THE ANHYDRIDE STRUCTURE OF SEVERAL PREVIOUSLY REPORTED STABLE ARENESELENENIC ACIDS<sup>1</sup>

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Abstract: The compounds previously reported<sup>2</sup> to be the stable areneselenenic acids, <u>o</u>-nitro-(La) and <u>o</u>-benzoylbenzeneselenenic acid (Lb), are shown actually to be the corresponding selenenic anhydrides (ArSeOSeAr). Solutions of the selenenic acids (ArSeOH), however, can be easily generated from the anhydrides by acid-catalyzed hydrolysis.

About 25 years ago Rheinboldt and Giesbrecht<sup>2</sup> described the preparation (via reduction of the corresponding seleninic acids with hydrazine sulfate) of two compounds which they believed to be the areneselenenic acids la and lb. These two compounds have represented the only

ArSeOH	ArSeOSeAr
$\frac{1}{2}$ , Ar = $\underline{o}^{-0} 2^{NC} 6^{H} 4^{-1}$	$2a$ , Ar = $-0_2 NC_6 H_4$ -
$\frac{1}{2}$ , Ar = <u>o</u> -PhC(0)C <sub>6</sub> H <sub>4</sub> -	$\frac{2b}{\sqrt{2}}$ , Ar = <u>o</u> -PhC(0)C <sub>6</sub> H <sub>4</sub> -

reported examples of relatively stable and isolable monosubstituted benzeneselenenic acids. Because of this they seemed ideal substrates to use in the initial phase of a planned general study of the mechanisms of reactions of areneselenenic acids. We therefore repeated the preparations of 1a and 1b as described by Rheinboldt and Giesbrecht<sup>2</sup> and in each instance isolated<sup>3</sup> compounds wnose melting point benavior, etc. were in agreement with those reported.<sup>2</sup> However, study of the chemical behavior of these compounds, as outlined in the remainder of this communication, demonstrates conclusively that they are not selenenic acids 1a and 1b as thought by Rheinboldt and Giesbrecht, but are in actuality the corresponding selenenic anhydrides 2a and 2b

Curve 1 of Figure 1A shows the UV absorption spectrum of a dilute solution of the <u>o</u>-nitrophenyl compound of Rheinboldt and Giesbrecht.<sup>2a</sup> In acidic 60% dioxane this spectrum gradually changes ( $t_{1/2} = 48 \text{ min in a 1:1 0.02 } \underline{M} \text{ CICH}_2\text{COOH/CICH}_2\text{COO}^-$  buffer at 25°C) to that



<u>Figure 1A</u>. Curve 1, UV spectrum of 2a (5 x  $10^{-5}$  <u>M</u>) in 60% dioxane. Curve 2, hydrolysis products of 2a (i.e., <u>1a</u>, 1.0 x  $10^{-4}$  <u>M</u>). Curve 3, calculated spectrum for solution 5 x  $10^{-5}$  <u>M</u> in both 3a and 1a; **O**, experimental data at end of first stage (eq 2) of the <u>n</u>-Bush-2a reaction. Curve 4, spectrum of 3a (1 x  $10^{-4}$  <u>M</u>). Curve 5, spectrum of ArSeSeAr + ArSeO<sub>2</sub>H (both 0.33 x  $10^{-4}$  <u>M</u>, Ar =  $0^{-0}2^{NC}_{6}H_{4}$ ).

Figure 1B. Curve 1, UV spectrum of 2b (5 x  $10^{-5}$  M) in 60% dioxane. Curve 2, hydrolysis products of 2b (i.e., 1b, 1.0 x  $10^{-4}$  M).

shown as Curve 2. The spectrum of Curve 2 is entirely different from the one (Curve 5) that would correspond to the occurrence of the reaction  $3 \operatorname{ArSeOH} \longrightarrow \operatorname{ArSeSeAr} + \operatorname{ArSeO}_2 H + H_2 O$ Therefore the change from Curve 1 to Curve 2 cannot represent the disproportionation of the selenenic acid. Furthermore, when a solution of the material having the spectrum of Curve 2 is diluted with water, the product extracted with chloroform, and the chloroform evaporated under reduced pressure, what is isolated (in essentially quantitative yield) is, not a substance having the spectrum of Curve 2, but rather that of Curve 1, i.e., the original starting material. This was established not only by UV and other spectral (IR, NMR) comparisons, but also by the fact that upon being redissolved in acidic 60% dioxane the material underwent the spectral change from Curve 1 to 2 at exactly the same rate as the original compound. The <u>o</u>-benzoyl compound of Rheinboldt and Giesbrecht<sup>2b</sup> exhibits analogous behavior (Curves 1 and 2 of Figure 1B), the only difference being that the spectral change from Curve 1 to 2 is considerably more rapid ( $t_{1/2} = 1.6$  min in a 1·1 0.02 M CICH<sub>2</sub>COOH/CICH<sub>2</sub>COO<sup>-</sup> buffer in 60% dioxane at 25°C).

This otherwise curious behavior is easily explained if the compounds isolated by Rheinboldt and Giesbrecht are in fact, <u>not</u> the selenenic acids La and 1b, but rather selenenic anhydrides 2a and 2b. The change from Curve 1 to Curve 2 in acidic aqueous dioxane represents the acid-catalyzed hydrolysis of the anhydride (2) to two molecules of the selenenic acid (eq la), but when the selenenic acid (1) is extracted from the final reaction solution into chloroform and the solvent removed, 1 reverts rapidly to 2 (eq lb), thereby accounting for the reisolation of the original starting material under such circumstances.



The behavior of the reaction of the <u>o</u>-nitro and <u>o</u>-benzoyl compounds with alkanethiols in acidic 60% dioxane further confirms that the substances are selenenic anhydrides (2), rather than selenenic acids. Thus, the reactions of both compounds with 1-butanethiol exhibit biphasic kinetics, the more rapid first stage corresponding to the reaction of the selenenic anhydride with the thiol according to eq 2, and the slower second stage to the reaction of the mole of selenenic acid formed in eq 2 with another mole of thiol to give a second mole of the selenenyl sulfide 3 (eq 3). With 2b in acetate buffers  $k_2$  is (depending on pH) from 4 5 to 15 times faster than  $k_3$ . With the <u>o</u>-nitro compound (2a) the difference in rates is much larger

with  $k_2$  being so much faster (factor of 80) than  $k_3$  in a 1 1 0.02 <u>M</u> HCOOH/HCOO<sup>-</sup> buffer that eq 2 is complete before reaction 3 has proceeded to any significant extent. As required by the reaction scheme in eqs 2 and 3, one finds that the UV spectrum of the reaction solution at the end of the first stage of the reaction of <u>n</u>-BuSH with 2a (Curve 3, Figure 1A) fits exactly with that calculated from the spectra of the hydrolysis products of 2a (2 moles la, Curve 2) and the final products of the thiol reaction (2 moles  $\frac{3a}{20}$ , Curve 4) for a reaction (eq 2) in which 2a yields one mole each of  $\frac{3a}{20}$  and  $\frac{1a}{20}$ .

In an accompanying communication Retch and co-workers,<sup>4</sup> using a quite different expermental approach, also show that the <u>o</u>-nitrophenyl compound of Rheinboldt and Giesbrecht<sup>2a</sup> is the anhydride 2a, rather than the selenenic acid. The important conclusion to be drawn from this work and that of Reich <u>et al.</u><sup>4</sup> is that the interconversion of areneselenenic acids (1) and their anhydrides (2) is a considerably more facile process than many might have imagined. Therefore, in systems in which areneselenenic acids are generated as intermediates in media containing negligible amounts of water one should always be alert for the possibility that subsequent observed reactions may actually be ones originating from the selenenic anhydride rather than from the acid.

The details of the kinetics of the acid-catalyzed hydrolyses of 2a and 2b, and of their reactions, and those of 1a and 1b, with alkanethiols, which show a number of most interesting features, including significant differences between the behavior of the <u>o</u>-nitro and <u>o</u>-benzoyl compounds, will be reported later in a full paper.

## References and Notes

- (1) This research supported by the National Science Foundation, Grant CHE-79-18877.
- (2) (a) H. Rheinboldt and E. Giesbrecht, <u>Chem. Ber.</u>, <u>88</u>, 666 (1955);
  (b) <u>Ibid.</u>, <u>89</u>, 631 (1956)
- (3) To purify the crude <u>o</u>-benzoyl compound we found it necessary to treat the material with carbon tetrachloride ( $\sim 2$  ml/g of material), filter to remove an insoluble impurity, and then precipitate the pure <u>o</u>-benzoyl compound by the addition of  $\sim 20$  ml of hexane to the carbon tetrachloride solution at room temperature.
- (4) H. J Reich, W W Willis, Jr, and S Wollowitz, <u>Tetrahedron Letters</u> (accompanying communication).

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