Peracid Oxidation of Naphtho[1,8-*cd*]-1,2-diselenole: Structure and Chemistry of the Monooxidation Product[1]

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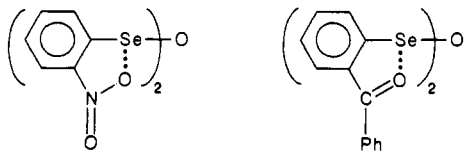
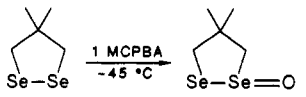
Oxidation of cyclic aryl diselenide **4** at −5 °C with 1 mol of *m*-chloroperoxybenzoic acid results in the formation of a surprisingly stable monooxidation product (**4-O**) that ^{1}H NMR shows is a mixture of naphtho[1,8-*cd*]-1,2-diselenole 1-oxide (**5**) and naphthalene-1,8-diselenenic anhydride (**6**). Cyclic selenenic anhydride **6** is the first areneselenenic anhydride not stabilized by coordination of an ortho substituent to selenium that is stable enough to be isolable, and selenolseleninate **5** is the first representative of that class of organoselenium compounds to have an appreciable lifetime at room temperature. Reaction of **4-O** with *t*-BuSH is very rapid and gives 1,8-bis[(*tert*-butylthio)seleno]naphthalene (**8**) in >90% yield. Reaction of **4-O** with hydrogen peroxide is interesting in that it leads to the formation of up to 0.5 mol of **4**/mol of **4-O** reacting. The mechanism in Scheme I is proposed to account for the formation of **4** in this reaction.

To date all areneselenenic anhydrides (ArSeOSeAr) long-lived enough to be isolable have been ones, such as *o*-nitro-[3ac] (**1a**) or *o*-benzoylbenzeneselenenic[3bc] (**1b**) anhydride, where the compound is stabilized by coordination of the ortho substituent to selenium. Isolable isomeric aryl areneselenolseleninates (ArSe(O)SeAr) have not been reported.



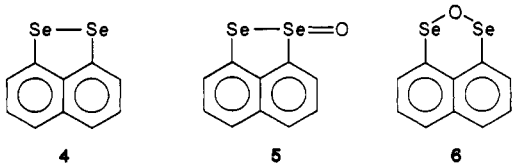
1a **1b**

Reich, Hoeger, and Willis[4] have shown that although no selenolseleninate RSe(O)SeR can be detected at the completion of the oxidation of an *acyclic* alkyl diselenide with 1 equiv of peracid at low temperature, the same is not true for the oxidation of a *cyclic*, five-membered diselenide, 4,4-dimethyl-1,2-diselenolane (**2**). Oxidation of **2** at −45 °C with 1 mol of *m*-chloroperoxybenzoic acid (MCPBA) (eq 1) gave a substance whose NMR spectrum established



2 **3** (1)

unequivocally that it was selenolseleninate **3**. Only upon warming to −20 °C did **3** decompose. Given the behavior of **2**, there seemed reason to hope that oxidation of naphtho[1,8-*cd*]-1,2-diselenole[5] (**4**) with 1 mol of peracid under suitable conditions might lead to a cyclic areneselenolseleninate **5**, or its isomeric areneselenenic anhydride **6**, having sufficient stability to be capable of isolation and study. Compound **5** would represent the first reported aryl selenolseleninate, while **6** would be the first areneselenenic anhydride without an ortho substituent coordinated to Se that was stable enough to be isolable.



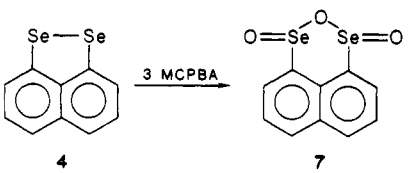
4 **5** **6**

The present paper describes the results of a study of the oxidation of **4** and of the structure and chemistry of its monooxidation product.

Results and Discussion

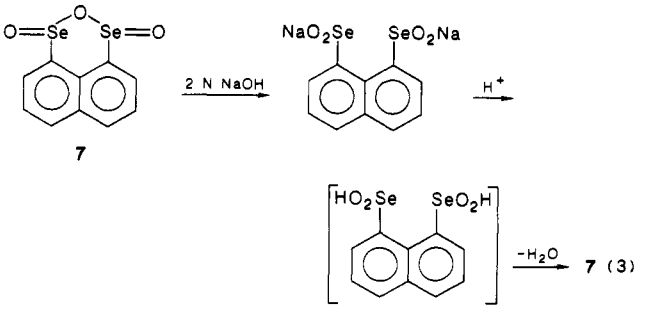
Oxidation of Naphtho[1,8-*cd*]-1,2-diselenole with Peracid. The oxidation of naphtho[1,8-*cd*]-1,2-diselenole (**4**) with peracid was investigated by using both 1 and 3 molar equiv of the oxidant.

Reaction of **4** with 3 molar equiv of MCPBA at room temperature led to the formation of naphthalene-1,8-diseleninic anhydride (**7**) (eq 2). This anhydride was so



4 **7** (2)

insoluble in all possible recrystallization solvents that its purification was effected by allowing **7** to react with 2 N sodium hydroxide to form sodium naphthalene-1,8-diseleninate. Acidification of a solution of the diseleninate resulted in the reprecipitation of the anhydride:



7 (3)

Addition of 1 mol of MCPBA to a solution of **4** in ether at −5 °C resulted in the rapid disappearance of **4** (as judged by the discharge of the purple color of the solution) and in the separation of a yellow-brown precipitate. This precipitate, which was purified by dissolving the material

(1) This research supported by the National Science Foundation, Grants GP-8215140 and GP-8519055.

(2) (a) University of Denver; (b) Texas Tech University.

(3) (a) Rheinboldt, H.; Giesbrecht, E. *Chem. Ber.* **1955**, *88*, 666, 1037, 1974. (b) Rheinboldt, H.; Giesbrecht, E. *Chem. Ber.* **1956**, *89*, 631. (c) Kice, J. L.; McAfee, F.; Slebocka-Tilk, H. *Tetrahedron Lett.* **1982**, *23*, 3323. Kice, J. L.; McAfee, F.; Slebocka-Tilk, H. *J. Org. Chem.* **1984**, *49*, 3100.

(4) Reich, H. J.; Hoeger, C. A.; Willis, W. W., Jr. *J. Am. Chem. Soc.* **1982**, *104*, 2936.

(5) Meinwald, J.; Dauplaise, D.; Wudl, F.; Hansen, J. J. *J. Am. Chem. Soc.* **1977**, *99*, 255.

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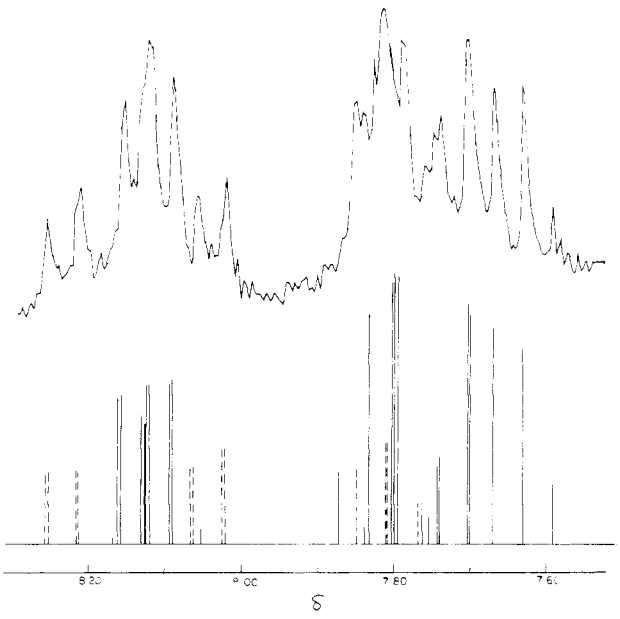


Figure 1. The ^1H NMR spectrum (200 MHz) of the monooxidation product of **4** (**4-O**) in $CDCl_3$ at 10 °C and stick plots of the computer-simulated NMR spectra of **5** (solid vertical lines) and **6** (dashed vertical lines).

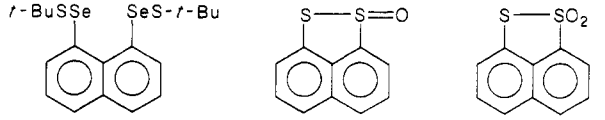
in cold chloroform and reprecipitating it by addition of hexane, analyzed for $C_{10}H_6OSe_2$ and was therefore a monooxidation product of **4**.

Although this monooxidation product (**4-O**) was stable for days at −20 °C in the dark, solutions in solvents such as chloroform showed evidence of some decomposition after a few hours at room temperature. This decomposition resulted in the formation of diselenide **4** (solution developed purple coloration; appearance of signals in ^1H NMR characteristic of **4**; absorption in UV at 375 nm λ_{max} of **4**) and an insoluble material, presumed to be **7** but not positively identified. Exposure of the solutions to light appeared to accelerate the decomposition. Although **4-O** was considerably more soluble than **7**, the solubility of **4-O** in organic solvents was still limited, the solubility in chloroform at 0 °C, for example, being only 10 mg/mL. The limited solubility of **4-O** and the thermal instability of its solutions hampered investigation of its structure by NMR.

We had hoped to use ^{77}Se NMR to determine whether **4-O** possessed structure **5** (two different ^{77}Se resonances) or **6** (single ^{77}Se resonance). However, despite several attempts, we were not able to obtain a satisfactory ^{77}Se FT NMR spectrum of **4-O**. Neither were we able to obtain a satisfactory ^{13}C NMR spectrum. This is discussed further in a footnote.[6] On the other hand, satisfactory ^1H NMR spectra of **4-O** were obtained, and the information they provided regarding the structure of **4-O** will now be presented and discussed.

^1H NMR Spectrum of the Monooxidation Product of 4. The ^1H NMR spectrum (200 MHz, $CDCl_3$) of a typical sample of **4-O** is shown in Figure 1. It is too complex to fit either **5** or **6** alone, but is compatible with **4-O** being a mixture of **5** and **6**. None of the lines observed can be due to the presence of **4** in the material since all of the resonances for the diselenide occur at δ <7.55 (vide infra). The relative intensity of certain of the signals varied somewhat from sample to sample in a manner indicating that the two doublets at δ 8.23 and 8.04 arose from one component of the mixture, while the apparent triplet at δ 8.12 (actually a pair of overlapping doublets) and the five-line pattern at 7.59–7.74 came from the other.

The ^1H NMR spectra of the aromatic protons of some related compounds were helpful in suggesting plausible ^1H NMR spectra for **5** and **6** and in establishing that the spectrum in Figure 1 is consistent with what might be expected for a mixture of **5** and **6**. The specific compounds whose ^1H NMR spectra were examined were as follows: (a) 1,8-bis[(*tert*-butylthio)seleno]naphthalene (**8**), cyclic diselenide **4**, and 1,8-dibromonaphthalene (examples of symmetrically, 1,8-disubstituted naphthalenes whose spectra should be indicative of that expected for **6**); and (b) naphtho[1,8-*cd*]-1,2-dithiole 1-oxide[7a] (**9**) and 1,1-dioxide[7b] (**10**) (examples of unsymmetrically 1,8-disubstituted naphthalenes whose spectra should be indicative of what might be expected for **5**).



8 **9** **10**

The ^1H NMR spectra of the aromatic protons of the three symmetrically disubstituted compounds are quite simple and consist in each case of two doublets of doublets (dd) ($J_1 \cong 8$ Hz, $J_2 \cong 1$ Hz) and one triplet ($J \cong 8$ Hz) with the two dd being further downfield than the triplet. The specific data are as follows:

compound	^1H NMR spectral data (arom protons), δ
8	8.38 (dd, 2 H), 7.75 (dd, 2 H), 7.40 (t, 2 H)
4	7.53 (dd, 2 H), 7.46 (dd, 2 H), 7.28 (t, 2 H)
1,8-dibromonaphthalene	7.95 (dd, 2 H), 7.82 (dd, 2 H), 7.27 (t, 2 H)

The two dd must represent the protons ortho and para to the 1- and 8-positions while the triplet represents the protons meta to those same positions. The dd furthest downfield presumably arises from the protons ortho to the 1,8-positions. From these spectra, that for **6** might therefore be anticipated to consist of two dd and a triplet with the two dd being *downfield* from the triplet.

The ^1H NMR spectra of **9** and **10** are more complex. The signals for the six protons in each compound (clarified by computer simulation[8] of the spectra) are as follows (for each dd, $J_1 \cong 8$ Hz, $J_2 \cong 1$ Hz; for each triplet, $J_1 \cong J_2 \cong 8$ Hz):

compound	^1H NMR spectral data, δ
9	8.16 (dd, 1 H), 8.12 (dd, 1 H), 7.79 (dd, 1 H), 7.78 (t, 1 H), 7.64 (t, 1 H), 7.57 (dd, 1 H)
10	8.16 (dd, 1 H), 8.08 (dd, 1 H), 7.80 (dd, 1 H), 7.78 (t, 1 H), 7.65 (t, 1 H), 7.49 (dd, 1 H)

(6) Initially we blamed the inability to obtain ^{77}Se or ^{13}C NMR spectra on the limited solubility of **4-O** and the restricted time for data collection (~1 h, in order to ensure no decomposition). However, equally dilute solutions of diselenide **4** gave weak, but detectable, spectra within this time period. The failure to get satisfactory ^{77}Se or ^{13}C NMR spectra for **4-O** is therefore puzzling. It is possible that **4-O** contains small amounts of paramagnetic impurities that, given the poor signal-to-noise situation, cause line broadening sufficient to obscure the signals in the ^{77}Se and ^{13}C spectra. However, the apparent absence of marked line broadening in the ^1H NMR spectrum of **4-O** makes this a less than completely satisfying explanation.

(7) (a) Boduszek, B.; Kice, J. L. *J. Org. Chem.* **1982**, *47*, 3199. (b) Boduszek, B.; Kice, J. L. *J. Org. Chem.* **1982**, *47*, 2055.

(8) The computer simulations of the ^1H NMR spectra were done by using the program DNMR3 by D. A. Klein and G. Binsch, obtained from the Quantum Chemistry Exchange Program. This program, most frequently used for dynamic NMR simulations, can also be used to simulate systems where exchange is not occurring simply by assuming that all rates of exchange are zero.

In both **9** and **10** the proton responsible for the triplet at δ 7.78 is *not* coupled to the proton giving the dd at essentially the same chemical shift (δ 7.79 or 7.80); in **9** it is coupled to the proton at δ 7.57 and one of the protons at δ >8.0, while in **10** it is coupled to the proton at δ 7.49 and one of the protons at δ >8.0. The proton responsible for the other triplet (δ 7.64 or 7.65) is coupled to the proton giving the dd at δ 7.8 and to the other proton at δ >8.0.

The two triplets in each spectrum are, of course, the protons meta to the 1- and 8-positions. Since the protons ortho to the 1- and 8-positions might be expected to have the largest chemical shift, we presume that the protons with δ >8.0 are those ortho to the 1- and 8-positions. This means that in one ring the proton para to the substituent (δ 7.79 or 7.80) is downfield from the meta proton (δ 7.64 or 7.65), similar to the situation with **8** or **4**; but in the other ring, the para proton (δ 7.57 for **9**, δ 7.49 for **10**) is upfield from the meta proton (δ 7.78). We are not sure in which ring $\delta_o > \delta_m > \delta_p$ applies and in which $\delta_o > \delta_p > \delta_m$. The key point, however, is that the spectra of **9** and **10** suggest that the ^{1}H NMR spectrum of **5** will have two dd (quite possibly overlapping) located downfield from the other resonances and due to the two protons ortho to the Se and Se=O functionalities, and that in one ring $\delta_o > \delta_m > \delta_p$ while in the other, $\delta_o > \delta_p > \delta_m$.

A computer-simulated[8] ^{1}H NMR spectrum for **5** was constructed by using the following chemical shifts and coupling constants:

ring I: δ_o 8.13, δ_m 7.82, δ_p 7.78; J_{om} = 7.7 Hz, J_{mp} = 8.0 Hz, J_{op} = 0.7 Hz

ring II: δ_o 8.10, δ_m, 7.64, δ_p, 7.72; J_{om} = 7.7 Hz, J_{mp} = 8.0 Hz, J_{op} = 0.7 Hz

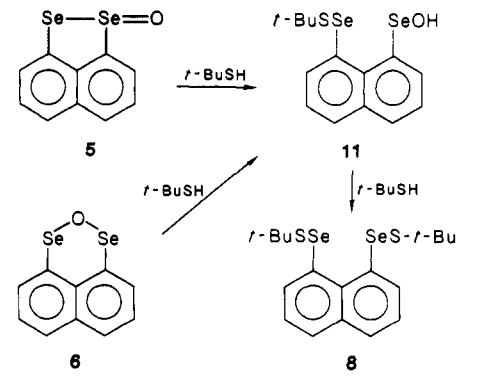
A stick plot of it is shown (solid lines) under the spectrum for **4-O** in Figure 1. One for **6** was constructed with the following δ and coupling constants: ortho H's, 8.23; meta H's, 7.81; para H's, 8.04; J_{om} = 7.7 Hz, J_{mp} = 8.0 Hz, J_{op} = 0.7 Hz. Its stick plot is given by the dashed lines in Figure 1. It is clear that these two spectra satisfactorily reproduce the features of the ^{1}H NMR spectrum for **4-O**. The success in simulating the ^{1}H NMR spectrum of **4-O** is consistent with the conclusion that **4-O** as isolated is a mixture of selenolseleninate **5** and cyclic selenenic anhydride **6**.

On the basis of the relative integrated intensities of the various signals, the sample in Figure 1 appears to be ~60% **5** and 40% **6**. The percentage of **5** in samples of **4-O** typically ran between 50% and 60%, although, in one case, for reasons unknown, the **4-O** isolated consisted of ~40% **5** and 60% **6**.

Reaction of the Monooxidation Product of 4 with a Thiol. The monooxidation product of **4** reacted very rapidly with 2 mol of 2-methyl-2-propanethiol (*t*-BuSH) in acidic aqueous dioxane to give 1,8-bis[(*tert*-butylthio)seleno]naphthalene (**8**) in over 90% yield (eq 4). Both

$$\text{4-O} + 2\,t\text{-BuSH} \rightarrow 8 + H_2O \qquad (4)$$

selenolseleninate **5** *and selenenic anhydride* **6** *would be* expected to react initially with the thiol to give **11** (eq 5); reaction of the selenenic acid functionality in **11** with a second mole of thiol will give **8**. Since attack by additional thiol on either of the sulfur atoms of **8** should be extremely slow due to steric hindrance,[9] further reaction of either selenenyl sulfide functionality with *t*-BuSH (RSH + ArSeSR → RSSR + ArSeH) is not a factor under the reaction conditions used.



(5)

The progress of the reaction could be followed by observing the increase with time in the absorbance (*A*) of the solution at 360 nm. Rates were measured in 60% dioxane (v/v) at 25 °C at pH's ranging from 2.0 to 7.8 and with the thiol (0.001–0.004 M) present in considerable stoichiometric excess over **4-O** (1×10^{-4} M). plots of log $(A_\infty - A)$ vs time were linear. The experimental first-order rate constants, k_1, obtained from the slopes of these plots, exhibited the following behavior: (1) At all pH's k_1 was strictly proportional to [*t*-BuSH], indicating that the reaction is first order in thiol; (2) in acid solution (0.001–0.01 M $HClO_4$), k_1 was proportional to a_{H^+} (showing that in this pH region the reaction is acid catalyzed), while in acetate buffers (pH 6.6–7.8), k_1 was proportional to $1/a_{H^+}$ (indicating that in this pH region reaction with *t*-BuS$^-$ is the kinetically important process); (3) studies in phosphate (pH 3.8–5.1) and formate buffers (pH 5.1–6.5) indicated that the change from $k_1 \sim a_{H^+}$ to $1/a_{H^+}$ occurred over a narrow pH range and that there was no pH region in which k_1 was independent of pH.

Since **4-O** is a mixture of **5** and **6**, and **5** and **6** may interconvert relatively easily, detailed interpretation of the kinetic results will not be attempted. It is, however, worth pointing out that the behavior of the present system differs significantly from the kinetic behavior of the reaction of an alkanethiol (*n*-BuSH) with *o*-nitrobenzeneselenenic anhydride (**1a**).[10] In that case, an acid-catalyzed reaction of the thiol with the substrate was not detectable, and a pH-independent reaction of **1a** with RSH was kinetically dominant over the pH range 2.0–8.0, with a term proportional to $1/a_{H^+}$ (reaction of RS$^-$ with **1a**) beginning to make a detectable contribution only at pH's above 7.5. Also worth noting is the fact that the rate constant for the $1/a_{H^+}$-dependent term for reaction of *t*-BuSH with **4-O** ($k_1(s^{-1}) = 3.1 \times 10^{-6}(1/a_{H^+})$[RSH]) is 2×10^3 larger than for **1a**, while at pH 2–3, the rate of reaction of **4-O** with *t*-BuSH ($k_1(s^{-1}) = 7.5 \times 10^5\ a_{H^+}$[RSH]) is 200–2000 times faster (depending on pH) than the rate of reaction of **1a** with *n*-BuSH.

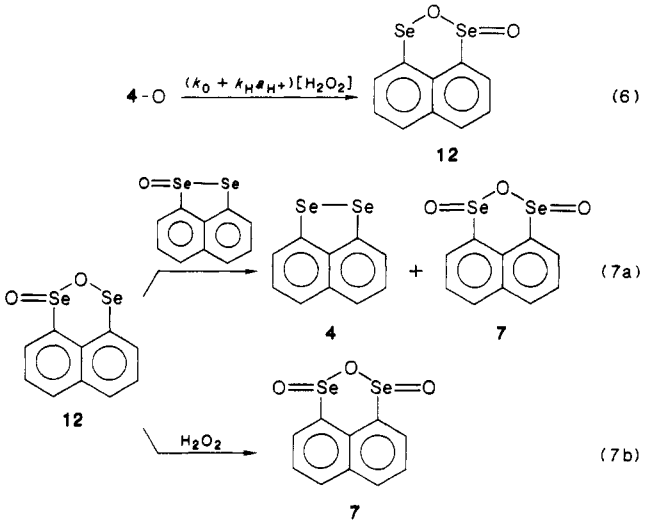
Oxidation of the Monooxidation Product of 4 by MCPBA and Hydrogen Peroxide. Oxidation of **4-O** (10^{-4} M) by excess MCPBA (0.0025–0.010 M) in 60% dioxane was accompanied by the disappearance of the absorbance at 335 nm (λ_{max} for **4-O**) and longer wavelengths. Plots of log $(A - A_\infty)$ vs time were linear, with the experimental first-order rate constant, k_1, being proportional to [MCPBA]. Measurement of the rate at 25 °C over the pH range 2.0–4.5 indicated the following:

$$k_1(s^{-1}) = (10^3 a_{H^+} + 8.0)[\text{MCPBA}]$$

(9) (a) Fava, A.; Iliceto, A.; Camera, E. *J. Am. Chem. Soc.* **1957**, *79*, 833. (b) Fava, A.; Iliceto, A. *J. Am. Chem. Soc.* **1958**, *80*, 3478. (c) Ciuffarin, E.; Fava, A. *Prog. Phys. Org. Chem.* **1968**, *6*, 84. (d) Kice, J. L.; Slebocka-Tilk, H. *J. Am. Chem. Soc.* **1982**, *104*, 7123.

(10) Kice, J. L.; McAfee, F.; Slebocka-Tilk, H. *J. Org. Chem.* **1984**, *49*, 3106.

Scheme I. Suggested Mechanism for the Reaction of 4-O with Hydrogen Peroxide



The pH-independent term (8.0 M^{-1} s^{-1}) is similar in magnitude to the rate constant (12.0 M^{-1} s^{-1}) for the oxidation of **1a** by MCPBA.[11] In the oxidation of **1a** by MCPBA, no acid-catalyzed term appears in the rate expression.

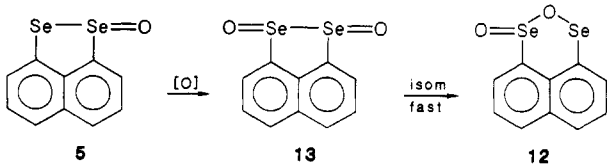
The behavior of the oxidation of **4-O** by excess hydrogen peroxide (0.025–0.10 M) was more complex. The disappearance of the λ_{max} for **4-O** at 335 nm was accompanied by the appearance of an absorption maximum at 375 nm due to the formation of cyclic diselenide **4**. Once formed, **4** slowly disappeared by reacting itself with H_2O_2, but the rate of this process was so much slower than the rate of its formation that the amount of **4** produced in the first reaction could be determined accurately. The amount of diselenide formed varied with reaction conditions (vide infra) but never exceeded 0.50 mol/mol of **4-O**. Plots of log $(A_\infty - A)$ at 375 nm vs time were linear; the experimental first-order rate constant, k_1, showed the following dependence on pH and $[H_2O_2]$ over a pH range from 2.0 to 5.1 at 25 °C:

$$k_1(s^{-1}) = (10.4a_{H^+} + 0.0093)[H_2O_2]$$

The fact that the rate of formation of **4** is proportional to $[H_2O_2]$ shows that the formation of **4** *cannot* be due to the disproportionation of **4-O** itself. The diselenide must arise from a process that has as its rate-determining step the reaction of **4-O** with hydrogen peroxide.

The amount of diselenide formed per mole of **4-O** decreased as the concentration of H_2O_2 increased; it also decreased as the pH increased. The lowest yield (0.11 mol/mol of **4-O**) occurred with $[H_2O_2]$ = 0.10 M in a phosphate buffer with pH 5.1; the highest yield (0.50 mol/mol of **4-O**) occurred at pH 2 (0.01 M $HClO_4$) with $[H_2O_2]$ = 0.025 M.[12]

The behavior of the H_2O_2 oxidation can be explained by the reaction sequence in Scheme I. Oxidation of **4-O** (mixture of **5** and **6**) by H_2O_2 is presumed to be rate determining and to lead to a dioxidation product of **4**, which is assigned structure **12**. Oxidation of **6** should give **12** directly. Oxidation of **5** would presumably give **13**, but the behavior of α-disulfoxides[13] in sulfur chemistry suggests that **13** should be extremely unstable and might be expected to isomerize rapidly to **12**. If reaction of **12** with



5 to form **4** and **7** occurs fast enough that reaction 7a is competitive in rate with oxidation of **12** by H_2O_2 (eq 7b), the formation of **4** in amounts up to 0.5 mol/mol of **4-O** can be explained.

m-Chloroperoxybenzoic acid is a much more reactive oxidant than H_2O_2. With MCPBA the rate of oxidation of **12** to **7** is fast enough that eq 7a is no longer competitive in rate with oxidation of **12**, and **4** is not formed in detectable amounts during the oxidation of **4-O** by MCPBA.

Conclusions. Oxidation of cyclic aryl diselenide **4** with 1 mol of peracid at −5 °C leads to the formation of a surprisingly stable monooxidation product (**4-O**) that, as isolated, is a mixture of selenolseleninate **5** and selenenic anhydride **6**. Cyclic aryl selenolseleninate **5**, which has a half-life of a number of hours in solution at room temperature, is considerably more stable than cyclic alkyl selenolseleninate **3**[4] (**3** decomposes at −20 °C) and is the first representative of this class of compounds stable enough to be isolated and studied. Cyclic selenenic anhydride **6** is the first areneselenenic anhydride not stabilized by coordination of an ortho substituent to selenium that has been isolated.

The monooxidation product (mixture of **5** and **6**) reacts very rapidly with an alkanethiol (*t*-BuSH) to give bis selenenyl sulfide **8** in >90% yield. Reaction of **4-O** with hydrogen peroxide in acid solution is surprising in that formation of up to 0.5 mol of **4**/mol of **4-O** reacting is observed. Scheme I, which features facile reaction of **12** with **5** to give **4** and **7**, is proposed to account for this behavior.

Experimental Section

1,8-Dibromonaphthalene was prepared as described by Hodgson and Whitehurst[14] and was purified by chromatography on silica gel (9:1 hexane–benzene as eluant) followed by two recrystallizatons from ethanol, mp 109–110 °C (lit.[15] mp 109–110 °C, lit.[16] mp 106–108 °C).

Naphtho[1,8-*cd*]-1,2-diselenole (4) was synthesized from 1,8-dibromonaphthalene by the method of Meinwald et al.[5] This involves conversion of the dibromo compound to 1,8-dilithionaphthalene by a modification of the procedure of Letsinger and co-workers[16] followed by reaction of the dilithio compound with selenium. A solution of 1,8-dibromonaphthalene (1.0 g, 3.5 mmol) in 15 mL of anhydrous tetrahydrofuran was cooled to −78 °C. To this was then added with good stirring 5.1 mL of a 1.6 M solution of *n*-butyllithium in hexane, and the solution was stirred for 45 min. At that point, black elemental selenium powder (0.65 g, 8.2 mmol) was added, and the mixture was stirred for 1 h. The reaction mixture was then warmed to room temperature and stirred in the presence of air for 30 min. The solvent was removed from the deep purple reaction mixture under reduced pressure.

(11) Kice, J. L.; Chiou, S. *J. Org. Chem.* **1986**, *51*, 290.

(12) At a given pH in H_3PO_4–$H_2PO_4^-$ buffers, an increase in total buffer concentraton led to an increase in **4**; for example, in a 1:1 H_3PO_4–$H_2PO_4^-$ buffer (pH 4.8) containing 0.075 M H_2O_2, increasing the buffer concentration from 0.005 to 0.02 M increased the yield of **4** from 0.19 to 0.38 mol/mol of **4-O**.

(13) (a) Freeman, F.; Angeletakis, C. N. *J. Org. Chem.* **1985**, *50*, 793. (b) Freeman, F.; Angeletakis, C. N. *J. Am. Chem. Soc.* **1983**, *105*, 4039. Freeman, F.; Angeletakis, C. N. *J. Am. Chem. Soc.* **1982**, *104*, 5766. (c) Freeman, F.; Angeletakis, C. N.; Maricich, T. J. *J. Org. Chem.* **1982**, *47*, 3403. (d) Freeman, F.; Angeletakis, C. N.; Pietro, W. J.; Hehre, W. *J. Am. Chem. Soc.* **1982**, *104*, 1161. (e) Freeman, F.; Angeletakis, C. N. *J. Am. Chem. Soc.* **1981**, *103*, 6232. (f) Chau, M. M.; Kice, J. L. *J. Am. Chem. Soc.* **1976**, *98*, 7711.

(14) Hodgson, H. H.; Whitehurst, J. S. *J. Chem. Soc.* **1947**, 80.

(15) Fieser, L. F.; Seligman, A. M. *J. Am. Chem. Soc.* **1939**, *61*, 136.

(16) Letsinger, R. L.; Gilpin, J. A.; Vullo, W. J. *J. Org. Chem.* **1962**, *27*, 672.

The residue was treated with methylene chloride, and the material that would not dissolve in methylene chloride was filtered off. Addition of hexane to the methylene chloride filtrate resulted in the precipitation of **4**. The crude diselenide was recrystallized three times from methylene chloride–hexane, giving 0.162 g (16%) of pure **4** as lustrous purple needles, mp 127–129 °C (lit.[5] mp 127–129 °C). The infrared, ultraviolet, ^{13}C NMR, and mass spectra of the product matched those reported by Meinwald et al.[5]

Oxidation of 4 with 3 mol of Peracid. Formation of 7. To a solution of 0.114 g (0.4 mmol) of **4** in 1.0 mL of dry chloroform was added rapidly with good stirring at room temperature 3.0 mL of chloroform containing 0.207 g of MCPBA. The violet color of the solution (due to **4**) was discharged rapidly, and a white precipitate separated. After 1 h, the precipitate was filtered off and washed several times with anhydrous ether.

The precipitate (0.11 g), which was slightly impure naphthalene-1,8-diseleninic anhydride (**7**), was purified by the following procedure. Anhydride **7** was dissolved with stirring in 2 N sodium hydroxide at 0 °C. The resulting solution was extracted with chloroform. After the extraction, the aqueous layer was acidified to pH <2 by addition of 6 N hydrochloric acid. The precipitate that separated was filtered off, washed several times with water, and then dried under vacuum at room temperature. There was obtained 0.086 g (65%) of **7**: mp 153 °C dec; IR (KBr) 3068, 3045, 3016, 2976, 1587, 1485, 1361, 1207, 1141, 1078, 889, 864, 850, 819, 758, and 628 cm^{-1}; UV (MeCN) λ_{max} 291 nm (ϵ 1.2 × 10^4). Anal. Calcd for $C_{10}H_6O_3Se_2$: C, 36.17; H, 1.82. Found: C, 35.96; H, 1.88.

The extremely low solubility of **7** in all common solvents precluded both its purification by recrystallization and the obtaining of a ^1H NMR spectrum.

Oxidation of 4 with 1 mol of Peracid. Formation of the Monooxidation Product of 4 (4-O). A solution of 0.057 g (0.33 mmol) of MCPBA in 3 mL of anhydrous ether was added slowly with good stirring at −5 °C to a solution of 0.085 g (0.3 mmol) of **4** in 15 mL of anhydrous ether. After the addition was complete, the reaction mixture was stirred at −5 °C for 30 min. The yellow-brown precipitate of **4-O** that had separated was filtered off, washed with ether, and then purified by dissolving the material in cold chloroform and reprecipitating it by the addition of hexane. There was obtained 0.083 g (93%) of the monooxidation product of **4** (**4-O**) as a fluffy yellow-brown solid: mp 90 °C dec; IR (KBr) 3041, 1581, 1547, 1483, 1442, 1375, 1199, 1039, 966, 814, 804, 756, and 690 cm^{-1}; UV (dioxane) λ_{max} 335 (ϵ 5 × 10^3), 257 nm (1.5 × 10^4). Anal. Calcd for $C_{10}H_6OSe_2$: C, 40.02; H, 2.02. Found: C, 39.87; H, 2.09.

The ^1H NMR spectrum (200 MHz, $CDCl_3$) of **4-O** is shown in Figure 1 and discussed in detail in the Results and Discussion. This spectrum indicates that **4-O** is a mixture of **5** and **6**, with the two being present in roughly equal amounts.

When solutions of **4-O** are allowed to stand at room temperature for more than an hour or two, a purple coloration begins to appear. This is due to the formation of **4**. Exposure of the solution to light appears to hasten this decomposition.

The mass spectrum of **4-O** does not show a molecular ion, the highest molecular weight peak being at *m/e* 286 ($M^+ - 16$). The same type of behavior was observed[17] in the mass spectra for selenenic anhydrides **1a** and **1b** and may therefore be a general characteristic of the mass spectral behavior of areneselenenic anhydrides and areneselenolseleninates.

Reaction of the Monooxidation Product of 4 with 2-Methyl-2-propanethiol. Products. The monooxidation product of **4** (0.030 g, 0.1 mmol) was dissolved in 25 mL of anhydrous dioxane, 15 mL of water was added, and a solution of 0.22 mL (2.0 mmol) of 2-methyl-2-propanethiol and 0.15 mL (2.0 mmol) of trifluoroacetic acid in 10 mL of 60% dioxane was added rapidly with good stirring. As soon as the addition was complete, the final reaction solution was extracted with chloroform, and the chloroform extract was washed with water until the washings were neutral. The chloroform extract was dried (Na_2SO_4), and the solvent was removed under reduced pressure at room temperature. Trituration of the oily residue with hexane resulted in the crystallization of 1,8-bis[(*tert*-butylthio)seleno]naphthalene (**8**): 0.042 g (92%); mp 84–85 °C; IR (KBr) 3053–2854, 1543, 1489, 1452, 1361, 1159, 808, and 754 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.24 (s, 12 H), 7.40 (t, 2 H), 7.75 (dd, 2 H), 8.38 (dd, 2 H); mass spectrum, *m/e* 464 (M^+, $^{80}Se^{80}Se$, 100), 462 (M^+, $^{80}Se^{78}Se$, 94), 460 (M^+, $^{78}Se^{78}Se$, 57); UV (dioxane) λ_{max} 345 nm. Anal. Calcd for $C_{18}H_{24}S_2Se_2$: C, 46.76; H, 5.23. Found: C, 46.60; H, 5.12.

Kinetics. All runs were carried out at 25 °C in 60% dioxane (v/v) as solvent at constant ionic strength (0.02). For pH ≤3.5 or ≥6.75, the rates were fast enough to require stopped-flow spectrophotometry. Runs in the pH range 3.8–6.4 could be followed by conventional UV–vis spectrophotometry.

Stock solutions of **4-O** (0.001 M) and of the thiol (0.6 M) in anhydrous dioxane were prepared immediately prior to use. In the runs followed by conventional spectrophotometry, a solution of 1.5 mL of dioxane and 1.2 mL of water containing the desired amount of buffer (plus any lithium perchlorate needed to maintain constant ionic strength) was placed in a 1-cm spectrophotometer cell in the thermostated cell compartment of a UV–visible spectrophotometer. To the cell was then added 300 μL of the stock solution of **4-O**. The reacton was initiated by adding 5–20 μL of the stock solution of the thiol, and the progress of the reaction was followed by measuring the increase in the absorbance of the solution at 360 nm.

In the runs followed by stopped-flow spectrophotometry, a 2 × 10^{-4} M solution of **4-O** in 60% dioxane was placed in one of the reservoir syringes of a Durrum-Gibson stopped-flow spectrophotometer, and a 60% dioxane solution containing the desired buffer (or $HClO_4$), thiol (0.002–0.01 M), plus any lithium perchlorate needed to maintain constant ionic strength was placed in the other reservoir syringe. The reaction was initiated by mixing the two solutions, and the increase in absorbance with time at 360 nm was recorded on the storage oscilloscope.

Kinetics of the Oxidation of 4-O by Hydrogen Peroxide or MCPBA. The runs with MCPBA as the oxidant were carried out at 25 °C by using stopped-flow spectrophotometry and monitoring the decrease in the absorbance of the solution with time at 340 nm. The procedure was the same as that just described for the reaction of **4-O** with *t*-BuSH, except that MCPBA replaced the thiol as one of the reagents in the second reservoir syringe.

The runs with hydrogen peroxide as the oxidant were enough slower that they could be followed by conventional spectrophotometry. Reactions were initiated by adding the desired amount of hydrogen peroxide to a solution of **4-O** (1 × 10^{-4} M) and buffer (or $HClO_4$), prepared in the same manner as described for the runs with the thiol, and contained in a 1-cm spectrophotometer cell. The progress of the reaction was followed by observing the increase in the absorbance of the solution at 375 nm due to the formation of **4**. The amount of **4** produced per mole of **4-O** was determined from the magnitude of the absorbance at 375 nm at the end of the first stage of the reaction. The much slower decline in absorbance at 375 nm due to subsequent oxidation of **4** by hydrogen peroxide was not followed kinetically.

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(17) Kice, J. L.; McAfee, F.; Slebocka-Tilk, H., unpublished results.