potassium carbonate, and water. After being dried ($MgSO_4$), the solvent was removed in vacuo to give 293 mg of two chlorides in an approximate ratio of 91:9.

Reduction with Bu_3SnH. To a stirred solution of the above chlorides and 50 mg of AIBN in 7 mL of cyclohexane was added a solution of 594 mg (2.04 mmol) of Bu_3SnH in 5 mL of cyclohexane at room temperature under nitrogen. The solution was heated at reflux for 1 h. The solvent was removed in vacuo, and the residue was chromatographed (eluent petroleum ether) to give 220 mg (86% from **22b** and **22c**) of a hydrocarbon that was identical (^{13}C NMR) with **22a**.

Similar transformation of 381 mg (1.98 mmol) of the carboxylic acids **20b** + **21b**, **22b**, and **22c** (in ratio of 11:59:30) as described above gave 205 mg (70% overall yield) of **20a** + **21a** and **22a** with a ratio of 12:88. The tricycloundecanes **20a** and **21a** were identified by their ^{13}C NMR spectra, and their ratio was approximately 4:1.

Modified Kochi reaction of 221 mg (1.14 mmol) of **4e** as described above gave a chloride that was identical (^{13}C NMR) with the known compound **4f**.[3]

Preparation of an Authentic Sample of 24. A solution of 1.20 g (7.32 mmol) of **3a** and 1.36 g (7.32 mmol) of tosylhydrazide in 25 mL of methanol was heated at reflux for 5 h. The solvent was removed in vacuo to give the crude tosylhydrazone: IR (KBr) 3210, 1590, 1330, 1165 cm^{-1}.

To a stirred solution of the hydrazone in 30 mL of dry ether was added dropwise 14.6 mL (17.6 mmol) of 1.2 M MeLi in ether at 20–25 °C under nitrogen. The resulting reaction mixture was stirred at the temperature for 16 h. A small amount of water was added carefully, and then additional water was added. The organic layer was separated and washed three times with water. The combined aqueous layers were extracted with ether. The combined organic layers were washed with brine, dried ($MgSO_4$), and concentrated carefully in vacuo. The residue was chromatographed (eluent petroleum ether) to give 587 mg (55% overall yield) of an olefin that was identical (MS, ^1H NMR, ^{13}C NMR) with **24**.

X-ray Analysis of 22b: formula $C_{12}H_{18}O_2$; M_r = 194.27; crystal selected from a sample recrystallized from hexane; triclinic, space group $P\bar{1}$; a = 6.354 (17) Å, b = 6.712 (2) Å, c = 13.441 (3) Å; d_{calcd} = 1.230 g cm^{-3}, d_{obsd} = 1.245 g cm^{-3}; Z = 2. The intensity data were measured on a CAD4 Enraf-Nonius diffractometer with graphite-monochromated Mo $K\alpha$ radiation (λ = 0.71069 Å) by θ–2θ scan technique. A total of 3043 independent reflections were measured for $\theta \leq 30°$, of which 2386 were considered to be observed [$I \geq 2\alpha(I)$]. The structure was solved by direct methods using MULTAN 82 and refined by full-matrix least-squares methods. In the final refinement anisotropic thermal parameters were used for non-hydrogen atoms. Hydrogen atoms were refined with isotropic thermal parameters. The final discrepancy indices were R = 8.33% and R_ω = 6.71% for the 2386 observed reflections. The final difference Fourier map was essentially featureless, with no peaks greater than ±0.2 e $Å^{-3}$.

Acknowledgment. We thank Dr. Y. Inamoto of Tochigi Research Laboratories, Kao Co., Ltd., for providing samples of **11** and the methyl ester of **21b**.

Supplementary Material Available: Tables IV–IX listing final atomic parameters, final anisotropic thermal parameters, bond lengths, and bond angles for **22b** and ORTEP drawing of **22b** (6 pages). Ordering information is given on any current masthead page.

The pK_a of Areneselenenic Acids[1]

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Received June 18, 1985

The pK_a's of *o*-nitrobenzeneselenenic acid (**1a**) and three 4-substituted-2-nitrobenzeneselenenic acids (**1b–d**) have been determined at 25 °C in water. A Hammett plot of the pK_a's gives a ρ value for the ionization of ArSeOH (eq 3) of +1.4. The pK_a of **1a** is 10.45, which makes it 2.8 times weaker as an acid than phenol. Areneselenenic acids are therefore surprisingly weak acids. If the only influence of the *o*-nitro group on the acidity of **1a** is its inductive effect, the pK_a of benzeneselenenic acid (which cannot be measured directly because of the instability of PhSeOH) is predicted to be 11.5.

Areneselenenic acids (ArSeOH) play an important role as reactive intermediates in organoselenium reactions. For example, an areneselenenic acid is the "other product" in the synthetically important olefin-forming elimination of alkyl aryl selenoxides (-CH-C-Se(O)Ar $\rightarrow$ >C=C< + ArSeOH),[2] and areneselenenic acids are thought to be generated as intermediates in the reduction of areneseleninic acids ($ArSeO_2H$) by a spectrum of reagents.[3]

In view of the relative ubiquity of areneselenenic acids as intermediates in selenium chemistry, information about their strength as acids would clearly be of considerable value. Such information has, regretably, not heretofore been available. This has undoubtedly been due to the fact that the vast majority of areneselenenic acids are of too limited stability and lifetime to permit straightforward measurement of their pK_a.

Previous research[4] in this laboratory has shown, however, that dilute solutions of *o*-nitrobenzeneselenenic acid, **1a** (ArSeOH, Ar = o-$O_2NC_6H_4$) are quite stable. These can be prepared either by hydrolysis of a solution of the corresponding selenenic anhydride (ArSeOSeAr + $H_2O \rightarrow$ 2 ArSeOH),[4] or by room-temperature decomposition of a concentrated solution of ethyl *o*-nitrophenyl selenoxide[5] ($ArSe(O)CH_2CH_3 \rightarrow ArSeOH + CH_2{=}CH_2$) followed by appropriate dilution.[6]

In the present work we have measured the pK_a of **1a** and of several 4-substituted-2-nitrobenzeneselenenic acids in water at 25 °C. We find that areneselenenic acids are surprisingly weak acids, much weaker than most organic

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[1] (1) This research was supported by the National Science Foundation, Grant CHE-82-15140.

[2] (2) (a) Reich, H. J.; Wollowitz, S.; Trend, J. E.; Chow, F.; Wendelborn, D. F. *J. Org. Chem.* **1978**, *43*, 1976. (b) Hori, T.; Sharpless, K. B. *Ibid.* **1978**, *43*, 1689.

[3] (3) (a) Labar, D.; Krief, A.; Hevesi, L. *Tetrahedron Lett.* **1978**, 2967. (b) Back, T. G.; Collins, S. *Ibid.* **1979**, 2961. (c) Back, T. G.; Collins, S.; Kerr, R. G. *J. Org. Chem.* **1981**, *46*, 1564. (d) Back, T. G. *Chem. Commun.* **1978**, 278. (e) Back, T. G.; Collins, S. *Tetrahedron Lett.* **1980**, *21*, 2213. (f) Gancarz, R. A.; Kice, J. L. *Ibid.* **1980**, *21*, 1697; *J. Org. Chem.* **1981**, *46*, 4899. (g) Faehl, L. G.; Kice, J. L. *J. Org. Chem.* **1979**, *44*, 2357.

[4] (4) Kice, J. L.; McAfee, F.; Slebocka-Tilk, H. *J. Org. Chem.* **1984**, *49*, 3100.

[5] (5) Reich, H. J.; Willis, W. W., Jr.; Wollowitz, S. *Tetrahedron Lett.* **1982**, *3319*.

[6] (6) Kang, S.-I.; Kice, J. L. *J. Org. Chem.* **1985**, *50*, 2968.

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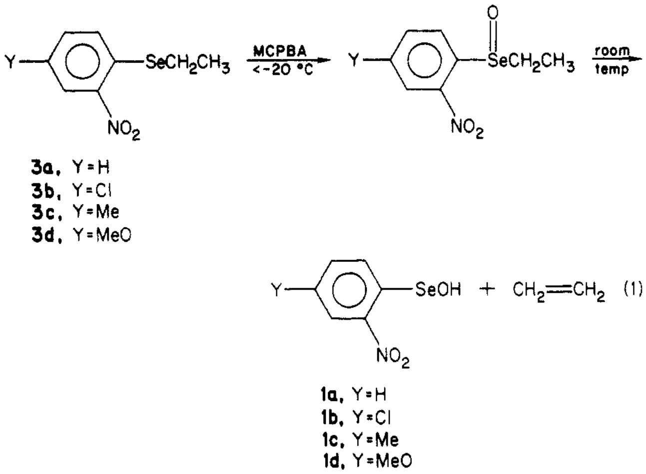
chemists would probably have expected.

Results

Preparation of Solutions of Selenenic Acids. Solutions of 4-substituted-2-nitrobenzeneselenenic acids (**1b–d**) were successfully prepared from appropriate ethyl 4-substituted-2-nitrophenyl selenides (**3b–d**) by the same reaction sequence, low temperature fragmentation of the selenoxide (eq 1), that has previously been employed[6] for



the synthesis of solutions of **1a**. The needed selenides (**3b–d**) were synthesized from the corresponding selenocyanates and ethanol by using the procedure of Grieco, Gilman, and Nishizawa.[7] Dilute (10^{-4}M) solutions of all of the selenic acids (**1a–d**) in water were quite stable, as evidenced by the lack of any change in the UV–visible spectrum of each solution over a period of observation of at least several hours.

Measurement of the pK_a of Selenenic Acids. An aqueous 10^{-4} M solution of o-$O_2NC_6H_4SeOH$ (**1a**) has a long wavelength λ_{max} at 425 nm (ϵ, 4600). Addition of 0.02 N NaOH causes this λ_{max} to shift to 550 nm (ϵ, 4900). Upon acidification the spectrum reverts to that for **1a** with λ_{max} at 425 nm, demonstrating that the equilibrium involving the selenenic acid under observation is instantaneously and quantitatively reversible. Since this spectral change is the only one evident over the pH range 4.0 to 13.0, this particular equilibrium is the sole one active in this pH range.

The equilibrium constants (K_{eq} = [complex$^-$]/[OH$^-$][ArH]) for Meisenheimer complex formation[8] from mononitro aromatics and hydroxide ion are so small ($\sim 10^{-9}$ to 10^{-13}) that the equilibrium under observation cannot be attributed to formation of a Meisenheimer complex from **1a** and OH^-.[9] The equilibrium must therefore be that between the selenenic acid and its anion, with the species having the λ_{max} at 550 nm being o-$O_2NC_6H_4SeO^-$ (**2a**).[10]

A similar bathochromic shift in λ_{max} to a wavelength where the selenenic acid itself has zero absorbance is observed upon addition of 0.02 N NaOH to aqueous solutions of the other selenenic acids and is presumed in each case to be due to the conversion of the selenenic acid to its anion (**1b** → **2b**, 432 to 562 nm; **1c** → **2c**, 435 to 560 nm; **1d** → **2d**, 485 to 585 nm). The fraction of the selenenic acid converted to its anion in any buffer solution, i.e., $f = [2]/([1] + [2])$, can therefore be accurately determined via measurement first of the optical density of a solution of the selenenic acid at λ_{max} for ArSeOH, followed by addition of the buffer and measurement of the optical density of the buffer solution at the λ_{max} for the anion.

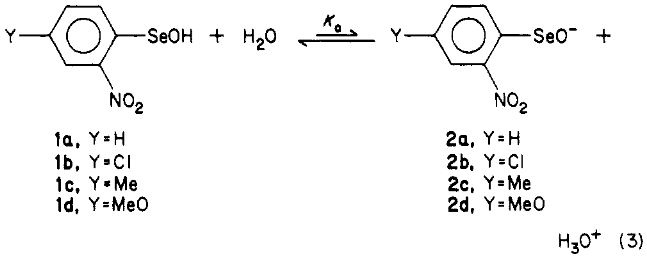
Measurements of this type were carried out on the four selenenic acids (**1a–d**) in a series of $NaHCO_3$–NaOH and K_2HPO_4–NaOH buffers[11] with pH's ranging from 9.9 to 11.2. For each selenenic acid measurements were made in at least five buffers over a pH range of 0.4 to 1.2 pH units. The results, expressed as $[ArSeO^-]/[ArSeOH]$, which is equal to $f/(1 - f)$, are given in Table I.[12] From $[ArSeO^-]/[ArSeOH]$ the pK_a for the selenenic acid was calculated using the relationship:

$$pK_a = pH - \log([ArSeO^-]/[ArSeOH]) \qquad (2)$$

These are listed in the last column of Table I. The average values of the pK_a's for the different selenenic acids calculated from these data are: **1a**, 10.45 ± 0.04; **1b**, 10.17 ± 0.04; **1c**, 10.73 ± 0.02; **1d**, 10.83 ± 0.07.

Discussion

The present measurements reveal that the pK_a (H_2O, 25 °C) for the ionization (eq 3, Y = H) of o-nitrobenzeneselenenic acid (**1a**) is 10.45, indicating that **1a** is



2.8 times *weaker* as an acid than phenol (pK_a = 10). The selenenic acid is therefore a surprisingly weak acid and will be completely converted to its anion only in solutions having a pH of 12.5 or greater.

The inductive effect of the o-NO_2 group on the strength of **1a** as an acid can be estimated as follows. A plot of log K_a vs. σ_Y for the ionization of **1a** and three 4-substituted-2-nitrobenzeneselenenic acids (**1b–d**) is linear with a slope, ρ, of +1.4. From this ρ value for eq 3, and the reported[13] σ value (+0.80) for o-NO_2, the o-NO_2 group would be predicted to be acid strengthening by 1.1 pK unit (1.4 × 0.8).

If the only influence of the o-nitro group on the acidity of **1a** is its inductive effect, the pK_a of benzeneselenenic acid (PhSeOH) should therefore be 1.1 pK units larger than that of **1a**, or 11.5. It should be kept in mind, however, that the stability of **1a** as compared to PhSeOH is believed[4,14] to be due to the coordination of the o-nitro group to selenium in the fashion shown in **4**. This coor-

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[7] Grieco, P. A.; Gilman, S.; Nishizawa, M. *J. Org. Chem.* **1976**, *41*, 1485.

[8] Strauss, M. J. *Chem. Rev.* **1970**, *70*, 667.

[9] The ^1H NMR spectrum of the species formed when **1a** is treated with excess OH^- is, based on the spectra[8] of known Meisenheimer complexes, also not consistent with its formulation as a Meisenheimer complex.

[10] A referee has pointed out that, rather than o-$O_2NC_6H_4SeO^-$, the structure of the anion of **1a** might be a hydrate of **2a**, i.e., o-$O_2NC_6H_4Se(OH)_2^-$, with the dissociation of **1a** being written:

$$ArSeOH + 2H_2O \rightleftharpoons ArSe(OH)_2^- + H_3O^+$$

rather than in the classical manner:

$$ArSeOH + H_2O \rightleftharpoons ArSeO^- + H_3O^+$$

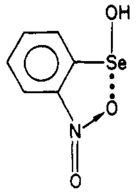
While we will write the anion as $ArSeO^-$ in the remainder of the paper, the possibility that it might actually be present as the hydrate, $ArSe(OH)_2$, should be kept in mind.

[11] Bates, R. G.; Bower, V. E. *Anal. Chem.* **1956**, *25*, 1322.

[12] See paragraph at end of paper regarding supplementary material.

[13] Shorter, J. *Q. Rev. Chem. Soc.* **1970**, *24*, 433.

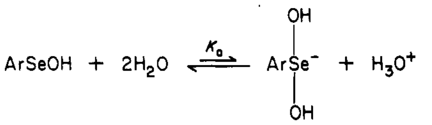
[14] (a) Austad, T. *Acta Chem. Scand., Ser. A* **1975**, *29A*, 895. (b) Austad, T. *Ibid.* **1977**, *31A*, 93. (c) Eriksen, R.; Hauge, S. *Ibid.* **1972**, *26*, 3153.



4

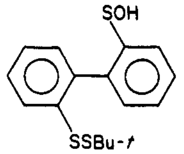
dination of the oxygen of the NO_2 group to Se could increase the electron density on selenium in **1a** over what it would otherwise be and make **1a** a weaker acid than would be expected from the purely inductive effect of the nitro group. For that reason the actual pK_a for PhSeOH could be somewhat smaller than the value of 11.5 estimated assuming that the only influence of the *o*-nitro group on the acidity of **1a** is its normal inductive effect.

As indicated earlier in a footnote,[10] it is possible that, rather than $ArSeO^-$, the anions of selenenic acids **1** could have the structure $ArSe(OH)_2^-$, which is a hydrate of **2**, and that the ionization of **1** should be written, not as in eq 3, but as shown in eq 4. In our opinion, given the tendency for intramolecular coordination of the nitro group to selenium in *o*-nitrobenzeneselenenyl derivatives,[4,14] the structure $ArSe(OH)_2^-$ seems less likely for anions of *o*-nitrobenzeneselenenic acids than for anions of areneselenenic acids where coordination of a substituent to selenium is not possible.



$$\mathrm{ArSeOH} + 2\mathrm{H_2O} \overset{K_a}{\rightleftharpoons} \mathrm{Ar}\overset{\mathrm{OH}}{\underset{\mathrm{OH}}{\mathrm{Se}^-}} + \mathrm{H_3O^+} \qquad (4)$$

Benzeneseleninic acid, $PhSeO_2H$ (pK_a = 4.79),[15] is ~3.5 pK units a weaker acid than benzenesulfinic acid, $PhSO_2H$ (pK_a = 1.2).[16] Whether a similar marked difference in pK_a also obtains for selenenic vs. sulfenic acids can't be determined with certainty since no quantitative data are yet available on the pK_a of any arenesulfenic acids. However, the behavior of sulfenic acid **5**, generated as an intermediate in a kinetic study in several basic solutions, indicates that its pK_a(H_2O) ≤ 9.6.[17] Sulfenic acid **5** is therefore *at least* 0.85 pK unit stronger acid than selenenic acid **1a**, suggesting that sulfenic acids may indeed also be considerably stronger acids than the corresponding selenenic acids. We hope in the near future to be able to measure accurately the pK_a of one or more sulfenic acids, either "stable" ones such as 1-anthraquinonesulfenic[18] or 9-triptycenesulfenic[19] acids, or one, like **5**, that can be generated and observed in well-defined kinetic systems.[17]



5

Experimental Section

Preparation of 4-Substituted-2-nitrophenyl Ethyl Selenides. All of the selenides were synthesized from the corresponding selenocyanates[20] and absolute ethanol using the synthetic procedure described by Grieco, Gilman, and Nishizawa.[7] Preparation of *o*-nitrophenyl ethyl selenide (**3a**) has been described previously.[6]

4-Methyl-2-nitrophenyl ethyl selenide (**3c**) was obtained, after recrystallization from hexane, in 16% yield as long needles, mp 45-46.5 °C (lit.[2a] 49.5-50 °C): ^{1}H NMR (acetone-d_6) δ 1.44 (t, 3 H), 2.42 (s, 3 H), 2.98 (quartet, 2 H), 7.30-8.15 (m, 3 H); mass spectrum, *m/e* 245 (M^+,^{80}Se), 216 ($M^+ - CH_3CH_2$).

4-Chloro-2-nitrophenyl ethyl selenide (**3b**) was isolated in 51% yield as yellow needles, mp 91-92.5 °C: IR (KBr) 3097, 3080, 2960, 2928, 1595, 1548, 1514, 1502, 1446, 1334, 1284, 1253, 1234, 1159, 1118, 1091, 1043, 887, 814, 765, 754, and 513 cm^{-1}; ^{1}H NMR (acetone-d_6) δ 1.47 (t, 3 H), 3.08 (quartet, 2 H), 7.65-8.35 (m, 3 H); mass spectrum, *m/e* 265 (M^+, ^{78}Se and ^{37}Cl, or ^{80}Se and ^{35}Cl). Anal. Calcd for $C_8H_8ClNO_2Se$: C, 36.32; H, 3.05. Found: C, 36.43; H, 3.10.

4-Methoxy-2-nitrophenyl ethyl selenide (**3d**) was obtained, after recrystallization from hexane, in 44% yield as shiny orange needles, mp 60-61 °C: IR (KBr) 3084, 2955, 2928, 2866, 2833, 1510, 1336, 1303, 1269, 1242, 1190, 1093, 1060, 914, 881, 808, 800, 771, 758, and 611 cm^{-1}; ^{1}H NMR (acetone-d_6) δ 1.46 (t, 3 H), 3.03 (quartet, 2 H), 3.95 (s, 3 H), 7.40-8.18 (m, 3 H); mass spectrum, *m/e* 261 (^{80}Se). Anal. Calcd for $C_9H_{11}NO_3Se$: C, 41.55; H, 4.26. Found: C, 41.60; H, 4.19.

Preparation of 4-Substituted-2-nitrobenzeneselenenic Acids. The 4-substituted-2-nitrophenyl ethyl selenide (1 mmol) was dissolved in 2 mL of methylene chloride and the solution was cooled to below −20 °C. To this was added with good stirring a solution of 1.2 mmol of *m*-chloroperoxybenzoic acid dissolved in 2 mL of ether. The reaction mixture was kept below −20 °C and stirred until TLC showed that no selenide remained unoxidized. The solution was then immediately transferred to a separatory funnel, additional cold methylene chloride (~10 mL) was added, and it was extracted with 5 mL of ice-cold 0.72 N aqueous potassium hydroxide. The organic layer was washed once, separated, dried ($MgSO_4$), and filtered. The dried filtrate containing the 4-substituted-2-nitrophenyl ethyl selenoxide was allowed to stand at room temperature until decomposition of the selenoxide to the selenenic acid was complete (5-12 h).

Dioxane (10 mL) was added to the CH_2Cl_2-ether solution of the selenenic acid, and the majority of the solvents were evaporated under reduced pressure at below room temperature. This removed the methylene chloride and ether. Sufficient additional dioxane was then added to give a stock solution of the selenenic acid in dioxane that was ~0.005 M. This was used promptly (before dehydration of selenenic acid to selenenic anhydride could become a problem) for the pK_a measurements.

Determination of pK_a's of 4-Substituted-2-nitrobenzeneselenenic Acids. To 3.0 mL of water contained in a 1-cm cell in the thermostatted cell compartment of a UV-visible spectrophotometer was added by microsyringe an amount (60 μL) of the 0.005 M stock solution of the selenenic acid in dioxane sufficient to give an optical density of 0.40 to 0.50 at the long wavelength λ_{max} for the selenenic acid (**1a**, 425 nm; **1b**, 432 nm; **1c**, 435 nm; **1d**, 458 nm). The absorption spectrum for the same concentration of the corresponding selenenate anion was then ascertained by adding to the solution by microsyringe sufficient 1 N sodium hydroxide to give a solution containing $[OH^-]$ = 0.04 M. The long wavelength absorption maximum for each of the $ArSeO^-$ ions (**2a-d**) was as follows: **2a**, 550 nm; **2b**, 562 nm; **2c**, 560 nm; **2d**, 585 nm. The reversibility of the formation of $ArSeO^-$ from ArSeOH was demonstrated by acidifying the solution containing the selenenate anion through addition of an appropriate amount of concentrated aqueous perchloric acid. In each case the absorption spectrum reverted to that observed for the selenenic acid prior to the addition of sodium hydroxide.

To determine the pK_a of each selenenic acid measured amounts of various $NaHCO_3$-NaOH or K_2HPO_4-NaOH buffers of known[11] pH were introduced by microsyringe into a solution of the selenenic acid in water prepared as described above, the solution was thoroughly mixed, and the absorbance of the solution at the wavelength corresponding to λ_{max} for the selenenate anion was measured immediately. For each selenenic acid determinations

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(15) McCullogh, J. D.; Gould, E. S. *J. Am. Chem. Soc.* **1949**, *71*, 674.

(16) Ritchie, C. D.; Saltiel, J. D.; Lewis, E. S. *J. Am. Chem. Soc.* **1961**, *83*, 4601.

(17) Boduszek, B.; Kice, J. L. *J. Org. Chem.* **1982**, *47*, 3199.

(18) Bruice, T. C.; Sayigh, A. B. *J. Am. Chem. Soc.* **1959**, *81*, 3416.

(19) Nakamura, N. *J. Am. Chem. Soc.* **1983**, *105*, 7172.

(20) Rheinboldt, H. "Methoden der organischen Chemie (Houben-Weyl)", 4th ed.; Georg Thieme Verlag: Stuttgart, 1955; Vol. 9, pp 942-947. See also references cited therein.

were made at from 5 to 11 different pH's separated by 0.1 pH unit. Because of the marked difference in the absorption spectra of $ArSeO^-$ and ArSeOH, particularly the lack of significant absorbance by the selenenic acid at the wavelength where the anion has its maximum, the fraction, f, of the selenenic acid present as the selenenate, $f = [ArSeO^-]/([ArSeO^-] + [ArSeOH])$, can be calculated easily from the optical density of the buffer solution at λ_{max} for $ArSeO^-$ plus the previously determined relationship between the ϵ's for ArSeOH and $ArSeO^-$ at their respective absorption maxima.

Registry No. **1a**, 56790-60-4; **1b**, 99809-29-7; **1c**, 65848-43-3; **1d**, 99809-30-0; **3a**, 99809-31-1; **3b**, 99809-32-2; **3c**, 65275-57-2; **3d**, 99809-33-3; *o*-nitrophenyl selenocyanate, 51694-22-5; *p*-chloro-*o*-nitrophenyl selenocyanate, 99809-34-4; *p*-methyl-*o*-nitrophenyl selenocyanate, 65275-29-8; *p*-methoxy-*o*-nitrophenyl selenocyanate, 63816-14-8; *o*-nitrophenyl ethyl selenoxide, 94650-41-6; *p*-chloro-*o*-nitrophenyl ethyl selenoxide, 99809-35-5; *p*-methyl-*o*-nitrophenyl ethyl selenoxide, 65275-44-7; *p*-methoxy-*o*-nitrophenyl ethyl selenoxide, 99809-36-6; benzeneselenenic acid, 5818-99-5; ethanol, 64-17-5.

Supplementary Material Available: Tabulation of the ratio of selenenate to selenenic acid and calculated pK_a's for selenenic acids in different buffers (Table I) (2 pages). Ordering information is given on any current masthead page.

Rates of Oxidation of *o*-Nitrobenzeneselenenyl Compounds by *m*-Chloroperoxybenzoic Acid and the Rate of Reaction of *o*-Nitrobenzeneselenol with *o*-Nitrobenzeneselenenic Acid[1a]

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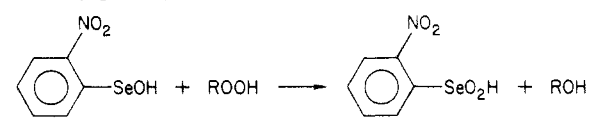
Department of Chemistry, Texas Tech University, Lubbock, Texas 79409

Received August 1, 1985

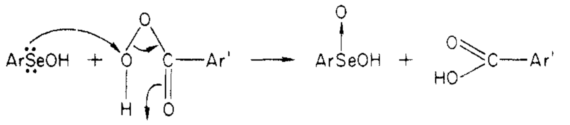
Rate constants for the oxidation of a series of *o*-nitrobenzeneselenenyl derivatives (Ar = o-$O_2NC_6H_4$) by *m*-chloroperoxybenzoic acid (MCPBA) have been measured at 25 °C in ethanol (compound, k_{PA} ($M^{-1}\,s^{-1}$)): ArSeH, 1.1×10^4; ArSeOH, 80; ArSeOSeAr, 12; ArSeOEt, 4; ArSeSeAr, 0.15. The rate constant ($k_{ArSeH} = 1.0 \times 10^2\ M^{-1}\,s^{-1}$) for the reaction of ArSeH with ArSeOH to give ArSeSeAr (eq 3), which is pH independent in acid solution, has also been determined. Significant practical consequences of these and related results include the following: (a) the rate of oxidation of selenol (ArSeH) to selenenic acid (ArSeOH) is enough faster than either the oxidation of ArSeOH to seleninic acid ($ArSeO_2H$) or eq 3 so that oxidation of the selenol with 1 molar equiv of MCPBA gives ArSeOH in high yield; (b) with a weaker oxidant, hydrogen peroxide, the rate of oxidation of the selenol is enough slower than the rate of eq 3 that the diselenide (ArSeSeAr) becomes the almost exclusive product; (c) the rate of oxidation of the diselenide is so much smaller than that of any of the other compounds that its initial oxidation to ArSeOSeAr is far and away the slowest step in its overall oxidation to seleninic acid by excess peracid.

In contrast to the vast majority of areneselenenic acids, solutions of *o*-nitrobenzeneselenenic acid, **1** (ArSeOH, Ar = o-$O_2NC_6H_4$), are quite stable, and the mechanisms of reactions of **1** are therefore subject to investigation in a straightforward fashion, something that is not possible with most selenenic acids. In earlier work,[2] the oxidation (eq 1) of **1** by peroxyacids (R = ArC(O)), hydroperoxides (R = *t*-Bu or $PhCMe_2$), and hydrogen peroxide (R = H) in 60% dioxane was examined. The mechanism for the oxidation of **1** by peroxyacids was found to be that shown in eq 2. This mechanism, which is analogous to that[3] for oxidation of alkyl sulfides by peracids, involves nucleophilic attack by the selenenic acid on one of the peroxide oxygens of the peracid.



(1)

1 2



(2)

It is of interest to determine how the rates of peroxyacid oxidation of other related *o*-nitrobenzeneselenenyl compounds (ArSeH, ArSeSeAr, ArSeOSeAr, ArSeOEt) compare with that of **1**. Also of interest is how the rate of

$$\underset{\mathbf{3}}{ArSeH} + \underset{\mathbf{1}}{ArSeOH} \xrightarrow{k_{ArSeH}} \underset{\mathbf{4}}{ArSeSeAr} + H_2O \qquad (3)$$

reaction of *o*-nitrobenzeneselenol (**3**) with **1** (eq 3) compares with the rate of oxidation of **3** (eq 4). Since the oxidation

$$\underset{\mathbf{3}}{ArSeH} + Ar'CO_3H \xrightarrow{k_{PA}} \underset{\mathbf{1}}{ArSeOH} + Ar'CO_2H \qquad (4)$$

$$Ar = o\text{-}O_2NC_6H_4;\ Ar' = m\text{-}ClC_6H_4$$

of the diselenide **4** is much slower than any of the other oxidations, the relative rates of eq 3 and 4 are critical in determining whether oxidation of selenol **3** by excess oxidant under a given set of conditions will lead primarily to seleninic acid **2** or to diselenide **4**. This paper reports the results of experiments providing information on these points.

Results

Oxidation of *o*-Nitrobenzeneselenol (3) by *m*-Chloroperoxybenzoic Acid (MCPBA). Solutions of o-$O_2NC_6H_4Se^-$ in ethanol were prepared by reduction of *o*-nitrophenyl selenocyanate (o-$O_2NC_6H_4SeCN$) with an equimolar amount of sodium borohydride.[4] Because of

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[1] (a) This research supported by the National Science Foundation, Grant CHE-82-15140. (b) Present address: Department of Chemistry, University of Denver, Denver, CO 80208.

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