of sodium bicarbonate (252 mg, 3.00 mmol) at 0 °C for 0.5 h. Acetone was evaporated in vacuo and the remaining aqueous portion was extracted with ether. All ethereal extracts were combined and washed with water and brine and were concentrated to provide the phenyl thio ester **5** in 64% yield.

**Hydrolysis of Sarkomycin Phenyl Thio Ester (5).** The phenylthio ester obtained by acetone-water-bicarbonate hydrolysis of the dichloro compound 4 prepared from 0.50 mmol of sulfide **3** was dissolved in a solution of benzene (5 mL) and THF (5 mL) and treated with silver trifluoroacetate (331 mg, 1.50 mmol), cadmium carbonate (517 mg, 6.00 mmol), and benzhydrol (92 mg, 0.50 mmol). The mixture was stirred at 25 °C for 24 h and filtered, the filtrate was dissolved in carbon tetrachloride, and the resulting solution was filtered again. To an ethereal solution of the concentrated filtrate was added an aqueous solution containing 504 mg (6.00 mmol) of sodium bicarbonate and a small amount of hydroquinone. The mixture was stirred at 25 °C for 0.5 h. The separated aqueous layer was acidified with hydrochloric acid and extracted with chloroform (15 mL + 3 × 5 mL) to which 3.6 mg of 3-*tert*-butyl-4-hydroxy-5-methylphenyl sulfide had been added. The overall yield of sarkomycin (**6**) from the concentrated extracts was 3% from the sulfide **3**; since the yield of thio ester starting from **3** and using the water-acetone-bicarbonate method is 64%, it follows that the yield of sarcomycin (**6**) starting from the thioester **5** is 5%.

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**Registry No.** **1**, 930-30-3; **2**, 76047-52-4; **3**, 96245-48-6; **4**, 96258-20-7; **5**, 96258-21-8; **6**, 69274-56-2; **8**, 13910-16-2; **9**, 83818-59-1; (*E*)-**10**, 96245-49-7; (*Z*)-**10**, 96245-50-0; **11**, 65842-42-4; PhSH, 108-98-5; $CH_2O$, 50-00-0; $Me_3SiCH_2OTf$, 64035-64-9; Chloreal, 87-90-1.

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# The Equilibrium between an Areneselenenic Acid and Its Anhydride[1]

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The equilibrium constants ($K_{eq} = [ArSeOH]^2/[H_2O][ArSeOSeAr]$) associated with the equilibrium (eq 1) between *o*-nitro- and *o*-benzoylbenzeneselenenic anhydrides (**2a** and **2b**) and the corresponding selenenic acids (**1a** and **1b**) have been determined in dioxane containing 0.25–1.5% water. For the **2b**–**1b** equilibrium, $K_{eq} = 0.16$ (25 °C) and $\Delta H° = +0.6$ kcal/mol. The equilibrium constant for the **2a**–**1a** system is ~10 times larger. That $\Delta H°$ for the hydrolysis of **2b** is slightly *endothermic* contrasts sharply with the exothermic nature of the hydrolysis of most common acid anhydrides. The values of $K_{eq}$ for both **2b** and **2a** are such that conditions can easily be encountered in media of low water content, where a significant fraction of the selenenic anhydride will remain unhydrolyzed at equilibrium, a situation without precedent in the chemistry of typical acid anhydrides.

Previous research[2] has shown that the compounds thought by Rheinboldt and Giesbrecht[3] to be *o*-nitro- and *o*-benzoylbenzeneselenenic acids (**1a** and **1b**) are, in actuality, the corresponding selenenic anhydrides (**2a** and **2b**).

$$\mathrm{ArSeOSeAr} + \mathrm{H_2O} \xrightleftharpoons{\mathrm{H^+}} 2\mathrm{ArSeOH} \qquad (1)$$

$$\begin{array}{ll} \mathbf{2a},\ \mathrm{Ar} = o\text{-}\mathrm{O_2NC_6H_4} & \mathbf{1a},\ \mathrm{Ar} = o\text{-}\mathrm{O_2NC_6H_4} \\ \mathbf{2b},\ \mathrm{Ar} = o\text{-}\mathrm{PhC(O)C_6H_4} & \mathbf{1b},\ \mathrm{Ar} = o\text{-}\mathrm{PhC(O)C_6H_4} \end{array}$$

In aqueous organic solvents these selenenic anhydrides undergo acid-catalyzed hydrolysis (eq 1) to afford stable solutions of the selenenic acids.[2] In the absence of water, however, **1a** and **1b** revert readily to anhydrides **2a** and **2b**,[2a] indicating the easily reversible nature of the equilibrium between **2** and **1**.

Since most areneselenenic acids, such as PhSeOH, are quite unstable and disproportionate ($3PhSeOH \rightarrow PhSeSePh + PhSeO_2H + H_2O$) so readily as to preclude any quantitative investigation of the equilibrium between acid and selenenic anhydride, the **1a**–**2a** and **1b**–**2b** systems offer a unique opportunity to probe the details of the equilibrium between an areneselenenic acid and the corresponding anhydride.

The kinetics and mechanisms of the acid-catalyzed hydrolyses of **2a** and **2b** in 60% aqueous dioxane were explored earlier.[2b] The objective of the present work was to determine the equilibrium constants and the enthalpy of reaction associated with the equilibria shown in eq 1 and to compare them, where possible, with equivalent data for other anhydride–acid equilibria.

Most measurements of $K_{eq}$ for eq 1 were done by starting with the selenenic anhydride and allowing the system to proceed to equilibrium. Some, however, were done by starting from a solution of the selenenic acid, the latter being prepared by allowing a sample of the appropriate ethyl aryl selenoxide (**3**) to undergo fragmentation[4] into ethylene and the selenenic acid (eq 2). In connection with

$$\mathrm{ArSe(O)CH_2CH_3} \rightarrow \mathrm{ArSeOH} + \mathrm{CH_2{=}CH_2} \qquad (2)$$

$$\begin{array}{ll} \mathbf{3a},\ \mathrm{Ar} = o\text{-}\mathrm{O_2NC_6H_4} & \mathbf{1a} \\ \mathbf{3b},\ \mathrm{Ar} = o\text{-}\mathrm{PhC(O)C_6H_4} & \mathbf{1b} \end{array}$$

this aspect of the work the kinetics of the decomposition of both **3a** and **3b** were measured over a range of temperatures in dioxane as solvent. The results and the ac-

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**Table I. Equilibrium Constants for the Equilibrium between *o*-Benzoylbenzeneselenenic Acid and Its Anhydride in Dioxane**

| temp, °C | **2b** or **1b** (range of $c_0$ used, M) | $c_{H_2O}$, M | no. of measurements | $K_{eq} = [\mathbf{1b}]_{eq}^2/[H_2O][\mathbf{2b}]_{eq}$ |
|---|---|---|---|---|
| 15.0 | **2b** (0.00495–0.0395) | 0.417 | 10 | 0.163 ± 0.013 |
| | | 0.556 | 8 | 0.160 ± 0.013 |
| 20.0 | **2b** (0.00495–0.0395) | 0.556 | 8 | 0.163 ± 0.02 |
| 25.0 | **2b** (0.00495–0.0395) | 0.417 | 8 | 0.167 ± 0.015 |
| | | 0.556 | 8 | 0.165 ± 0.013 |
| | | 0.833 | 4 | 0.153 ± 0.016 |
| | **1b** (0.0080–0.064) | 0.556 | 4 | 0.173 ± 0.018 |
| 33.9 | **2b** (0.00495–0.0395) | 0.417 | 7 | 0.176 ± 0.02 |
| | | 0.556 | 7 | 0.174 ± 0.02 |
| 40.0 | **2b** (0.00495–0.0395) | 0.417 | 4 | 0.175 ± 0.007 |
| | | 0.556 | 4 | 0.170 ± 0.017 |

tivation parameters for their decomposition are also included in the paper.

## Results

**Measurement of the Equilibrium Constant for Selenenic Anhydride–Selenenic Acid Equilibria. General Considerations.** For both the *o*-nitro and *o*-benzoyl compounds the UV spectra[2a] of the selenenic acid **1** and the anhydride **2** are sufficiently different that the ratio $([\mathbf{1}]/[\mathbf{2}])_{eq}$ can be reliably estimated under conditions where the ratio $[\mathbf{1}]/[\mathbf{2}]$ at equilibrium is 0.3–15.

Because of the stoichiometry of eq 1 the ratio $([\mathbf{1}]/[\mathbf{2}])_{eq}$ at a given water concentration will be smaller the larger the initial concentration of **2** (or **1**) used. Preliminary studies in aqueous dioxane indicated, however, that even when $[\mathbf{2b}]_0$ was as high as 0.004–0.04 M the water concentration needed to be below ~1.5% (0.84 M $H_2O$) in order for there to be enough **2b** remaining at equilibrium so that $([\mathbf{1b}]/[\mathbf{2b}]) \leq 15$. Reliable equilibrium constants for the **1b**–**2b** equilibrium were therefore able to be measured experimentally only in media containing 1.5% or less water. For the **1a**–**2a** equilibrium, considerably lower water concentrations (~0.25% $H_2O$) were necessary. This led to other experimental difficulties that precluded measuring $K_{eq}$ for the **1a**–**2a** equilibrium as accurately as that for **1b**–**2b**.

Expeditious achievement of equilibrium requires acid catalysis. Although both **1a** and **1b** are stable in the presence of dilute perchloric acid in dioxane containing 10% or more water, in media of much lower water content the selenenic acids are apparently oxidized by perchlorate. For this reason other strong acids had to be used as catalysts. For the **1b**–**2b** equilibrium trifluoroacetic acid was satisfactory; sulfuric acid was used with the **1a**–**2a** equilibrium.

**The 1b–2b Equilibrium.** Most measurements of $K_{eq}$ for the **1b**–**2b** equilibrium were done by starting from solutions containing the selenenic anhydride **2b** and allowing the system to proceed to equilibrium. If $c_0$ is the initial concentration of **2b** and $\alpha$ is the fraction of selenenic anhydride converted to **1b**, the relationship indicated in eq 3 is expected at equilibrium; $\alpha$ was determined by

$$K_{eq} = \frac{[\mathrm{ArSeOH}]^2}{[\mathrm{H_2O}][\mathrm{ArSeOSeAr}]}$$

$$\frac{\alpha^2}{(1-\alpha)} = \left(\frac{K_{eq}c_{H_2O}}{4}\right)\left(\frac{1}{c_0}\right) \qquad (3)$$

comparing the change in absorbance ($\Delta A_{eq}$) at 430 nm with the change that corresponded to complete hydrolysis of **2b** to **1b** ($\Delta A_{100\%}$); i.e., $\alpha = \Delta A_{eq}/\Delta A_{100\%}$.

Equation 3 indicates that for a series of experiments at a given water concentration with varying initial concentrations of **2b** a plot of $\alpha^2/(1-\alpha)$ vs. $1/c_0$ should be linear, the slope being equal to $(K_{eq}c_{H_2O}/4)$. Figure 1, which shows plots of this type for the data obtained at 40 °C, demonstrates that the expected relationship is indeed observed.

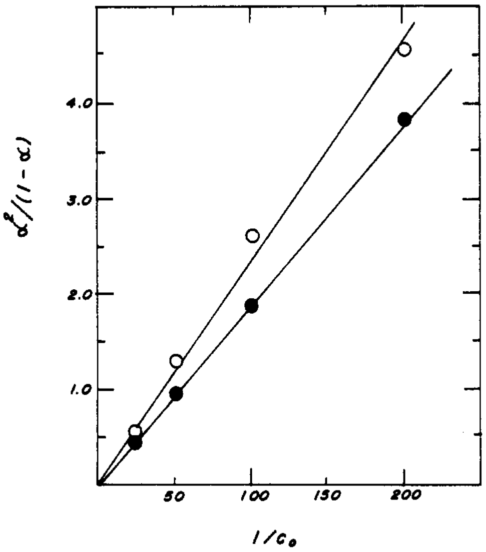


**Figure 1.** Plot of data for the equilibrium between **2b** and **1b** at 40 °C according to eq 3; $\alpha$ equals the fraction of **2b** converted to **1b** at equilibrium, $c_0$ equals the initial concentration of **2b**. Data for $H_2O$ = 0.556 M (○); data for $H_2O$ = 0.417 M (●).

To verify that the same value of $K_{eq}$ would be obtained regardless of the direction from which equilibrium was approached, a series of measurements was also carried out starting with solutions of selenenic acid **1b** (prepared, as outlined in the Experimental Section, by fragmentation of ethyl *o*-benzoylphenyl selenoxide). In these experiments the expected relationship (eq 4) between initial concentration of **1b** ($c_0'$) and the fraction ($\beta$) of the selenenic acid converted to **2b** at equilibrium was observed, and $K_{eq}$ was the same, within experimental error, as that determined by starting with solutions of selenenic anhydride **2b**.

$$\frac{(1-\beta)^2}{\beta} = \left(\frac{K_{eq}c_{H_2O}}{2}\right)\left(\frac{1}{c_0'}\right) \qquad (4)$$

Table I summarizes the results of the measurements of $K_{eq}$ for the **2b**–**1b** equilibrium. Each entry in the table indicates whether $K_{eq}$ was measured by allowing the system to reach equilibrium starting from **2b** or **1b**, the range of initial concentrations of these reagents used, the number of separate determinations of $K_{eq}$ made for a particular temperature and water concentration, and the average value of $K_{eq}$ and its standard deviation.

Table I shows that $K_{eq}$ varies little with temperature and that $\Delta H°$ for the **2b**–**1b** equilibrium is close to zero. From plots of ln $K_{eq}$ vs. $1/T$ for the data with 0.417 and 0.556 M $H_2O$ $\Delta H°$ for the equilibrium is estimated as 0.6 ± 0.1 kcal/mol; $\Delta S°$ is −1.6 ± 0.3 eu.

**The 1a–2a Equilibrium.** Experiments with $[\mathbf{2a}]_0 = 0.02$ M in dioxane containing 0.556 M $H_2O$ revealed that approximately 92% of the selenenic anhydride was hydrolyzed to the selenenic acid at equilibrium and that $([\mathbf{1a}]/[\mathbf{2a}])_{eq}$ was therefore too large under such conditions for $K_{eq}$ to be able to be estimated accurately, although a rough estimate was that it was approximately 10 times larger than $K_{eq}$ for the **2b**–**1b** equilibrium.

In dioxane containing only 0.139 M $H_2O$ $([\mathbf{1a}]/[\mathbf{2a}])_{eq}$ was enough smaller so that it and $K_{eq}$ could be measured satisfactorily. Equilibrium was approached starting from solutions of **1a** (0.01–0.04 M), prepared by fragmentation of ethyl *o*-nitrophenyl selenoxide. Because solutions of **1a** undergo slow decomposition in the presence of acid in this very low water content medium, the value for $K_{eq}$ (1.8 ± 0.8) obtained from these experiments is considerably less precise than those for the **2b**–**1b** equilibrium in Table I. Because of the problems in obtaining precise values for $K_{eq}$ for the **2a**–**1a** equilibrium, measurement of $K_{eq}$ at other temperatures was not attempted.

**Kinetics of Decomposition of Ethyl *o*-Nitrophenyl (3a) and *o*-Benzoylphenyl (3b) Selenoxides.** Since selenenic acids **1a** and **1b** are stable in anhydrous dioxane in the absence of strong acid, the kinetics of the decomposition (eq 2) of selenoxides **3a** and **3b** can be followed conveniently by monitoring the increase in absorbance at the long wavelength $\lambda_{max}$ for the selenenic acid (420 nm for **1a**, 395 nm for **1b**). Plots of log $(A_\infty - A)$ vs. time showed excellent linearity. The first-order rate constants, $k_1$, evaluated from the slopes of such plots, for **3a** at different temperatures are (temperature, $k_1 \times 10^3$, $s^{-1}$) as follows: 20.0 °C, 0.73 ± 0.01; 25.0 °C, 1.23 ± 0.01; 30.0 °C, 2.04 ± 0.08; 34.0 °C, 3.00 ± 0.03. For **3b** the corresponding data are as follows: 20.0 °C, 0.53 ± 0.01; 25.0 °C, 0.96 ± 0.01; 30.0 °C, 1.74 ± 0.05; 34.0 °C, 2.48 ± 0.05. From these data the activation parameters for the decompositions are as follows: **3a**, $\Delta H^{\ddagger} = 17.6$ kcal/mol, $\Delta S^{\ddagger} = -12.9$ eu; **3b**, $\Delta H^{\ddagger} = 19.5$ kcal/mol, $\Delta S^{\ddagger} = -7.1$ eu.

## Discussion

**Enthalpy of Reaction and Equilibrium Constants for the Hydrolysis of Selenenic Anhydrides.** The hydrolysis of most anhydrides is substantially exothermic, $\Delta H°$ ranging from −8 to −18 kcal/mol (eq 5–8). Because of this, $K_{eq}$ for the equilibrium

$$\text{anhydride} + H_2O \rightleftharpoons 2\text{acid} \qquad (K_{eq} = [\text{acid}]^2/[H_2O][\text{anhydride}])$$

is extremely large, and even in media containing virtually no water the anhydride is completely hydrolyzed to the acid at equilibrium.

$$CH_3C(O)OC(O)CH_3 + H_2O \rightarrow 2CH_3COOH \qquad \Delta H° = -14.0 \text{ kcal/mol (ref 5)} \quad (5)$$

$$(HO)_2P(O)OP(O)(OH)_2 + H_2O \rightarrow 2H_3PO_4 \qquad \Delta H° = -7.6 \text{ kcal/mol (ref 6)} \quad (6)$$

$$Ph_2P(O)OP(O)Ph_2 + H_2O \rightarrow 2Ph_2PO_2H \qquad \Delta H° = -17.6 \text{ kcal/mol (ref 7)} \quad (7)$$

$$PhSO_2SO_2Ph + H_2O \rightarrow PhSO_3H + PhSO_2H \qquad \Delta H° = -16 \text{ kcal/mol (ref 8)} \quad (8)$$

In marked contrast, the hydrolysis of *o*-benzoylbenzeneselenenic anhydride (eq 9) is slightly *endothermic*, $\Delta H°$ being +0.6 kcal/mol, and $K_{eq} = [ArSeOH]^2/[H_2O][ArSeOSeAr]$ is only 0.16 at 25 °C. Although $K_{eq}$

$$ArSeOSeAr + H_2O \rightarrow 2ArSeOH \qquad \Delta H° = +0.6 \text{ kcal/mol} \quad (9)$$

$$(Ar = o\text{-}PhC(O)C_6H_4)$$

for the hydrolysis of *o*-nitrobenzeneselenenic anhydride ($Ar = o\text{-}O_2NC_6H_4$) is about 10 times larger, it too is many orders of magnitude smaller than the equilibrium constants for the hydrolyses in eq 5–8. This means that in media of low water content conditions can easily be encountered where a significant fraction of selenenic anhydride **2b** or **2a** will remain unhydrolyzed at equilibrium, a situation without precedent in the chemistry of anhydrides such as those in eq 5–8.

The sulfur analogues of selenenic acids are sulfenic acids. The tendency of arenesulfenic acids (ArSOH) to form the corresponding thiosulfinate (sulfenic anhydride) is well documented.[9] Because of the instability of arenesulfenic acids and their tendency to undergo decomposition, no quantitative data on either $\Delta H°$ or $K_{eq}$ for the thiosulfinate–sulfenic acid equilibrium (eq 10) has ever been

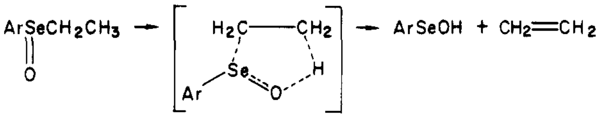
$$ArS(O)SAr + H_2O \rightleftarrows 2ArSOH \quad K_{eq} = [ArSOH]^2/[H_2O][ArS(O)SAr] \quad (10)$$

obtained. However, the qualitative behavior that has been observed[9] would appear to indicate that $K_{eq}$ for eq 10 is probably extremely small. Unusual thermodynamic stability of anhydride relative to acid therefore appears to be a distinctive and noteworthy aspect of the chemistry of *both* sulfenic and selenenic acids.

**Rates of Elimination of Selenoxides 3a and 3b.** Although the response of the rate of syn elimination of aryl alkyl selenoxides to a number of reaction variables has been established,[4c] enthalpies and entropies of activation for such eliminations have not been reported. In the present work we have determined the activation parameters for the decomposition (eq 2) of selenoxides **3a** and **3b**. These are (selenoxide, $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$) as follows: **3a**, 17.6 kcal/mol, −12.9 eu; **3b**, 19.5 kcal/mol, −7.1 eu. These may be compared with $\Delta H^{\ddagger}$ (25–28 kcal/mol) and $\Delta S^{\ddagger}$ (−11 to −16 eu) for the syn eliminations of aryl *n*-propyl sulfoxides (eq 11).[10] The enthalpy of activation for the decomposition of **3a** and **3b** (eq 2) is seen to be from 8 to 10 kcal/mol less than $\Delta H^{\ddagger}$ for the analogous decomposition of $ArS(O)CH_2CH_2CH_3$. The enormous difference in rates of syn elimination of selenoxides vs. sulfoxides is therefore, as might have been expected, primarily due to a much lower $\Delta H^{\ddagger}$ for the selenoxide decomposition.

$$ArS(O)CH_2CH_2CH_3 \rightarrow ArSOH + CH_2{=}CHCH_3 \quad (11)$$

The $\Delta S^{\ddagger}$ for the syn elimination of **3a** (−12.9 eu) is closely comparable to $\Delta S^{\ddagger}$ for eq 11 and is consistent with a mechanism[11] (eq 12) in which there is much less freedom of rotation in the transition state than in the selenoxide.



(12)

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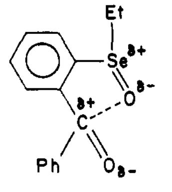
The origin of the 6 eu less negative $\Delta S^{\ddagger}$ for the decomposition of **3b** is not certain. One attractive hypothesis is that in **3b** there is some stabilizing interaction between the highly polar seleninyl and carbonyl groups in the fashion shown in 7. This would lead to less freedom of rotation in **3b** than in **3a** and would mean that going from selenoxide to transition state will result in a less negative $\Delta S^{\ddagger}$ for **3b**. At the same time such a stabilizing interaction should decrease somewhat the enthalpy of **3b** and could therefore explain why $\Delta H^{\ddagger}$ for the decomposition of this selenoxide is 2 kcal/mol greater than for **3a**.



7

## Experimental Section

**Preparation and Purification of Materials.** *o*-Nitro- and *o*-benzoylbenzeneselenenic anhydrides (**2a** and **2b**) were prepared as previously described.[2b] *o*-Nitrophenyl and *o*-benzoylphenyl ethyl selenide were both synthesized from the corresponding selenocyanates[3] and ethanol by using the synthetic procedure described by Grieco, Gilman, and Nishizawa.[12] The *o*-nitrophenyl selenide, a compound that has been prepared previously,[13] is an orange oil: IR (neat) 3086, 2692, 1591, 1564, 1510, 1452, 1330, 1303, 1226, 1097, 1037, 852, 783, 729 cm$^{-1}$; $^1$H NMR (acetone-$d_6$) δ 1.45 (t, 3 H), 3.03 (q, 2 H), 7.20–7.80 (m, 3 H), 8.15–8.35 (m, 1 H); mass spectrum, *m/e* 231 ($M^+$, $^{80}$Se), 202, 186, 156, 117, 106, 78; UV (dioxane) $\lambda_{max}$ 388 nm (ε 2250). *o*-Benzoylphenyl ethyl selenide was obtained in 90%g yield as a yellow oil: IR (neat) 3059, 2960, 2922, 2866, 1666, 1657, 1597, 1579, 1448, 1269, 925, 806, 761, 736, 725, 698, 638 cm$^{-1}$; $^1$H NMR ($CDCl_3$) δ 1.37 (t, 3 H), 2.83 (q, 2 H), 7.0–8.0 (m, 9 H); mass spectrum, *m/e* 290 ($M^+$, $^{80}$Se), 260 ($M^+$ − Et), 181, 151, 105; UV (dioxane) $\lambda_{max}$ 356 nm (ε 1630). Anal. Calcd for $C_{14}H_{14}OSe$: C, 62.29; H, 4.88. Found: C, 62.50; H, 4.87.

Dioxane was purified to remove peroxides and water,[14] and after fractional distillation, the anhydrous solvent was frozen and stored at −20 °C to prevent the formation of peroxides prior to use. All water used in studies of the equilibria between 1 and 2 was doubly distilled from glass. All other reagents were of the highest purity commercially available and were used without further purification.

**Preparation of 3b by Oxidation of *o*-Benzoylphenyl Ethyl Selenide.** To a solution of *o*-benzoylphenyl ethyl selenide (0.58 g, 2.0 mmol) in 15 mL of methylene chloride was added at −20 °C 0.46 g (2.1 mmol) of *m*-chloroperoxybenzoic acid (85%, Aldrich) dissolved in 3 mL of ether. The resulting solution was allowed to stand at −20 °C for 30 min, before being extracted twice with ice-cold, dilute aqueous sodium hydroxide, washed with ice water, and dried ($Na_2SO_4$) and the solvent removed under reduced pressure at 0 °C. The residue, *o*-benzoylphenyl ethyl selenoxide (**3b**) was a colorless crystalline solid: mp 48.5–50 °C dec; IR (KBr) 3061, 1643, 1282, 829 cm$^{-1}$; $^1$H NMR ($CDCl_3$) δ 1.31 (t, 3 H), 3.15 (q, 2 H), 7.1–8.6 (m, 9 H); UV (dioxane) $\lambda_{max}$ 250 nm. At room temperature a dioxane solution of **3b** underwent decomposition to yield selenenic acid **1b**, the yield of **1b** being determined from the final absorbance of the solution at 395 nm.

**Preparation of 3a by Oxidation of *o*-Nitrophenyl Ethyl Selenide.** Oxidation of *o*-nitrophenyl ethyl selenide with *m*-chloroperoxybenzoic acid at −20 °C in $CH_2Cl_2$–ether and workup using the procedure just described gave *o*-nitrophenyl ethyl selenoxide (**3a**).[13] The purity of **3a** was estimated by dissolving a weighed amount in dioxane, allowing it to undergo decomposition at room temperature, and measuring the amount of **1a** formed from the optical density of the solution at 420 nm.

**Kinetics of the Decomposition of 3a and 3b.** Immediately after isolation of the selenoxide, a 0.01 M solution in dioxane was prepared, and 35 μL of this solution was added by microsyringe to 3.5 mL of dioxane in a 1-cm stoppered cell in the thermostated cell compartment of a Perkin-Elmer Lamda 5 spectrophotometer. The increase in the absorbance ($A$) with time at the appropriate wavelength (420 nm for **3a**, 395 nm for **3b**) was followed. The final absorbance ($A_\infty$) of the solution was stable. The rate constant for the syn elimination of the selenoxide was determined from the slope of a plot of log $(A_\infty - A)/(A_\infty - A_0)$ vs. time.

**Measurement of Equilibrium Constants for Selenenic Anhydride–Selenenic Acid Equilibria. Runs Starting from the Selenenic Anhydride.** Four solutions containing different concentrations (0.04, 0.02, 0.01, 0.005 M) of **2b** and the desired concentration of water were prepared by appropriate dilution of aliquots of a 0.05 M solution of **2b** with dioxane and addition of water and were thermostated. Before initiating hydrolysis an aliquot of each solution was removed and diluted with solvent (ranging from an 800-fold dilution for the 0.04 M solution down to a 100-fold dilution for the 0.005 M solution) and the absorbance ($A_0$) at 430 nm measured. Hydrolysis of **2b** was initiated by addition to each solution of 0.01 M $CF_3CO_2H$. Once approximately four half-lives had elapsed, aliquots of each solution were periodically removed and diluted with solvent in precisely the same manner as in the measurement of $A_0$ for the same solution, and the absorbance ($A$) at 430 nm was measured immediately. Dilution of the aliquot decreases [$CF_3CO_2H$] by 100- to 800-fold. Since attainment of the **2b**–**1b** equilibrium is acid-catalyzed, this slows any change in the [1]/[2] ratio to the point that it does not change detectably during the short time required for dilution and measurement of the optical density; this was confirmed by measurements of $A$ at 430 nm for short periods of time after completion of the initial measurement.[15] When successive aliquots from a given solution indicated no further change in the absorbance, this value of $A$ was taken to be $A_{eq}$ and $\Delta A_{eq}$ as $A_0 - A_{eq}$. At the same time that these experiments were being done, a $5 \times 10^{-5}$ M solution of **2b** in dioxane containing the same concentration of water and 0.01 M $CF_3CO_2H$ was allowed to undergo hydrolysis to **1b**. The final absorbance ($A_\infty$) of this solution was used to determine the absorbance change ($\Delta A_{100\%}$) corresponding to complete hydrolysis of **2b**: $\Delta A_{100\%} = A_0 - A_\infty$.

The procedure used to examine the **2a**–**1a** equilibrium was the same, except that, because of the lower solubility of **2a** in dioxane, the maximum initial concentration of **2a** that could be used was 0.02 M. Also, the very slow rate of hydrolysis of **2a** in the presence of 0.01 M $CF_3CO_2H$ in dioxane containing 0.5–1.5% water dictated that 0.01 M sulfuric acid be used instead as the acid catalyst; $\Delta A$ and $\Delta A_{100\%}$ were measured at 465 nm.

**Runs Starting from the Selenenic Acid.** A 0.08 M solution of selenoxide **3b** in dixoane was allowed to undergo thermal decomposition (eq 2) to ethylene and selenenic acid **1b** at room temperature. The concentration of **1b** in the final solution was determined by measuring the absorbance of a diluted aliquot at 395 nm. Four solutions containing different concentrations (0.064, 0.032, 0.016, 0.008 M) of **1b** and 0.56 M water were prepared from aliquots of this solution by appropriate dilution with dioxane and addition of the proper amount of water; these were thermostated at 25 °C. Before equilibration of **1b** with **2b** was initiated an aliquot of each solution was removed and diluted with solvent (*an 800-fold dilution for the 0.064 M solution, a 400-fold dilution for the 0.032 M solution, etc.*), and the absorbance at 430 nm was determined. Equlibration was initiated by the addition of 0.01 M $CF_3CO_2H$. Once the time necessary for the system to get close

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[15] We had originally planned to neutralize the trifluoroacetic acid completely by making the dilution of the aliquot into a solution containing a large excess of an *n*-alkanecarboxylate, RCOO$^-$. However, although the rate of reaction of acetate ion with **2b** in 60% dioxane is so slow as to be negligible,[2b] we found that the same is not true in the essentially aprotic media used in the current study. Since tetra-*n*-butylammonium *n*-hexanoate (the hexanoate was used rather than acetate because of its much greater solubility in dioxane–1% $H_2O$) reacted relatively rapidly with **2b** in this medium, this experimental approach was abandoned in favor of the one described.

to equilibrium had elapsed aliquots of each solution were periodically removed and diluted with solvent in exactly the same manner as in the measurement of $A_0$ for the same solution, and the absorbance ($A$) at 430 nm was immediately ascertained. When successive aliquots from a given solution showed no further increase in absorbance, the absorbance of the solution was considered to have reached its equilibrium value, $A_{eq}$; $\Delta A_{eq} = A_{eq} - A_0$. To determine $\Delta A_{100\%}$, the absorbance change that would correspond to complete conversion of **1b** to the selenenic anhydride, the optical density ($A_{100\% \text{ anhyd}}$) of a 4 × $10^{-5}$ M solution of **2b** in dioxane–0.56 M $H_2O$ was measured at 430 nm, and $\Delta A_{100\%}$ was taken as equal to $A_{100\% \text{ anhd}} - A_0$.

The procedure for studying the equilibration of **1a** with **2a** was generally the same. The initial concentrations of **1a** in the different solutions used ranged from 0.01 to 0.04 M. The concentration of water was 0.14 M. Because **1a** seemed to be somewhat unstable in the presence of 0.01 M $H_2SO_4$ in this very low water content medium, only a trace of strong acid and rather long reaction times (overnight) were employed.

**Kinetics of the Hydrolysis of Selenenic Anhydrides.** In connection with the study of the equilibria between selenenic anhydrides and selenenic acids some rates of hydrolysis of both **2a** and **2b** under various conditions were also determined. The general procedure used in carrying out these kinetic runs was that described previously[2b] for studying the kinetics of the hydrolyses of **2a** and **2b** in 60% dioxane.

The experimental first-order rate constants for the hydrolysis of **2b** (5 × $10^{-5}$ M) in dioxane–0.56 M $H_2O$ in the presence of 0.01 M $CF_3CO_2H$ at various temperatures were as follows (temperature, $k_1 \times 10^3$, $s^{-1}$): 15.0 °C, 1.22 ± 0.07; 20.0 °C, 1.77 ± 0.08; 25.0 °C, 2.59 ± 0.20; 33.9 °C, 5.18 ± 0.50. For the hydrolysis of **2a** in the same reaction medium with 0.01 M sulfuric acid as catalyst the rate constants were as follows (temperature, $k_1 \times 10^3$, $s^{-1}$): 15.0 °C, 0.20 ± 0.001; 20.0 °C, 0.31 ± 0.004; 25.0 °C, 0.39 ± 0.009; 30.0 °C, 0.48 ± 0.01; 33.9 °C, 0.62 ± 0.01. The rate of hydrolysis of **2a** in the presence of 0.01 M $CF_3CO_2H$ was much slower than in the presence of the same concentration of sulfuric acid, $k_1$ being only 2.5 × $10^{-6}$ $s^{-1}$ at 25 °C. As already noted, this very slow rate was the reason that $H_2SO_4$, rather than $CF_3CO_2H$, was used as acid catalyst for establishment of the equilibrium between **2a** and **1a**.

Rates of hydrolysis of **2a** in the presence of 0.01 M perchloric acid were also measured at 25 °C in dioxane containing from 5% to 40% water. The first-order rate constants were as follows (% water, $k_1 \times 10^3$, $s^{-1}$): 40, 4.2; 20, 2.4; 10, 1.6; 5, 1.2.

**Registry No. 1a**, 56790-60-4; **1b**, 84250-81-7; **2a**, 84250-76-0; **2b**, 84250-80-6.

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# Barriers to Rotation of Peri Methyl Groups in 1,8-Dimethylquinolinium Iodide and Related Compounds

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To investigate peri steric interactions in heterocyclic compounds, rotational barriers of methyl groups in 1,8-dimethylquinolinium iodide (**3**) and related compounds are determined from the temperature dependence of the $^1H$ spin–lattice relaxation times in the solid state. The barrier to rotation of the 8-methyl ($C_{sp^2}$–$CH_3$) group (3.41 ± 0.26 kcal $mol^{-1}$) in **3** is in good agreement with that in 1,8-dimethylnaphthalene, whereas the barrier to rotation of the 1-methyl ($N_{sp^2}$–$CH_3$) group (2.42 ± 0.07 kcal $mol^{-1}$) in **3** is appreciably smaller. Similarly, the barriers obtained for methyl groups bonded to $N_{sp^2}$ atoms are smaller than the respective barriers for methyl groups bonded to $C_{sp^2}$ atoms in the corresponding carbon systems, suggesting facile bending of the $N_{sp^2}$–$CH_3$ groups in the rotational transition state. Also, the steric effect of the lone-pair electrons of the $sp^2$ nitrogen atom in 1-methyl-1,10-phenanthrolinium iodide (**5**) on the rotation of the 1-methyl group is estimated to be 1.7 Å in terms of the van der Waals radius. This value is notably larger than that (1.1 Å) for the side-on steric effects of the lone-pair electrons of the $sp^2$ nitrogen atom.

There is continuing interest in steric strain in overcrowded molecules.[1] The magnitude of steric strain between substituents at the peri positions in naphthalene derivatives has been investigated extensively.[2] Quinoline derivatives are also of interest since they have similar geometry. Packer et al.[3] have estimated the steric strain in methylnaphthalenes from the rates of the Menschutkin reaction of methyl iodide with quinoline derivatives in nitrobenzene, assuming the "strained homomorph" concept of Brown.[4] To our knowledge, however, the "strained homomorph" assumption has not been investigated quantitatively. In this regard, a comparison of the barrier to rotation of the 8-methyl group in 1,8-dimethylquinolinium iodide (**3**) with that of the methyl groups in 1,8-dimethylnaphthalene (**9**) reported previously should reveal differences in steric interactions in the two ring systems.[5-8]

Furthermore, it is of interest to determine whether there is any difference in the barriers to rotation of the 1-methyl and 8-methyl groups in **3**. For rotation about $N_{sp^2}$–$C_{sp^3}$ bonds, Balaban et al.[9] studied hindered rotation of the

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