met by a mechanism of the following general type.

$$(+)\text{-I} + \text{H}^+ \underset{K_a}{\rightleftharpoons} (+)\text{-IH}^+$$

$$\text{Nu:} + (+)\text{-IH}^+ \xrightarrow[\substack{\text{rate}\\ \text{determining}}]{k_{Nu}} \text{intermediates} \xrightarrow{k_{-1}} \text{Nu:} + (\pm)\text{-IH}^+ \longrightarrow (\pm)\text{-I} + \text{H}^+$$

$$k_2 \Big\downarrow \substack{\text{ArSO}_2\text{H,}\\ \text{fast}} \qquad\qquad \substack{\text{R}'\text{SH,}\\ \text{fast}} k_3 \searrow$$

$$\text{H}^+ + \text{Nu:} + \text{PhSSR}'$$

$$\text{H}^+ + \text{Nu:} + \text{Ar}\overset{\text{O}}{\underset{\text{O}}{\overset{\|}{\underset{\|}{\text{SSPh}}}}}$$

$$k_2(\text{ArSO}_2\text{H}) \text{ and } k_3(\text{R}'\text{SH}) \gg k_{-1}$$

In our opinion the only completely satisfactory mechanism of this type that can be written is the one shown in Chart I. This involves rate-determining attack of the nucleophile on the sulfenyl sulfur of sulfinyl-portonated I (eq 4). In the absence of added ArSO$_2$H or R'SH the intermediates (PhSOH + PhSNu) produced in eq 4 recombine to give racemic I (eq 5). On the other hand, when ArSO$_2$H or R'SH are present PhSNu reacts rapidly with them, as shown in eq 6; this prevents its return to I via eq 5.[11] The sulfenic acid PhSOH is also effectively scavenged by these same reagents, but, whether this occurs by the reaction sequence of eq 7 followed by eq 6 or, directly, as in eq 8, is not known at present.

The mechanism proposed in Chart I for the acid- and nucleophile-catalyzed reactions of I with sulfinic acid or mercaptan is the same one suggested[3c,8] for the acid and alkyl sulfide catalyzed reaction of I with these same reagents in acetic acid–water. In agreement with this picture k_S (Tables III and IV) for the n-Bu$_2$S-catalyzed reactions (eq 4, Nu$^-$ = n-Bu$_2$S, k_{Nu} = k_{Bu_2S}), which

(IH$^+$)/(I) on going from one medium to the other, the observed change in k_S is entirely consistent with the idea that the several sulfide-catalyzed reactions do indeed have the same mechanism in the two different solvents.

Before deciding on the mechanism in Chart I we explored and were able to reject a number of alternatives. These differed from it in such matters as the point of attack of the nucleophile, the site of protonation of the thiolsulfinate, etc. Our reasons for rejecting certain of these mechanisms are perhaps worth noting briefly. One possible alternative was that attack of the nucleophile catalyst occurred at the oxygen of the protonated thiolsulfinate. Reoxidation of the

$$\text{R}_2\text{S} + (+)\text{-PhS}\overset{+}{\underset{\text{OH}}{\text{SPh}}} \xrightarrow[\text{determining}]{\text{rate}} \text{R}_2\text{S}{=}\text{O} + \text{PhSSPh} + \text{H}^+ \longrightarrow$$

$$\text{R}_2\text{S} + (\pm)\text{-PhS}\overset{\text{O}}{\underset{}{\overset{\|}{\text{SPh}}}} + \text{H}^+$$

disulfide would then give $(\pm)$-I. This mechanism could be rejected because independent experiments showed

Chart I. Mechanism of the Nucleophile- and Acid-Catalyzed Reactions of I

$$(+)\text{-PhS}\overset{\text{O}}{\underset{}{\overset{\|}{\text{SPh}}}} + \text{H}^+ \underset{K_a}{\rightleftharpoons} (+)\text{-PhS}\overset{+}{\underset{\text{OH}}{\text{SPh}}} \tag{3}$$

$$\text{Nu}^- + (+)\text{-PhS}\overset{+}{\underset{\text{OH}}{\text{SPh}}} \xrightarrow[\substack{\text{rate}\\ \text{determining}}]{k_{Nu}} \text{PhSNu} + \text{PhSOH} \tag{4}$$

$$\text{PhSNu} + \text{PhSOH} \longrightarrow \text{Nu}^- + \text{H}^+ + (\pm)\text{-PhS}\overset{\text{O}}{\underset{}{\overset{\|}{\text{SPh}}}} \text{ (racemization)} \tag{5}$$

$$\text{PhSNu} + \substack{\text{ArSO}_2\text{H}\\ \text{or}\\ \text{R}'\text{SH}} \longrightarrow \text{Nu}^- + \text{H}^+ + \substack{\text{ArSO}_2\text{SPh (reacn with ArSO}_2\text{H)}\\ \text{or}\\ \text{R}'\text{SSPh (reacn with R}'\text{SH)}} \tag{6}$$

$$\text{PhSOH} + \text{Nu}^- + \text{H}^+ \rightleftharpoons \text{PhSNu} + \text{H}_2\text{O} \tag{7}$$

$$\text{PhSOH} + \substack{\text{ArSO}_2\text{H}\\ \text{or}\\ \text{R}'\text{SH}} \longrightarrow \text{H}_2\text{O} + \substack{\text{ArSO}_2\text{SPh (reacn with ArSO}_2\text{H)}\\ \text{or}\\ \text{R}'\text{SSPh} \quad \text{(reacn with R}'\text{SH)}} \tag{8}$$

should be given by $k_{Bu_2S}K_a a_{H^+}$, is about 300 times smaller in 60% dioxane–0.3 M HClO$_4$ (H_0 = +1.81)[12] than it is[3c,8] in acetic acid–0.56 M H$_2$O–0.10 M H$_2$SO$_4$ (H_0 = −1.13).[13] Since k_{Bu_2S} may be slightly dependent on solvent and the change in H_0 may not be exactly the correct function to describe the change in log

that an acidic solution of an alkyl sulfoxide is incapable of oxidizing phenyl disulfide to I. Other alternative mechanisms involve attack by the nucleophile at the sulfinyl sulfur. In one of these the rate-determining step is

$$\text{Nu}^- + \text{PhS}\overset{+}{\underset{\substack{\|\ \ \|\\ \text{O} \ \text{H}}}{\text{SPh}}} \longrightarrow \text{PhSNu} + \text{PhSH} \overset{\text{O}}{\underset{\|}{}}$$

It is unacceptable on at least two counts. First, for reasons already outlined,[3c] it cannot account for the stoichiometry of the sulfide-catalyzed I–ArSO$_2$H reaction. Second, it is unable to explain the acid- and nucleophile-catalyzed disappearance of thiolsulfinate in

(11) Equations 5 and 6 are similar in that both involve nucleophilic attack by a reagent on the sulfur of PhSNu. In eq 5 the attacking reagent is PhSOH; in eq 6 it is either ArSO$_2$H or R'SH. We believe that the ability of added ArSO$_2$H or R'SH to compete so successfully with PhSOH for the capture of PhSNu is due largely to the fact that they are always present in much larger concentration.

(12) C. A. Bunton, J. B. Ley, A. J. Rhind-Tutt, and C. A. Vernon, *J. Chem. Soc.*, 2327 (1957).

(13) J. Rocek, *Collection Czech Chem. Commun.*, **22**, 1 (1957).

the presence of added mercaptan, since rapid reaction of PhS(O)Nu with mercaptan would only regenerate thiolsulfinate. A second mechanism involving attack at the sulfinyl group would postulate as the rate-determining step

$$Nu^- + (+)\text{-Ph}\overset{+}{S}SPh \longrightarrow (+)\text{-Ph}\overset{\overset{\displaystyle Nu}{|}}{\underset{\underset{\displaystyle OH}{|}}{S}}SPh$$

$$\underset{\displaystyle II}{}$$

In order to make this mechanism consistent with the data on the acid- and nucleophile-catalyzed reactions of I with $ArSO_2H$ and $R'SH$, one would have to assume: (1) that attack of $R'SH$ or $ArSO_2H$ occurs more readily on the sulfenyl sulfur of II than it does on the same atom in sulfinyl-protonated I; (2) that reaction of $ArSO_2H$ or $R'SH$ with II occurs more rapidly than II reverts to Nu^- and protonated I. The first assumption seems extremely unrealistic since PhS^+OH^- should certainly be a better leaving group than $PhSOHNu^-$. The second assumption also seems unlikely to be correct, particularly for those cases where $Nu^- = R_2S$. One final alternative involving attack on the sulfinyl sulfur would have the direct displacement of OH^- in the rate-determining step, i.e.

$$Nu^- + Ph\overset{+}{S}SPh \longrightarrow Ph\overset{+}{S}SPh + OH^-$$
$$\underset{\underset{\displaystyle III}{\underset{\displaystyle OH}{|}}}{} \qquad \underset{\underset{\displaystyle Nu}{|}}{}$$
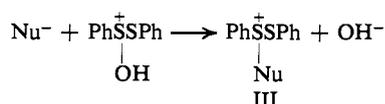
In our opinion this mechanism has at least several serious faults. (1) In a reaction of this kind, since PhS^- is presumably the better leaving group, it should be displaced in preference to OH^-. (2) In the case of the alkyl sulfide catalyzed reactions III would correspond to $PhS^+(SPh)S^+R_2$, an energetically most unattractive intermediate.

We therefore feel quite confident that the mechanism of the several acid- and nucleophile-catalyzed reactions of I is accurately represented by the scheme in Chart I and that the nucleophilic catalysis which is observed involves attack of the nucleophile on the sulfenyl sulfur of protonated I.

Relative Reactivity of Nucleophiles toward Sulfenyl Sulfur. The slopes of the plots in Figure 1 give k_{Nu}' (eq 1a) for each of the nucleophiles involved. In terms of the mechanism shown in Chart I k_{Nu}' is equal to $k_{Nu}K_a$. The values of $k_{Nu}K_a$ for the acid- and nucleophile-catalyzed reactions of I in 60% dioxane are shown in the first column of Table V. Since K_a, which refers to the equilibrium involving protonation of I, is the same for all the nucleophile-catalyzed reactions, the relative

Table V. Nucleophilic Reactivity toward the Sulfenyl Sulfur of Protonated I[a]

Nucleophile	$k_{Nu}' = k_{Nu}K_a$,[b] M^{-2} sec^{-1}	k_{Nu}/k_{Cl}
Cl$^-$	0.0057	(1.0)
Br$^-$	0.20	35
SCN$^-$	31	5.4×10^3
I$^-$	78	1.4×10^4
n-Bu$_2$S	4.7[c]	8.2×10^2

[a] All data are in 60% dioxane at a constant ionic strength of 0.50. [b] k_{Nu}' is defined in eq 1a. k_{Nu} and K_a are as defined in Chart I. [c] k_s' (eq 1b).

reactivity of two nucleophiles toward the sulfenyl sulfur of protonated I, k_{Nu_1}/k_{Nu_2}, can be obtained simply by taking k_{Nu_1}'/k_{Nu_2}'. Such data on the relative reactivity of the various nucleophiles in eq 4 are shown in the last column of Table V, using chloride ion as the nucleophile to which the reactivity of all the others is compared.

Comparison of these k_{Nu}/k_{Cl} values for a substitution at sulfenyl sulfur with those (first column of Table VI) found[4] for a nucleophilic substitution at sulfinyl sulfur (eq 9) in the same protic solvent reveals that

$$Nu^- + Ar\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O}{\|}}{S}}\text{---}\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O}{\|}}{S}}Ar \xrightarrow{k_{Nu}} ArSNu + Ar\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O}{\|}}{S}}^- \qquad (9)$$
$$\underset{\displaystyle IV}{}$$

$$Ar = p\text{-CH}_3OC_6H_4$$
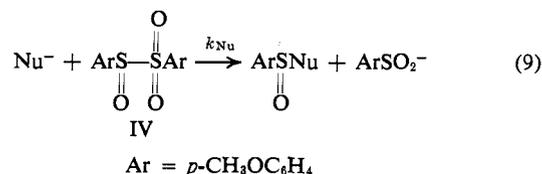
highly polarizable, weakly basic nucleophiles, like iodide and thiocyanate, are much more reactive relative to chloride in the substitution involving attack on sulfenyl sulfur than they are in the one involving attack on sulfinyl sulfur. In the parlance of hard and soft acid and base theory (HSAB),[14,15] highly polarizable nucleophiles like iodide or thiocyanate are considered much softer bases than the less polarizable chloride ion.

Table VI. Relative Nucleophilicity of Some Common Nucleophiles in Various Substitution Reactions

| Nucleophile | k_{Nu}/k_{Cl} | |
	Subst at sulfinyl sulfur (eq 9)[a]	Subst at peroxide oxygen (eq 10)[b]
Cl$^-$	(1.0)	(1.0)
Br$^-$	5.4	2.8×10^2
SCN$^-$	14	5.0×10^2
I$^-$	83	2.0×10^5
(HOCH$_2$CH$_2$)$_2$S	..	4.6×10^2

[a] Reference 4; solvent, 60% dioxane. [b] Reference 17; solvent, water.

In HSAB soft nucleophiles are considered to react to particular advantage with soft electrophilic centers, while hard nucleophiles (nonpolarizable species like F$^-$ or OH$^-$) are thought to enjoy a special advantage in reaction with hard electrophilic centers. According to HSAB the fact that softer nucleophiles react faster relative to chloride in the substitution at sulfenyl sulfur indicates that sulfenyl sulfur represents a softer electrophilic center than sulfinyl sulfur, i.e., that ArS$^+$ is a softer electrophile than ArS$^+$O. Since other work[4b] indicates that sulfonyl sulfur is a considerably harder electrophilic center than sulfinyl sulfur, ArS$^+$, ArS$^+$O, and ArSO$_2^+$ represent a series of increasing hardness as electrophiles. This is in accord with expectations, since each covalent bond to oxygen decreases by one the number of unshared pairs of outer-shell electrons on sulfur, and it is easily excited outer-shell electrons which are one of the hallmarks of a soft electrophilic center.[15]

Pearson and Songstad[15] have pointed out that having a soft base as the leaving group in a substitution can make a given center more reactive toward soft nucleo-

(14) R. G. Pearson, J. Am. Chem. Soc., 85, 3533 (1963); Science, 151, 172 (1966).

(15) R. G. Pearson and J. Songstad, J. Am. Chem. Soc., 89, 1827 (1967).

philes than would otherwise be the case, while a hard base as the leaving group can enhance its reactivity toward hard nucleophiles. They call effects of this kind "symbiotic effects." Since $ArSO_2^-$ (eq 9) and PhSOH (eq 4) presumably do not differ too much in their softness as bases, with $ArSO_2^-$ probably being if anything the softer,[16] a symbiotic effect cannot be responsible for the fact that soft nucleophiles exhibit a greater reactivity relative to chloride ion in eq 4 than they do in eq 9. The observed behavior must be due to sulfenyl sulfur being inherently a softer electrophilic center than sulfinyl sulfur.

One electrophilic center which is generally considered quite soft is the divalent oxygen of a peroxide. The prediction had been that sulfenyl sulfur would be a significantly harder electrophilic center than peroxide oxygen.[5] However, comparison of Edwards' data[17] (last column of Table VI) on the acid-catalyzed reaction of nucleophiles with hydrogen peroxide in aqueous solution (eq 10) with the k_{Nu}/k_{Cl} values in Table V reveals

$$Nu^- + HO\overset{+}{O}H_2 \xrightarrow{k_{Nu}} NuOH + H_2O \quad (10)$$

that eq 4 and 10 are not too different in their response to changes in the softness of the attacking nucleophile. This suggests that sulfenyl sulfur is about as soft an electrophilic center as peroxide oxygen;[18] it is therefore somewhat softer as an electrophilic center than had been predicted.[5]

Solvent Effects on Nucleophile Reactivity in Substitutions at Sulfenyl Sulfur. In nucleophilic substitutions at saturated carbon involving anions the transfer of the reaction from a polar protic solvent to a dipolar aprotic one generally leads to dramatic increases in reaction rate.[19] Because these rate increases are considerably smaller when the attacking nucleophilic anion is a soft base than when it is a harder one, one actually gets a quite different order of nucleophilic reactivity ($Cl^- > Br^- > SCN^-$) for such reactions in dipolar aprotic solvents than the one which is observed in protic solvents.[19b]

Comparison of the data in Table V with data which have been obtained by Fava and Koch[2c] for the reactivity of the same nucleophiles in the nucleophile-catalyzed racemization of (+)-I in anhydrous acetone, a process that presumably involves eq 11 as the rate-de-

$$Nu^- + (+)\text{-PhSSPh} \longrightarrow PhSNu + PhSO^- \quad (11)$$
$$\overset{\parallel}{O}$$
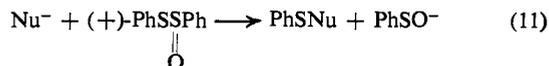
termining step, shows that the same sort of alteration of the nucleophilic reactivity order also occurs on transferring a nucleophilic substitution occurring at sulfenyl sulfur from a protic solvent (60% dioxane) to a dipolar aprotic one (acetone). Thus in acetone nucleophilic reactivity in eq 11 decreases in the order $Cl^- > Br^- > I^- > SCN^-$,[2c] which is, of course, very different from the pattern of $I^- > SCN^- >> Br^- >> Cl^-$ found in 60% dioxane for eq 4.

Experimental Section

Preparation of (+)-I. (+)-Percamphoric acid was prepared from (+)-camphoric anhydride by the procedure of Milas and McAlevy.[20] Over a period of 1 hr, 250 ml of a 0.1 M solution of the peracid in chloroform was added with stirring to a solution of 5.7 g of phenyl disulfide in 250 ml of chloroform kept at $-5°$. After the addition was complete the cooling bath was removed, and the final mixture was allowed to warm to room temperature. After 1 hr, the mixture was filtered to remove the camphoric acid which had precipitated. The chloroform filtrate was washed several times with aqueous bicarbonate to remove the last traces of camphoric acid; it was then dried over anhydrous magnesium sulfate. The chloroform was removed under reduced pressure, and the residue was recrystallized several times by dissolving it in the minimum amount of chloroform at room temperature, adding n-hexane and then cooling. The resulting optically active phenyl benzenethiolsulfinate, mp 69°, gave $[\alpha]_{436}$ +8.5-+14.0° (dioxane) depending on the sample. The variation in rotation is due to variations in the amount of racemization of (+)-I that occurs during synthesis and work-up.

Purification of Solvents and Other Reagents. Dioxane was purified by the procedure described by Wiberg.[21] The n-butyl sulfide, potassium bromide, potassium iodide, and lithium perchlorate were those employed in a previous investigation.[3b] Lithium chloride, potassium thiocyanate, and perchloric acid (72%) were analytical reagent grade and were not further purified. Benzenesulfinic acid was purified as outlined in an earlier paper;[3c] the same was true for benzyl sulfide and thiodipropionic acid. n-Butyl mercaptan was purified by distillation under nitrogen.

Procedure for Measurement of Racemization Rates. Standard solutions of perchloric acid, the catalyzing nucleophile, and lithium perchlorate in 60% dioxane (v/v)[22] were prepared. The proper amount of (+)-I was weighed out, the desired amounts of the standard solutions were added, and the whole was made up to volume with additional 60% dioxane. The solution was placed in a jacketed polarimeter cell which was kept at 39.1°, and the change in rotation at 436 mμ was followed with time using a Perkin-Elmer Model 141 polarimeter. The final rotation of the reaction solution was always zero. Plots of log α vs. time were always nicely linear.

Runs with either bromide, thiocyanate, or n-butyl sulfide showed that during the period required for complete loss of optical activity there was no significant change in the ultraviolet absorption spectrum of the solution; this shows that there is no significant change in the concentration of I during the period required for loss of optical activity. Loss of optical activity therefore occurs solely as a result of racemization of (+)-I.

Procedure for Kinetic Study of the Reactions of I with Sulfinic Acid or Mercaptan. For study of the reaction of I with sulfinic acid, standard solutions of each of the following in 60% dioxane were prepared: thiolsulfinate, benzenesulfinic acid, nucleophilic catalyst (either n-butyl sulfide or bromide ion), and perchloric acid. The reactions were carried out in the special spectrophotometer reaction cell described in an earlier publication.[23] A measured amount of the standard solution of the thiolsulfinate was placed in chamber A. Measured amounts of the remaining reagents and any additional 60% dioxane required were placed in chamber B. The solutions

(16) Dr. B. Saville has pointed out that the softness of a base is determined in large measure by its possessing vacant orbitals of fairly low energy which may overlap with filled orbitals of a (soft) acid, or electrophile, to generate a π bond, this contributing to over-all acid–base bonding. In a sulfinate ion acting as an S-nucleophile, V, the S 3d orbitals

O   OH
$\parallel$ $\mid$
ArS:⁻   ArS:
$\parallel$
O

V   VI

should be energetically more accessible by virtue of the formally higher oxidation state than they would be in the sulfenic acid VI wherein S^{II} experiences only a slight inductive effect of a single σ-bonded oxygen.

(17) J. O. Edwards, "Peroxide Reaction Mechanisms," J. O. Edwards, Ed., Interscience Division, John Wiley and Sons, Inc., New York, N. Y., 1962, pp 67–106.

(18) We feel that water and 60% dioxane are both sufficiently aqueous solvents so that the fact that eq 10 was studied in the former and eq 4 in the latter does not introduce any large solvent effect into the two sets of (k_{Nu}/k_{Cl})'s, such as would have been the case if one set of ratios had been obtained in a protic solvent and the other in an aprotic one.

(19) (a) A. J. Parker, Quart. Rev. (London), 16, 163 (1962); (b) J. Chem. Soc., 1328, 4398 (1961).

(20) N. A. Milas and A. McAlevy, J. Am. Chem. Soc., 55, 350 (1933).

(21) K. B. Wiberg, "Laboratory Technique in Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1960, p 245.

(22) The per cent dioxane was calculated after the fashion of Bunton, et al.[12]

(23) J. L. Kice, G. Guaraldi, and C. G. Venier, J. Org. Chem., 31, 3561 (1966).

in the two chambers were brought to temperature and then mixed. The final solution was poured into spectrophotometer cell C, and the apparatus was placed in the thermostated cell compartment of a Cary Model 15 spectrophotometer. The decrease in optical den-

sity at 296 mμ with time was followed. Plots of log $(A - A_\infty)$ vs. time were nicely linear. For the runs with mercaptan the same procedure was used except that a standard solution of the mercaptan was used in place of that of the sulfinic acid.

The Relative Nucleophilicity of Some Common Nucleophiles toward Sulfinyl Sulfur. The Nucleophile-Catalyzed Hydrolysis of Aryl Sulfinyl Sulfones[1]

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Abstract: The relative reactivity of seven common nucleophiles in a displacement reaction at sulfinyl sulfur (eq 8) may be determined from kinetic data on their catalysis of the hydrolysis of an aryl sulfinyl sulfone (IIa) in aqueous dioxane. These data for sulfinyl sulfur (Table IV) are compared with analogous data for substitutions at sulfenyl sulfur (eq 11), peroxide oxygen (eq 9), sp^3 carbon (eq 10), and sulfonyl sulfur (eq 12). This comparison reveals the following interesting points. (1) The substitution at sulfonyl sulfur shows a completely different pattern of reactivity ($F^- > AcO^- \gg Cl^-$) than the one at sulfinyl sulfur ($Cl^- > AcO^- > F^-$). (2) In the substitutions at both sulfenyl sulfur and peroxide oxygen, nucleophiles such as iodide or thiocyanate show a considerably greater reactivity compared to chloride ion than they do in the one at sulfinyl sulfur. (3) The relative reactivities of the various nucleophiles in the substitutions at sulfinyl sulfur and sp^3 carbon are very similar. These facts are discussed with reference to the theory of hard and soft acids and bases (HSAB). The conclusions are (a) that sulfonyl sulfur is a much harder and sulfenyl sulfur a significantly softer electrophilic center than sulfinyl sulfur, and (b) that sulfinyl sulfur is a medium soft electrophilic center analogous to sp^3 carbon.

E quation 1 is a generalized representation of a nucleophilic substitution reaction. In a protic

$$Nu^- + SX \longrightarrow NuS + X^- \qquad (1)$$
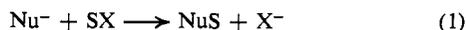
solvent the relative reactivity of a series of nucleophiles in such a reaction depends greatly on the nature of the center in the substrate SX which is being attacked by the nucleophile.[2] Nucleophiles which are "hard" bases,[3] i.e., of low polarizability and high proton basicity, show up to particular advantage in substitutions involving attack on such centers as carbonyl carbon[4] or tetracoordinate phosphorus.[5] On the other hand, nucleophiles which are "soft" bases,[3] i.e., of high polarizability and low proton basicity, do particularly well in substitutions involving centers such as divalent oxygen[6] or Pt^{2+}.[7] Edwards and Pearson,[8] in what has become a classic paper, attempted to evaluate and explain the relative importance of basicity, polarizability, and other effects in determining the reactivity of a nucleophile toward these and other centers in protic

solvents. Recently, Pearson and Songstad[9] have shown how the various data and conclusions can also be easily understood within the framework of the theory of hard and soft acids and bases (HSAB).

In their paper, Edwards and Pearson[8] made some predictions about the reactivity patterns that might be observed for nucleophiles reacting with different sulfur centers, but they pointed out that unfortunately no quantitative data were yet available for any of these centers. In fact for sulfinyl sulfur, $-S(=O)-$, there were not even any qualitative data. Since there has been much interest in recent years in reactions involving substitution at the sulfinyl sulfur of sulfoxides, sulfinate esters, and related compounds,[10–16] it would seem that having quantitative data for sulfinyl sulfur would be of considerable value. Furthermore, comparison of this data with suitable data for substitutions at other sulfur

(1) This research supported by the Directorate of Chemical Sciences, Air Force Office of Scientific Research, Grant AF-AFOSR-106-65. Preliminary communication: J. L. Kice and G. Guaraldi, *Tetrahedron Letters*, 6135 (1966).

(2) J. O. Edwards, "Inorganic Reaction Mechanisms," W. J. Benjamin, Inc., New York, N. Y., 1965, pp 51–72.

(3) R. G. Pearson, *J. Am. Chem. Soc.*, **85**, 3533 (1963); *Science*, **151**, 172 (1966).

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(5) Reference 2, pp 39–63, 177–180.

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(8) J. O. Edwards and R. G. Pearson, *J. Am. Chem. Soc.*, **84**, 16 (1962).

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