Tetrahedron Letters Vol. 21, pp 1697 - 1700
© Pergamon Press Ltd. 1980. Printed in Great Britain

0040-4039/80/0429-1697$02.00/0

THE REACTION OF SULFINIC ACIDS WITH BENZENESELENINIC ACID[1]

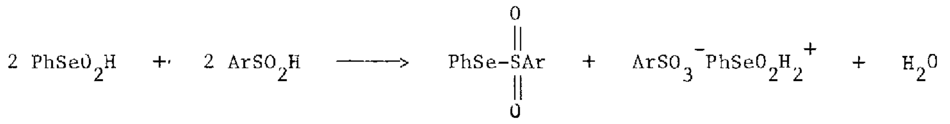
Roman A. Gancarz and John L. Kice*

Department of Chemistry, Texas Tech University
Lubbock, Texas 79409

Abstract: Aromatic sulfinic acids are rapidly oxidized at 0°C by benzeneseleninic acid, setting in motion a reaction sequence whose final products are (a) the arenesulfonate salt of benzeneseleninic acid (**2**) and (b) the Se-phenyl areneselenosulfonate (**1**).

We wish to report a novel and very facile reaction between arenesulfinic acids ($ArSO_2H$) and benzeneseleninic acid ($PhSeO_2H$) that leads to the oxidation of part of the sulfinic acid to the corresponding sulfonic acid and to the conversion of the remainder to the phenyl areneselenosulfonate, $ArSO_2SePh$ (**1**).

When dilute solutions of p-toluenesulfinic acid and benzeneseleninic acid in acetonitrile are mixed at 0°C in equimolar proportions a rapid reaction ensues, as evidenced by the crystallization from the solution after ~5 min. of one of the reaction products, a strongly acidic salt (m.p. 175°, equiv. wt., 360) whose infrared spectrum, NMR, and elemental analysis show it to be the p-toluenesulfonic acid salt of benzeneseleninic acid (**2**, Ar = p-$CH_3C_6H_4$); the amount of **2** formed is 0.5 mmole/mmole $ArSO_2H$. The other major product, which can be isolated from the acetonitrile solution by careful work-up,[2] is Se-phenyl p-tolueneselenosulfonate[3] (**1**, Ar = p-tolyl). The approximate stoichiometry of the reaction is shown in eq. 1.[4] Other sulfinic acids (Ar = C_6H_5, p-ClC_6H_4) react in exactly analogous fashion.

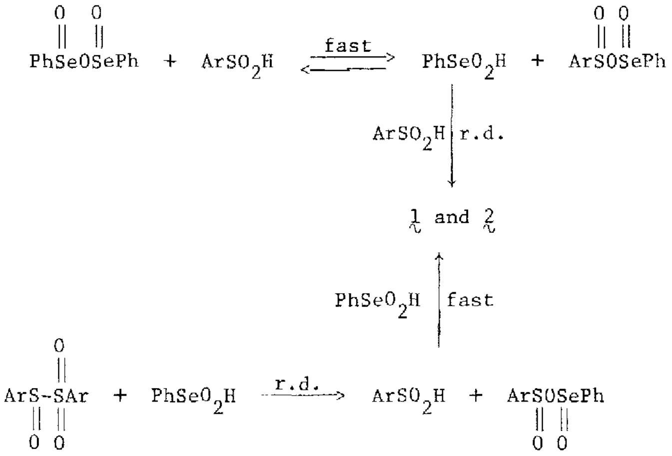


$$2\ PhSeO_2H + 2\ ArSO_2H \longrightarrow PhSe\text{-}\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}Ar + ArSO_3^-PhSeO_2H_2^+ + H_2O \qquad (1)$$

1 **2**

The same products, **1** and **2**, are also formed rapidly if one reacts one mole of $ArSO_2H$ with 0.5 mole of benzeneseleninic anhydride, PhSe(O)OSe(O)Ph, or more slowly, if one reacts 0.5

mole of the aryl sulfinyl sulfone $ArS(O)SO_2Ar$ with one mole of $PhSeO_2H$. In these two cases the initially absent component of the reacting pair of acids is generated either rapidly (eq. 2) or considerably more slowly (eq. 3), from the seleninic anhydride and sulfinyl sulfone, respectively.



$$Ph\overset{O}{\overset{\|}{Se}}O\overset{O}{\overset{\|}{Se}}Ph + ArSO_2H \xrightleftharpoons{fast} PhSeO_2H + Ar\overset{O}{\overset{\|}{S}}O\overset{O}{\overset{\|}{Se}}Ph \qquad (2)$$

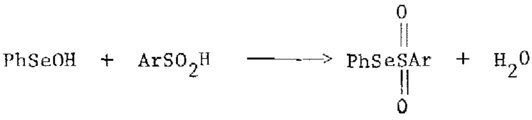
$$PhSeO_2H \xrightarrow[r.d.]{ArSO_2H} 1 \text{ and } 2 \xleftarrow[fast]{PhSeO_2H} ArSO_2H$$

$$Ar\underset{O}{\underset{\|}{S}}-\overset{O}{\underset{O}{\overset{\|}{\underset{\|}{S}}}}Ar + PhSeO_2H \xrightarrow{r.d.} ArSO_2H + Ar\underset{O}{\underset{\|}{S}}O\underset{O}{\underset{\|}{Se}}Ph \qquad (3)$$

The initial step in eq. 1 is presumably a redox reaction between $PhSeO_2H$ and $ArSO_2H$ (eq. 4). The sulfonic acid $ArSO_3H$ formed in eq. 4 protonates a second molecule of the seleninic acid (seleninic acids are known[6] to be weak bases) forming salt 2 (eq. 5). The benzenselenenic acid (PhSeOH) from eq. 4 is consumed primarily by reaction with sulfinic acid (eq. 6), forming 1, although a small amount of PhSeOH evades capture by sulfinic acid and undergoes disproportionation.

$$PhSeO_2H + ArSO_2H \longrightarrow PhSeOH + ArSO_3H \qquad (4)$$

$$PhSeO_2H + ArSO_3H \longrightarrow \underset{2}{PhSeO_2H_2^{+}ArSO_3^{-}} \qquad (5)$$



$$PhSeOH + ArSO_2H \longrightarrow \underset{1}{PhSe\overset{O}{\underset{O}{\overset{\|}{\underset{\|}{S}}}}Ar} + H_2O \qquad (6)$$

That eq. 6 is competitive in rate with eq. 4 is shown by the fact that reaction of 1.0 mmole of $PhSeO_2H$ with <u>only 0.5 mmole</u> of $ArSO_2H$ still leads to the formation of a significant amount of selenosulfonate 1(~25% of the amount produced when a 1:1 molar ratio of reactants is used). Were the rate of eq. 4 much faster than that of eq. 6 no 1 would be formed under such conditions, because all of the sulfinic acid would be consumed by reaction with $PhSeO_2H$ in eq. 4 before any could be consumed by eq. 6.[7]

The ability of the seleninic acid to oxidize so readily the organic sulfur acid of equivalent oxidation state is an example of the marked difference in the chemistries of these two neighboring Group VI elements that derives from the fact that while S(VI) is a stable oxidation state for sulfur relative to S(IV) exactly the reverse is true for Se(VI) *vs.* Se(IV). Besides the present oxidation of sulfinic acids, seleninic acids have also recently been shown to oxidize phosphines,[8a] phosphites,[8d] alkyl sulfides,[8a] hydrazines,[8b] and acyl hydrazides.[8c] The present oxidation, and that of acyl hydrazides,[8c] differ from the other oxidations in that the selenenic acid (PhSeOH) produced is trapped by the substrate (sulfinic acid reaction), or an oxidation product derived from the substrate (acyl hydrazide reaction), rather than undergoing disproportionation[5] to diphenyl diselenide.

The $PhSeO_2H$-$ArSO_2H$ reaction (eq. 1) also occurs readily in acetic acid, ether, or ethanol. When ethanol is the solvent medium precipitation of salt **2** does not occur, while the solubility of the areneselenosulfonate **1** is low enough so that it can be induced to crystallize from the reaction medium in good yield in a very pure state upon removal of most of the ethanol. Thus, reaction of 5 mmoles of $ArSO_2H$ and 5 mmoles of $PhSeO_2H$ in ethanol (20 ml) for 0.5 hr., followed by removal at room temperature of 10-15 ml of the ethanol, leads to the isolation, after cooling, of pure areneselenosulfonate **1** in yields (based on the stoichiometry of eq. 1) of 61% (Ar = Ph or *p*-tolyl) to 70% (Ar = *p*-ClC_6H_4). The simplicity of this procedure and the high purity of the product suggest this as an attractive route for the preparation of Se-aryl areneselenosulfonates, an interesting class of compounds whose chemistry to date has received only very limited study,[9] but which are now under investigation in this laboratory.

References and Notes

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

(2) The acetonitrile solution was treated with anhydrous, solid sodium carbonate to neutralize the traces of **2** still present in solution, filtered, and then evaporated to dryness at room temperature. The ultraviolet spectrum of the residue shows that **1** is present in an amount ~70% of that expected from the stoichiometry of eq. 1. Pure **1** may be isolated by extraction of the residue with hexane and concentration of the hexane extract, followed by cooling in the refrigerator, at which point **1** (Ar = *p*-tolyl, mp 75-77°C; lit.[3], 77-79°C) crystallizes out.

(3) D. H. R. Barton, M. R. Britten-Kelly, and D. Ferreira, *J. Chem. Soc.*, *Perkin I*, 1682 (1978).

(4) A small amount of diphenyl diselenide, PhSeSePh, is also formed. This presumably arises because some of the benzeneselenenic acid (PhSeOH) produced in eq. 4 escapes being trapped by $ArSO_2H$ and undergoes disproportionation.[5] Because of this the yield of **1**

is only about 70% of that predicted by the stoichiometry of eq. 1.

(5) (a) H. J. Reich, J. M. Renga, and I. L. Reich, *J. Am. Chem. Soc.*, **97**, 5734 (1975);
(b) O. Behagel and H. Deibert, *Chem. Ber.*, **66**, 708 (1933);
(c) H. Rheinboldt and K. Giesbrecht, *Chem. Ber.*, **89**, 631 (1956).

(6) (a) R. Paetzold, H.-D. Schumann, and A. Simon, *Z. Anorg. Allg. Chem.*, **305**, 98 (1960);
(b) H. J. Backer and W. van Dam, *Recl. Trav. Chim. Pays-Bas.*, **54**, 531 (1935).

(7) The fact that use of a 1.0:0.5 molar ratio of $PhSeO_2H:ArSO_2H$ leads to the formation of ~25% of the amount of **1**, but to *~70%* of the amount of **2**, produced when a 1:1 molar ratio of reactants is employed also shows that the rate of eq. 6 *cannot be much faster* than the rate of eq. 4, for if that were the case the yields of *both* **1** and **2** would be reduced by the *same extent* from what is found for reaction of $PhSeO_2H$ with $ArSO_2H$ in 1:1 molar proportions.

(8) (a) L. G. Faehl and J. L. Kice, *J. Org. Chem.*, **44**, 2357 (1979);
(b) T. G. Back, *Chem. Commun.*, **278** (1978);
(c) T. G. Back and S. Collins, *Tetrahedron Letters*, 2661 (1979);
(d) D. Labar, A. Krief, and L. Hevesi, *Tetrahedron Letters*, 3967 (1978).

(9) (a) O. Foss, *J. Am. Chem. Soc.*, **69**, 2236 (1947);
(b) T. Austad, *Acta Chem. Scand.*, **30A**, 479 (1976).

(Received in USA 29 January 1980)