1,4-Diisopropyl-1,4-dihydronaphthalene. This compound was prepared from naphthalene (4 g) according to the above procedure, using a normal quench with isopropyl bromide. GLPC of the reaction mixture (5.2 g) indicated above 60% of the desired compound, with the remainder being 1-isopropyl-1,4-dihydronaphthalene. Fractional distillation provided an analytical sample (bp 120–124 °C (5 mm)): NMR (CDCl$_3$) δ 7.1 (b s, 4 H), 5.9 (b d, 2), 3.3 (m, 2), 2.0 (b m, 2), 0.95 (d, 6), 0.7 (d, 6).

Anal. Calcd for C$_{16}$H$_{22}$: C, 89.65; H, 10.34. Found: C, 89.87; H, 10.07.

Oxidation of Sulfides and Phosphines by Aromatic Selenonic and Seleninic Acids[1]

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Both alkyl sulfides and triphenylphosphine are readily oxidized by *p*-chlorobenzeneselenonic acid to alkyl sulfoxides and triphenylphosphine oxide, the selenonic acid itself being reduced to *p*-chlorobenzeneseleninic acid. The seleninic acid, in an acid-catalyzed reaction, then even more rapidly oxidizes additional sulfide to sulfoxide (or Ph$_3$P to phosphine oxide) and is itself reduced to a diselenide. Study of the mechanism of this oxidation of sulfides by aromatic seleninic acids indicates that the rate-determining step is nucleophilic attack by the sulfide on the protonated seleninic acid, ArSe(OH)$_2^+$, to give the sulfoxide, a proton, and the selenenic acid, ArSeOH. The selenenic acid can then disproportionate to the diselenide, ArSeSeAr, and the seleninic acid. Despite the strong inherent oxidizing power of *p*-chlorobenzeneselenonic acid and its facile oxidation of alkyl sulfides and Ph$_3$P, it does not oxidize such other potentially oxidizable organic functionalities as alcohols, alkenes, or ketones.

The chemistry of aromatic selenonic acids (ArSeO$_3$H) has been explored previously in only a very limited way.[2] Like aromatic sulfonic acids (ArSO$_3$H) selenonic acids are strong acids.[2] However, quite unlike sulfonic acids, they are also apparently strong oxidizing agents,[2] strong enough reportedly to oxidize hydrogen chloride to chlorine.[3] This led us to wonder if selenonic acids might not be effective oxidizing agents for a variety of organic substrates and if their reactions with a number of compounds might not take an interesting course and be of potential synthetic value. For this reason we undertook a study of the reactions of a typical aromatic selenonic acid with a variety of different types of organic compounds.

This study revealed that, despite the ability of the selenonic acid to readily oxidize a halide ion such as bromide ion to Br$_2$, it is remarkably inert toward many organic functionalities that one might think it would oxidize.

We did find, however, two organic substrates that the selenonic acid would readily oxidize, alkyl sulfides and triphenylphosphine. In examining these two oxidations in more detail, we discovered, somewhat to our surprise, that, provided a strong acid is present as catalyst, the corresponding seleninic acid (ArSeO$_2$H) will actually oxidize either alkyl sulfides or triphenylphosphine faster than does the selenonic acid. The present paper describes what we have been able to learn about the character and mechanism of the oxidations of these two substrates by the two different types of organoselenium acids.

Results

p-Chlorobenzeneselenonic acid (1), which has been prepared and carefully characterized by Rebane,[4] was the aromatic selenonic acid selected for study. The corresponding seleninic acid, *p*-ClC$_6$H$_4$SeO$_2$H, and benzeneseleninic acid (PhSeO$_2$H) were the seleninic acids used. Because of the limited solubility of 1 in all common organic solvents except acetic acid and acetonitrile, acetonitrile was used as the solvent medium for most of the reactions.

Oxidation of Sulfides by *p*-Chlorobenzeneselenonic Acid. Treatment of dibenzyl sulfide with an equimolar amount of *p*-chlorobenzeneselenonic acid (1) in acetonitrile at room temperature resulted in quantitative oxidation of the sulfide to dibenzyl sulfoxide and in the formation of approximately 0.2 mol of bis(*p*-chlorophenyl) diselenide/mol of sulfide oxidized. Similar stoichiometry was observed in an oxidation carried out in acetic acid.

We also examined the oxidation of a diaryl sulfide, Ph$_2$S, by 1. In this case after a reaction time (18 h at room temperature in acetonitrile) far more than that sufficient for complete oxidation of dibenzyl sulfide to the sulfoxide

(1) This research was supported by the National Science Foundation, Grant CHE-76-13346.

(2) D. L. Klayman, "Organic Selenium Compounds: Their Chemistry and Biology", D. L. Klayman and W. H. H. Gunther, Eds., Wiley, New York, N.Y., 1973, pp 141–3.

(3) (a) H. W. Doughty, *Am. Chem. J.*, **41**, 326 (1909); (b) R. Lesser and R. Weiss, *Chem. Ber.*, **46**, 2640 (1913).

(4) E. Rebane, *Acta Chem. Scand.*, **23**, 1819 (1969).

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Table I. Kinetics of the Reaction of Alkyl Sulfides with Benzeneseleninic Acid in Acetonitrile[a]

% H₂O (v/v)	[HClO₄], M	R₂S	[R₂S], M	$10^3 k_1$, s⁻¹	$k_1/[R_2S]$, M⁻¹ s⁻¹
1.0	0.005	n-Bu₂S	0.010	33	3.3
			0.0050	21	4.2
			0.0025	9.7	3.9
			0.0010	3.4	3.4
		EtSCH₂CH₂OH	0.010	5.3	0.53
			0.0050	3.1	0.62
			0.0025	1.5	0.59
		(HOCH₂CH₂)₂S	0.010	1.6	0.16
			0.0050	0.75	0.15
		(HOOCCH₂CH₂)₂S	0.010	0.56	0.06
1.0	0.005	n-Bu₂S	0.010	33	3.3
2.0				3.1	0.31
3.0				0.92	0.092
1.0	0.001	n-Bu₂S	0.0050	5.8	1.17
	0.002			11	2.17
	0.003			19	3.78
	0.005			21	4.20
	0.010			22	4.4
3.0	0.005	n-Bu₂S	0.010	0.92	0.092
	0.010			1.85	0.185
	0.020			3.5	0.35
	0.040			3.8	0.38

[a] All runs are at 25 °C in acetonitrile containing the percentage of water indicated; $[PhSeO_2H]_0 = 1.0 \times 10^{-4}$ M.

the oxidation of diphenyl sulfide was still incomplete, only 70% of the original sulfide having been converted to diphenyl sulfoxide and the remaining 30% being recovered unchanged.

Oxidation of Sulfides by Aromatic Seleninic Acids. When an alkyl (n-Bu₂S) or aralkyl sulfide (dibenzyl sulfide) was treated with p-chlorobenzeneseleninic acid (**2a**) *alone* in acetonitrile, no reaction was detected, even after 24 h. However, as soon as some strong acid (0.25 mol of p-toluenesulfonic acid/mol of ArSeO₂H) was added to the solution a rapid reaction occurred, and from a solution containing initially 1.03 mmol of (PhCH₂)₂S and 1.1 mmol of **2a** in 10 mL of acetonitrile there was isolated 1.0 mmol of dibenzyl sulfoxide and 0.31 mmol of bis(p-chlorophenyl) diselenide. n-Butyl sulfide was also oxidized to n-butyl sulfoxide in high yield by the seleninic acid under the same conditions.

Kinetics of the Alkyl Sulfide–Seleninic Acid Reaction. The kinetics of the oxidation of alkyl sulfides by aromatic seleninic acids could be examined experimentally by employing alkyl sulfides that do not absorb significantly (at concentrations up to 0.01 M) in the 240–400-nm region, having the sulfide present in large stoichiometric excess over benzeneseleninic acid (**2b**) ($[PhSeO_2H] \approx 1 \times 10^{-4}$ M), and following the increase in absorbance (A) at 240 nm that accompanies the conversion of PhSeO₂H to PhSeSePh. Under such conditions plots of log ($A_\infty - A$) vs. time show good linearity, indicating that the reaction is presumably first order in seleninic acid. An experimental first-order rate constant k_1 for each run may be obtained from the slope of such a plot.

The kinetics were investigated at 25 °C in acetonitrile containing 1–3% water, using perchloric acid as the strong acid catalyst. The effects of the following reaction variables on rate were investigated: (a) alkyl sulfide concentration; (b) alkyl sulfide structure; (c) strong acid concentration; (d) water concentration. The data for the various runs are collected in Table I.

The results in Table I show that, at a fixed concentration of water and strong acid, k_1 for any alkyl sulfide varies linearly with sulfide concentration. The reaction is therefore kinetically first order in sulfide.

There is a marked dependence of rate on sulfide structure. A plot of log ($k_1/[R_2S]$) for the different sulfides studied vs. $\sum \sigma^*$ for the two groups attached to the sulfur is nicely linear with a slope (ρ^*) of -2.0, showing that the reaction is markedly retarded by electron-withdrawing substituents in the alkyl groups of the sulfide.

The dependence of k_1 on strong acid concentration is somewhat unusual. In acetonitrile–1% H₂O at low acid concentrations ($[HClO_4] = 0.001-0.002$ M) k_1 increases approximately linearly with $[HClO_4]$. However, at higher acid concentrations ($[HClO_4] = 0.005-0.010$ M) k_1 becomes virtually independent of strong acid concentration. The same sort of phenomenon is also observed in acetonitrile–3% H₂O, but in this medium the leveling off in k_1 with increasing $[HClO_4]$ does not occur until $[HClO_4]$ reaches 0.02 M.

An increase in the water content of the solvent medium from 1 to 3% leads to a very marked decrease in k_1. With acetonitrile containing 0.005 M HClO₄, for example, the rate of the reaction is about 35 times slower in the presence of 3% water than it is when only 1% water is present.

While the kinetics of the sulfide–seleninic acid reaction could be studied easily, we were not able to develop a simple, reliable method for monitoring the kinetics of the reaction of selenonic acid 1 with sulfides.

Oxidation of Triphenylphosphine by p-Chlorobenzeneselenonic Acid. Treatment of triphenylphosphine at 0 °C in acetonitrile with an equimolar amount of p-chlorobenzeneselenonic acid led to rapid oxidation of the phosphine quantitatively to triphenylphosphine oxide and to the formation of slightly over 0.20 mol of bis(p-chlorophenyl) diselenide/mol of phosphine oxidized.

The oxidation of Ph₃P by 1, unlike the oxidation of sulfides by 1, was amenable to kinetic study. The disappearance of Ph₃P (1×10^{-4} M) in the presence of excess selenonic acid ($(0.4-1.0) \times 10^{-3}$ M) could be followed kinetically at 25 °C in acetonitrile–10% H₂O as solvent by monitoring the decrease in absorbance (A) of the solution at 278 nm. Plots of log ($A - A_\infty$) vs. time exhibited good first-order kinetics, indicating the reaction is presumably first order in the phosphine. The experimental first-order rate constant k_1 varied linearly with [1], showing that the reaction is also first order in the selenonic acid. The value of $k_1/[1]$ was 15.4 ± 0.2 M⁻¹ s⁻¹.

Oxidation of Triphenylphosphine by Aromatic Seleninic Acids. Even at 0 °C in acetonitrile both PhSeO₂H and p-ClC₆H₄SeO₂H rapidly oxidize triphenylphosphine to triphenylphosphine oxide. The only selenium-containing reduction product isolated is the diaryl diselenide. For each mol of phosphine oxidized there is obtained 1.0 mol of phosphine oxide and 0.33 mol of the diselenide.

In contrast to the oxidation of alkyl sulfides by ArSeO₂H, no strong acid catalyst is required to get the reaction to take place. However, the reaction is more rapid in the presence of a small amount of added strong acid.

The extinction coefficients of the reactants and products of the Ph₃P–ArSeO₂H reaction in acetonitrile dictated that its kinetics be examined under conditions where the aromatic seleninic acid ($(4.0-10.0) \times 10^{-4}$ M) was present in stoichiometric excess over triphenylphosphine ($[Ph_3P] = 1 \times 10^{-4}$ M) with the reaction being monitored by following at 265–280 nm the decrease in absorbance that

Table II. Kinetics of the Reaction of Triphenylphosphine with Aromatic Seleninic Acids in Acetonitrile[a]

seleninic acid	% H_2O (v/v)	[ArSeO$_2$H], M	$10^3 k_1$, s^{-1}	$k_1/$ [ArSeO$_2$H], M^{-1} s^{-1}
p-ClC$_6$H$_4$-SeO$_2$H	5.0	0.0010	12.8	12.8
		0.0008	10.0	12.5
		0.0006	7.1	11.9
		0.0004	4.5	11.3
	10.0	0.0010	7.2	7.2
		0.0008	5.6	7.0
		0.0006	4.2	7.0
		0.0004	2.8	7.0
		0.0010 (TsOH)[b]	too fast to measure	>150
PhSeO$_2$H	10.0	0.0010	12.6	12.6
		0.0008	10.0	12.5
		0.0006	7.5	12.5
		0.0004	5.0	12.5

[a] All runs at 25 °C in acetonitrile containing the percentage of water (v/v) indicated; [Ph$_3$P]$_0$ = 1 × 10^{-4} M.
[b] p-Toluenesulfonic acid (5 × 10^{-4} M) added.

accompanies the conversion of the phosphine to the phosphine oxide. In contrast to the alkyl sulfide–seleninic acid reaction (vide supra) where plots of the logarithm of the absorbance change vs. time generally showed excellent linearity, plots of log $(A - A_\infty)$ vs. time for the reaction of the phosphine with either PhSeO$_2$H or p-ClC$_6$H$_4$SeO$_2$H invariably showed some downward curvature, the apparent slope of the plot increasing in the later stages of the reaction. Whether this curvature actually represents some acceleration in the conversion of Ph$_3$P to Ph$_3$P=O as the reaction proceeds or whether it is merely an artifact is not known. However, because of its existence we have used only the initial linear portion of each plot of log $(A - A_\infty)$ vs. time to estimate the experimental first-order rate constant k_1 for that run. The values of k_1 so obtained are summarized in Table II.

Examination of these data shows that k_1 varies linearly with [ArSeO$_2$H], indicating the reaction is first order in seleninic acid. An increase in the water content of the solvent from 5 to 10% leads to a modest decrease in rate constant. While the reaction proceeds quite readily in the absence of any added strong acid, addition of even as little as 5 × 10^{-4} M p-toluenesulfonic acid led to such a large increase in rate that k_1 became too fast to measure by conventional spectrophotometry. Changing the aryl group of the seleninic acid from p-ClC$_6$H$_4$ to C$_6$H$_5$ led to a small increase in rate.

Other Attempted Oxidations with p-Chlorobenzeneselenonic Acid. We had thought that perhaps 1 might be able to oxidize ketones to esters in a fashion akin to peracids in the Baeyer–Villiger reaction. However, heating equimolar amounts of 1 and benzophenone in acetonitrile at 80 °C for 6 h led to the recovery of all of the benzophenone unchanged.

The selenonic acid also does not apparently oxidize alcohols. Treatment of benzhydrol with 1 in acetonitrile at 80 °C for 2 h did not result in the formation of any benzophenone. Instead, *N*-benzhydrylacetamide was isolated in 37% yield. This amide presumably arises by 1 acting as a strong acid to promote the formation of Ph$_2$CH$^+$ from the alcohol, with the carbocation then reacting with acetonitrile in a Ritter reaction to give Ph$_2$CH$^+$N≡CCH$_3$, which is then hydrolyzed by water to give the amide.

Neither was the carbon–carbon double bond of a simple alkene (cyclohexene) oxidized by 1. When an acetonitrile

solution of 1 and cyclohexene was allowed to stand at room temperature for 20 h, little reaction occurred, and that which did led to the formation of a small amount of a compound whose infrared and NMR spectra suggested it was *N*-cyclohexylacetamide. Protonation of the alkene by 1 and reaction of the resulting carbonium ion with acetonitrile would account for the formation of this product.

Discussion

Oxidation of Alkyl Sulfides by Aromatic Seleninic Acids. In acetonitrile solvent in the presence of a strong acid catalyst alkyl sulfides can be cleanly oxidized to the corresponding sulfoxide by an aromatic seleninic acid. The stoichiometry of the reaction is shown in eq 1.

$$R_2S + {}^2/_3 ArSeO_2H \xrightarrow{H^+}$$
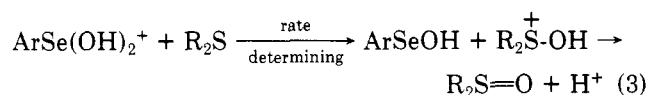$$R_2S{=}O + {}^1/_3 ArSeSeAr + {}^1/_3 H_2O \quad (1)$$
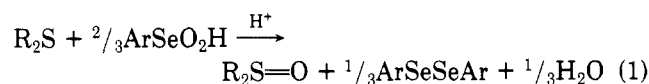
Kinetic studies of the reaction indicate that it is first order in both alkyl sulfide and seleninic acid. The pronounced dependence of rate on sulfide structure ($\rho^* = -2.0$ from a plot of log k_{R_2S} vs. $\sum \sigma^*$ for the R groups in the sulfide) shows that there is a significant decrease in the electron density on the sulfur atom of the sulfide on going to the transition state of the rate-determining step.

As noted above, the reaction does not occur at a significant rate in the absence of added strong acid. Before considering the probable mechanistic significance of the particular dependence of rate on strong acid concentration that is observed, we review briefly what is known about both the acidity and basicity of seleninic acids. Benzeneseleninic acid is a weak acid with a pK_a in water (4.79) almost identical with that of acetic acid.[5] For this reason benzeneseleninic acid should not be significantly dissociated to PhSeO$_2$$^-$ in acetonitrile containing 1–3% water. In the absence of added strong acid effectively all of the seleninic acid should be present as PhSeO$_2$H. Seleninic acids are, however, known[6] to be fairly basic and to undergo protonation quite readily by strong acids (HY) to give salts of the type RSe(OH)$_2$$^+Y^-$.
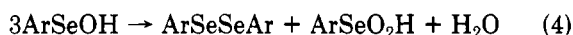
The behavior of the rate of the alkyl sulfide–seleninic acid reaction with respect to concentration of added strong acid indicates that in acetonitrile containing 1 to 3% water PhSeO$_2$H (1 × 10^{-4} M) is protonated by H$^+$ to give a species reactive toward the alkyl sulfide and that in CH$_3$CN–1% H$_2$O protonation of the seleninic acid is almost complete once the concentration of added strong acid reaches 3 × 10^{-3} M. In CH$_3$CN–3% H$_2$O a higher strong acid concentration (0.02 M) is required before protonation of the seleninic acid is complete. Given the apparent substantial basicity of seleninic acids,[6] it does not seem unreasonable to assume that PhSeO$_2$H could be almost completely protonated to PhSe(OH)$_2$$^+$ under such conditions.

A mechanism for the alkyl sulfide–seleninic acid reaction consistent with the observed effect of changes in sulfide structure on rate, and with the other aspects of the kinetics of the reaction, is given in eq 2–4. Selenenic acids

$$ArSeO_2H + H^+ \rightarrow ArSe(OH)_2^+ \quad (2)$$

$$ArSe(OH)_2^+ + R_2S \xrightarrow[\text{determining}]{\text{rate}} ArSeOH + R_2\overset{+}{S}\text{-OH} \rightarrow$$
$$R_2S{=}O + H^+ \quad (3)$$

(5) J. D. McCullough and E. S. Gould, *J. Am. Chem. Soc.*, **71**, 674 (1949).
(6) R. Paetzold, H.-D. Schumann, and A. Simon, *Z. Anorg. Allg. Chem.*, **305**, 98 (1960); H. J. Backer and W. van Dam, *Recl. Trav. Chim. Pays-Bas*, **54**, 531 (1935).

$$3ArSeOH \rightarrow ArSeSeAr + ArSeO_2H + H_2O \quad (4)$$

(ArSeOH) are known[7] to disproportionate readily to diselenides and seleninic acids, so that suggesting eq 4 (whose detailed mechanism is not yet known) as the route for the formation of the diaryl diselenide that is the other final product of the reaction seems very reasonable.[8]
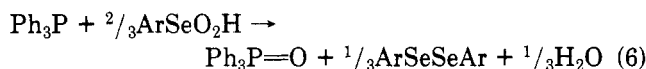
The rate of reaction of $PhSe(OH)_2^+$ with the alkyl sulfide is greatly decreased by an increase in the water content of the acetonitrile from 1 to 3%. In our opinion $PhSe(OH)_2^+$ may well be subject to significant stabilization by hydrogen bonding to water molecules. If so, this could explain the large decrease in rate that is observed with an increase in the water content of the medium.

Barnard and Woodbridge[9] have found that in an acidic solvent, such as acetic acid, but not in solvents like methanol or benzene, dibenzyl or diphenyl selenoxide will oxidize alkyl sulfides to sulfoxides. They suggested the reaction involves attack of the sulfide on the protonated selenoxide (eq 5). The similarity between eq 5 and the

$$R_2\overset{+}{S}e{-}OH + R'_2S \rightarrow R_2Se + R'_2S{=}O + H^+ \quad (5)$$
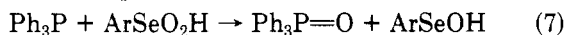
rate-determining step (eq 3) in the oxidation of alkyl sulfides by aromatic seleninic acids is readily apparent.

Oxidation of Triphenylphosphine by Aromatic Seleninic Acids. The reaction of triphenylphosphine with $ArSeO_2H$ (eq 6) has the same sort of stoichiometry

$$Ph_3P + {}^2/_3ArSeO_2H \rightarrow$$
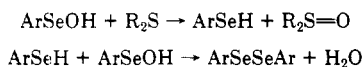$$Ph_3P{=}O + {}^1/_3ArSeSeAr + {}^1/_3H_2O \quad (6)$$

as the reaction of the alkyl sulfides (eq 1). Kinetically it too is first order in $[ArSeO_2H]$ and also first order in the concentration of the compound being oxidized, in this case the phosphine. The main difference kinetically between the two reactions is that in the oxidation of the phosphine the reaction proceeds at a relatively rapid rate even in the absence of added strong acid. Thus the more easily oxidized substrate Ph_3P can apparently attack the seleninic acid itself at a reasonable rate, whereas with the sulfides reaction occurs at a significant rate only with the protonated seleninic acid, $ArSe(OH)_2^+$. We presume that the rate-determining step of the reaction is simply attack of the phosphine on the seleninic acid to form the phosphine oxide and the selenenic acid (eq 7). Once formed, the selenenic acid can then go on to form the diselenide in the same manner (eq 4) as outlined earlier.

$$Ph_3P + ArSeO_2H \rightarrow Ph_3P{=}O + ArSeOH \quad (7)$$

Oxidation of Alkyl Sulfides and Triphenylphosphine by Aromatic Selenonic Acids. Treatment of an alkyl sulfide with an aromatic selenonic acid $(ArSeO_3H)$ leads to the oxidation of the sulfide to the sulfoxide and to the formation of the corresponding diaryl diselenide $(ArSeSeAr)$. From the amounts of sulfoxide and diselenide formed the stoichiometry of the reaction appears

to be as shown in eq 8. Oxidation of triphenylphosphine to triphenylphosphine oxide exhibits a similar stoichiometry (eq 9).

$$R_2S + {}^2/_5ArSeO_3H \rightarrow$$
$$R_2S{=}O + {}^1/_5ArSeSeAr + {}^1/_5H_2O \quad (8)$$

$$Ph_3P + {}^2/_5ArSeO_3H \rightarrow$$
$$Ph_3P{=}O + {}^1/_5ArSeSeAr + {}^1/_5H_2O \quad (9)$$

We have seen that aromatic seleninic acids $(ArSeO_2H)$ can also oxidize sulfides to sulfoxides (eq 1) and Ph_3P to $Ph_3P{=}O$ (eq 6). These oxidations are markedly catalyzed by small amounts of added strong acids. Kinetic studies of eq 9 and eq 6 show that in the presence of as little as 5×10^{-4} M p-toluenesulfonic acid the rate of oxidation of Ph_3P by $ArSeO_2H$ is *at least* 10 times faster than the rate of oxidation of the phosphine by $ArSeO_3H$. When we remember that a selenonic acid is itself a strong acid,[2] the origin of the diselenide and the particular stoichiometry observed for eq 9 become easily understood. First, reaction of the phosphine with the selenonic acid takes place according to eq 10. Then the seleninic acid $ArSeO_2H$ formed

$$Ph_3P + ArSeO_3H \rightarrow Ph_3P{=}O + ArSeO_2H \quad (10)$$

in eq 10 is rapidly consumed by reaction with additional phosphine in the fast, acid-catalyzed reaction between these two species that has already been discussed and that has the stoichiometry shown in eq 6. Summation of eq 10 and 6 gives the overall stoichiometry for the process shown in eq 9.

A similar sequence of events, reaction of the selenonic acid with sulfide according to eq 11, followed by more rapid

$$R_2S + ArSeO_3H \rightarrow R_2S{=}O + ArSeO_2H \quad (11)$$

reaction of the seleninic acid produced in eq 11 with additional sulfide in the manner shown in eq 1, is presumably involved in the oxidation of sulfides by the selenonic acid, and would, of course, result in the overall stoichiometry for the reaction shown in eq 8.

Failure of Selenonic Acids to Oxidize Other Organic Functionalities. Despite their ability to oxidize sulfides and phosphines, we find aromatic selenonic acids to be ineffectual as oxidizing agents for alkenes, alcohols, or ketones. This certainly suggests that they are *not* generally useful oxidizing agents for organic functionalities. This, combined with the fact that they are in many cases somewhat difficult to prepare, means that they are unlikely to be of significant use as reagents in organic synthesis.

Experimental Section

Benzeneseleninic Acid (2b). Diphenyl diselenide (Eastman), purified by recrystallization from hexane, was oxidized to benzeneseleninic acid by using the procedure described by McCullough and Gould;[5] mp 120–121 °C (lit[5] mp 121 °C).

p-**Chlorobenzeneseleninic Acid (2a).** Bis(*p*-chlorophenyl) diselenide, mp 88–90 °C, was prepared by the procedure of Foster.[10] *p*-Chlorobenzeneseleninic acid was then prepared from this diselenide in the manner described by McCullough and Gould.[5] It was recrystallized from water; mp 170–180 °C (lit.[3] mp 170–185 °C).

p-**Chlorobenzeneselenonic Acid (1).** This was prepared from *p*-chlorobenzeneseleninic acid by oxidation of the seleninic acid with potassium permanganate according to the procedure of Rebane,[4] mp 145–147 °C (lit.[4] mp 146–147.5 °C).

Other Materials. The acetonitrile used was a special grade supplied by Eastman Organic Chemicals containing less than 0.05% water and was used without further purification. The

(7) H. Rheinboldt and E. Giesbrecht, *Chem. Ber.*, **89**, 631 (1956); H. J. Reich, S. Wollowitz, J. E. Trend, F. Chow, and D. F. Wendelborn, *J. Org. Chem.*, **43**, 1697 (1978); T. Hori and K. B. Sharpless, *ibid.*, **43**, 1689 (1978).
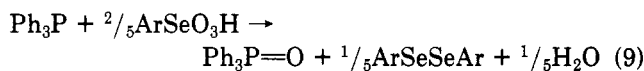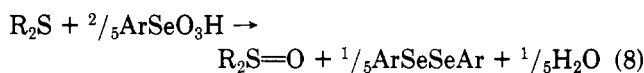
(8) Although eq 4 represents a perfectly reasonable route for the formation of the diselenide, the possibility exists that ArSeOH may be able under the reaction conditions also to oxidize the sulfide to the sulfoxide, being itself reduced to ArSeH, and that the diselenide could then be formed by reaction of ArSeH with ArSeOH:

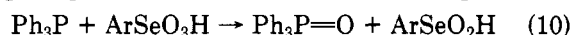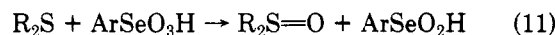$$ArSeOH + R_2S \rightarrow ArSeH + R_2S{=}O$$

$$ArSeH + ArSeOH \rightarrow ArSeSeAr + H_2O$$

Either route for the formation of the diselenide leads to the same predicted overall stoichiometry for the reaction of $ArSeO_2H$ with R_2S.

(9) D. Barnard and D. T. Woodbridge, *Chem. Ind. (London)*, 1603 (1959).

(10) D. G. Foster, "Organic Syntheses", Collect. Vol. III, Wiley, New York, N.Y., 1953, p 771.

sulfides, sulfoxides, triphenylphosphine, and triphenylphosphine oxide were all the highest purity materials commercially available, and examination indicated that all were of a sufficient purity to be used without further purification.

Reaction of Triphenylphosphine with Seleninic Acids. To 0.51 g (2.3 mmol) of *p*-chlorobenzeneseleninic acid dissolved in 9 mL of acetonitrile and cooled to 0 °C was added 0.58 g (2.2 mmol) of triphenylphosphine, and the solution was allowed to stand at 0 °C for 1 h. The reaction solution was then poured into about five times its volume of water, and the aqueous mixture was extracted with methylene chloride. The methylene chloride extracts were washed first with 10% aqueous sodium carbonate to remove unreacted seleninic acid and were then washed with water. Removal of the methylene chloride under reduced pressure left a residue that was subjected to chromatography on silica gel, using pentane or 1:1 pentane–benzene as eluents. From the chromatography there was isolated 0.62 g (2.2 mmol) of triphenylphosphine oxide and 0.28 g (0.74 mmol) of bis(*p*-chlorophenyl) diselenide. The identity of both the phosphine oxide and the diselenide was proven by appropriate comparisons with known samples.

In the same way reaction of benzeneseleninic acid (0.25 g, 1.32 mmol) with triphenylphosphine (0.35 g, 1.33 mmol) gave upon similar workup and chromatography 0.135 g (0.43 mmol) of diphenyl diselenide and 0.356 g (1.28 mmol) of triphenylphosphine oxide.

Reaction of Alkyl Sulfides with Seleninic Acids. Dibenzyl sulfide (0.22 g, 1.03 mmol) and *p*-chlorobenzeneseleninic acid (0.26 g, 1.14 mmol) were dissolved in 10 mL of acetonitrile, and the solution was allowed to stand at room temperature for 24 h. Workup at the end of this time gave quantitative recovery of the sulfide, indicating that no reaction had occurred. However, if 0.05 g (0.29 mmol) of *p*-toluenesulfonic acid was also added to the original solution of the sulfide and the seleninic acid, then after 24 h upon workup, using the same general procedure as in the phosphine–seleninic acid reactions, there was obtained after chromatography of the residue 0.126 g (0.33 mmol) of bis(*p*-chlorophenyl diselenide and 0.214 g (0.93 mmol) of dibenzyl sulfoxide. The identity of both products was proved by appropriate comparison with known samples.

n-Butyl sulfide (0.33 g, 2.23 mmol) was added to a solution of 0.50 g (2.2 mmol) of *p*-chlorobenzeneseleninic acid and 0.10 g of 70% perchloric acid in 5 mL of acetonitrile. After standing overnight at room temperature the reaction solution was poured into water and worked up in the same way as for the benzyl sulfide reaction. Chromatography of the residue on silica gel, using pentane as eluent, afforded 0.179 g (0.57 mmol) of bis(*p*-chlorophenyl) diselenide. Elution with pentane–acetone (1:1) gave 0.326 g (2.01 mmol) of *n*-butyl sulfoxide, identical in all respects with a known sample.

Kinetic Studies of Seleninic Acid Reactions. A solution (volume 3.5 mL) containing the desired concentration of the seleninic acid, water, and, if used, perchloric acid in acetonitrile was placed in a 1-cm spectrophotometer cell in the thermostated cell compartment of a Cary Model 17 spectrophotometer. After this solution had come to temperature the reaction was initiated by adding to the cell via a microsyringe a small amount ($\leq$35 μL) of a stock solution of, as appropriate, either the alkyl sulfide or triphenylphosphine in acetonitrile. In the runs with the sulfides the increase in the absorbance of the solution at 240 nm was then monitored; in the runs with Ph_3P and $PhSeO_2H$ the change in the absorbance at 280 nm was followed, while in the runs with the phosphine and *p*-chlorobenzeneseleninic acid the wavelength used was 265 nm.

Reaction of 1 with Triphenylphosphine. Products. To 0.51 g (2.1 mmol) of 1 dissolved in 9 mL of acetonitrile was added 0.55 g (2.1 mmol) of triphenylphosphine, and the solution was allowed to stand at 0 °C for 10 min. It was then poured into about five times its volume of water and the aqueous mixture was extracted with methylene chloride. The methylene chloride extracts were washed first with 10% aqueous sodium carbonate and then with water. The methylene chloride was removed under reduced pressure to leave a residue which was subjected to chromatography on silica gel, using 1:1 pentane–benzene as the eluent. From the chromatography there was isolated 0.54 g (1.94 mmol, 92%) of triphenylphosphine oxide and 0.20 g (0.54 mmol)

of bis(*p*-chlorophenyl) diselenide, each identical in all respects with known samples of the same compounds.

Kinetics. A solution (3.5 mL) of the selenonic acid ((0.4–1.0) × 10^{-3} M) in acetonitrile–10% water was placed in a 1-cm spectrophotometer cell in the thermostated cell compartment of a Cary Model 17 spectrophotometer. Once it had come to temperature 35 μL of a 0.01 M solution of triphenylphosphine in acetonitrile was then added with thorough mixing, and the change in the absorbance (*A*) of the solution with time at 278 nm was then followed. Plots of log ($A - A_\infty$) vs. time were nicely linear. The experimental first-order rate constants for the runs at the different concentrations of selenonic acid used were as follows (concentration of $ArSeO_3H$, k_1): 0.0010 M, 0.016 s^{-1}; 0.0008 M, 0.012 s^{-1}; 0.0006 M, 0.0094 s^{-1}; 0.0004 M, 0.0062 s^{-1}.

Reaction of 1 with Benzyl Sulfide. Benzyl sulfide (1.0 g, 4.68 mmol) and 1 (1.0 g, 4.2 mmol) were dissolved in 9 mL of acetonitrile and the solution was allowed to stand at room temperature for 18 h. The solution was then poured into water, extracted with methylene chloride, and further worked up in the same fashion as for the reaction of 1 with Ph_3P. Chromatography on silica gel of the residue remaining after removal of the methylene chloride, using carbon tetrachloride–acetone 4:1 as the eluting solvent, gave 1.04 g (4.52 mmol, 96%) of dibenzyl sulfoxide, identical in all respects with a known sample, and 0.40 g (1.05 mmol) of bis(*p*-chlorophenyl) diselenide.

An otherwise identical run in acetic acid as solvent and using a reaction time of 24 h gave 1.07 g (4.68 mmol) of dibenzyl sulfoxide and 0.40 g (1.05 mmol) of bis(*p*-chlorophenyl) diselenide.

Reaction of 1 with Phenyl Sulfide. Diphenyl sulfide (0.76 g, 4.1 mmol) and 1.0 g (4.1 mmol) of 1 were dissolved in 9 mL of acetonitrile and the solution was allowed to stand at room temperature for 18 h before being worked up in the same fashion as in the experiments with benzyl sulfide. Chromatography of the residue remaining after the removal of the methylene chloride gave 0.24 g (1.3 mmol, 31%) of unreacted diphenyl sulfide, 0.56 g (2.8 mmol, 68%) of diphenyl sulfoxide, identical in all respects with a known sample, and 0.15 g (0.39 mmol) of bis(*p*-chlorophenyl) diselenide.

Other Attempted Oxidations with 1. Benzophenone (0.36 g, 2.0 mmol) and 1 (0.50 g, 2.0 mmol) were dissolved in 9 mL of acetonitrile and the solution was heated to 80 °C for 6 h. The solution was then worked up in the same fashion as described earlier for the sulfides and triphenylphosphine. Upon evaporation of the methylene chloride all of the benzophenone was recovered unchanged.

A solution of benzhydrol (0.37 g, 2.0 mmol) and 1 (0.5 g, 2.0 mmol) in 9 mL of acetonitrile was heated at 80 °C for 2 h. After workup in the fashion already described, the residue remaining after removal of the methylene chloride was recrystallized from ethanol to afford 0.165 g (0.73 mmol) of *N*-benzhydrylacetamide: mp 148–151 °C (lit.[11] mp 149–150 °C); NMR (CDCl$_3$) δ 1.95 (s, 3 H), 6.21 (d, 1 H), 6.5 (broad peak, 1 H), 7.1–7.4 (m, 10 H). The infrared spectrum showed a strong peak at 1640 cm^{-1} and other absorptions consistent with the structure $Ph_2CHNHC(O)CH_3$.

Cyclohexene (0.5 g, 6.1 mmol) and 1 (1.0 g, 4.0 mmol) were dissolved in 6 mL of acetonitrile and the solution was allowed to stand at room temperature for 20 h. At that time the solution was poured into water and worked up in the same fashion as in the cases above. Removal of the methylene chloride left a small amount of a brownish oil. From this there was isolated on chromatography a small amount (50 mg) of a material whose infrared and NMR spectra suggested it was *N*-cyclohexylacetamide.

(11) L. Skulski, G. C. Palmer, and M. Calvin, *Roczn. Chem.*, **38**, 789 (1964).