Procedure for Product Analysis by GC. The reduction of 1,2-butylene oxide is representative. In a 50-mL flask fitted with a rubber syringe cap on an inlet port, a magnetic stirring bar, and a reflux condenser connected to a mercury bubbler were placed 4.8 mL (5.09 mmol) of a 1.06 M solution of Li9-BBNH and 0.2 mL of THF. Then 5.0 mL of a 1.0 M solution of 1,2-butylene oxide in THF was introduced while the mixture was vigorously stirred at room temperature. After 3 h, the excess hydride was destroyed with 0.5 mL of water. Then the reaction mixture was oxidized by the addition of 1.6 mL (6.4 mmol) of 4 N aqueous sodium hydroxide, followed by 1.5 mL (13 mmol) of 30% hydrogen peroxide and heating at 50 °C for 1 h. The aqueous layer was saturated with 3 g of potassium carbonate and the dry THF layer was subjected to GC analysis on a 10% Carbowax 20M column, 6 ft × 0.125 in., indicating the presence of 99% 2-butanol and 1% 1-butanol. A similar procedure was employed for examining the stereochemistry of the reduction of cyclic and bicyclic ketones with Li9-BBNH. The other compounds discussed were also examined in this manner by using the appropriate internal standard.

Procedure for Competitive Reaction. The reaction of ethyl benzoate in the presence of caproic acid is representative. 9.4 mL of a 1.06 M Li9-BBNH solution (20 mmol in hydride) and 5.6 mL of purified THF were introduced into a dried, 50-mL flask fitted with a rubber syringe cap on an inlet port, a magnetic stirring bar, and a reflux condenser connected to a mercury bubbler. The flask was maintained at room temperature with stirring and 5 mL of THF solution containing 5 mmol of ethyl benzoate and 5 mmol of caproic acid was injected slowly. After 30 min, the remaining hydride was destroyed with water. Then the reaction mixture was oxidized with $NaOH–H_2O_2$, followed by addition of 5 mmol of *n*-octanol in THF (5 mL) as internal standard. GC analysis of the mixture on a 5% Carbowax 20M column, 6 ft × 0.125 in., revealed the presence of 5 mmol of benzyl alcohol and the absence of 1-hexanol.

Acknowledgment. The financial support from the United States Army Research Office (Durham), DAAG 29-79-C-0027, and the Ministry of Education, Korean Government, for this research is gratefully acknowledged.

Registry No. 1-Hexanol, 111-27-3; benzyl alcohol, 100-51-6; 3-hexanol, 623-37-0; 3-ethyl-3-pentanol, 597-49-9; phenol, 108-95-2; 2,6-di-*tert*-butylphenol, 128-39-2; *n*-hexylamine, 111-26-2; benzenethiol, 108-98-5; 1-hexanethiol, 111-31-9; caproaldehyde, 66-25-1; benzaldehyde, 100-52-7; 2-heptanone, 110-43-0; norcamphor, 497-38-1; camphor, 76-22-2; acetophenone, 98-86-2; benzophenone, 119-61-9; 2,2,4,4-tetramethyl-3-pentanone, 815-24-7; cinnamaldehyde, 104-55-2; 2-methylcyclohexanone, 583-60-8; 4-*tert*-butylcyclohexanone, 98-53-3; *p*-benzoquinone, 106-51-4; anthraquinone, 84-65-1; caroic acid, 142-62-1; benzoic acid, 1005-01-2; acetic anhydride, 108-24-7; succinic anhydride, 108-30-5; phthalic anhydride, 85-44-9; caproyl chloride, 142-61-0; benzoyl chloride, 98-88-4; ethyl caproate, 123-66-0; ethyl benzoate, 93-89-0; phenyl acetate, 122-79-2; γ-butyrolactone, 96-48-0; phthalide, 87-41-2; isopropenyl acetate, 108-22-5; 1,2-butylene oxide, 106-88-7; styrene oxide, 96-09-3; cyclohexene oxide, 286-20-4; 1-methyl-1,2-cyclohexene oxide, 1713-33-3; 2-phenyldioxolane, 936-51-6; 2-methyl-2-ethyldioxolane, 126-39-6; triethyl orthoformate, 122-51-0; caproamide, 628-02-4; benzamide, 55-21-0; *N,N*-dimethyl acetamide, 127-19-5; *N,N*-dimethyl benzamide, 611-74-5; capronitrile, 628-73-9; benzonitrile, 100-47-0; 1-nitropropane, 108-03-2; nitrobenzene, 98-95-3; azobenzene, 103-33-3; azoxybenzene, 495-48-7; cyclohexanone oxime, 100-64-1; phenyl isocyanate, 103-71-9; pyridine, 110-86-1; pyridine *N*-oxide, 694-59-7; di-*n*-butyl disulfide, 629-45-8; diphenyl disulfide, 882-33-7; methyl phenyl sulfide, 100-68-5; dimethyl sulfoxide, 67-68-5; tetramethylene sulfone, 126-33-0; diphenyl sulfone, 127-63-9; methanesulfonoic acid, 75-75-2; *p*-toluenesulfonic acid monohydrate, 6192-52-5; *n*-octyl tosylate, 3386-35-4; cyclohexyl tosylate, 953-91-3; *n*-octyl chloride, 111-85-3; *n*-octyl bromide, 111-83-1; 2-bromopentane, 107-81-3; *n*-hexyl iodide, 638-45-9; *cis*-2-methylcyclohexanol, 7443-70-1; *cis*-4-*tert*-butylcyclohexanol, 7214-18-8; *endo*-bicyclo[2.2.1]heptan-2-ol, 497-36-9; *exo*-1,7,7-trimethylbicyclo[2.2.1]heptan-2-ol, 124-76-5; lithium 9-boratabicyclo[3.3.1]nonane, 91083-44-2.

Protonation and Sulfur Trioxide Sulfonation of Some 1,6-Methano[10]annulenes[1]

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The sulfonation of 1,6-methano[10]annulene (1), 2-methoxy-1, 11-fluoro-1, and 11,11-difluoro-1 with SO_3 in dioxane at 35 °C and the low temperature protonation of the two fluoro-containing substrates in the $HSO_3F–SO_2ClF$ (1:2 v/v) solvent system has been studied. The sulfonation and protonation of all substrates occur at the α-positions. The subsequent sulfonation of 2-methoxy-5-sulfo-1 occurs at the 3-, 8-, and 9-position. The protonation of 11-fluoro-1,6-methano[10]annulene (3) occurs 36% at the 2-position and 64% at the 7-position, whereas the sulfonation yields 47% of the 2- and 53% of the 7-sulfonic acid. Rate studies have shown that the increase in the free energy of activation on replacing the methylene hydrogens of 1 successively by fluorine is additive.

The bridged monocyclic 10π-electron 1,6-methano[10]-annulene (1)[2] is an intriguing aromatic[3] hydrocarbon in view of the nonplanarity of the annulene perimeter[4,5] and its transannular interaction.[5–7] We now report on the products and reactivities in the sulfonation of the 1,6-methano[10]annulene derivatives **3–5**. In order to obtain

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(7) In 11,11-dimethyl- and 11-cyano-11-methyl-1,6-methano[10]-annulene the distance between C(1) and C(6) is so short (1.83–1.77[8] and 1.85–1.77 Å,[9] respectively) that these compounds are regarded as bis(norcaradiene) derivatives, whereas the C(1)–C(6) of 1, its 2-carboxylic acid, and **5** are relatively large (2.24,[4] 2.26,[10] and 2.27 Å,[11] respectively), illustrating the true [10]annulene nature of these compounds.

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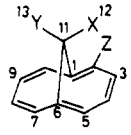
Table II. Sulfonation of 1,6-Methano[10]annulenes with SO_3

no.	reactn conditions: SO_3 equiv	solvent	temp, °C	time, h	sulfonic acid products, % (±2%)[a]	unconverted substrate, %
1	2	[$^2H_8$]dioxane	17	0.5	2-S (>96)	<2
	3	[$^2H_8$]dioxane	17	0.5	2-S (77), 2,7-S_2 (23)	0
	4	dioxane	12	0.5	2,7-S_2 (>96)[12]	
2	0.9	dioxane	12	0.5	2-S (≥98)[12]	
	4	dioxane	12	0.5	2-S (≥98)[12]	
3	1	[$^2H_8$]dioxane	35	1.0	2-S (48), 7-S (52)	36
	2	[$^2H_8$]dioxane	35	1.0	2-S (47), 7-S (53)	16
	8	[$^2H_8$]dioxane	35	1.0	2-S (47), 7-S (53)	4
4	2	[$^2H_8$]dioxane	35	24	2-S (>96)	5
5[b]	1	[$^2H_8$]dioxane	17	0.5	5-S (>96)	57
	2	[$^2H_8$]dioxane	17	0.5	5-S (73), 3,5-S_2 (4), 5,8-S_2 (7[c]), 5,9-S_2 (16[c])	0

[a] S stands for SO_3H. [b] Reaction of **5** with more than 4 equiv of SO_3 led to decomposition of the [10]annulene moiety. [c] These data may be the reverse, cf., subscript *k* of Table I.

information on the relative stabilities of the σ-complex intermediates in the sulfonation of **3**, we have also studied the low temperature HSO_3F protonation of **3** and **4**.



1 X = Y = Z = H
2 X = Y = H ; Z = Me
3 X = F ; Y = Z = H
4 X = Y = F ; Z = H
5 X = Y = H ; Z = OMe
10 X = Y = H ; Z = SO_3H
11 X + Y = CH_2

Results

Substrates **1** and **3–5** have been sulfonated with SO_3 in an aprotic solvent. The ^1H NMR spectra of the sulfonic acids and certain potassium sulfonates, are listed in Table I (supplementary material). The sulfonic acid product distributions are collected in Table II. All substrates yield very predominantly, if not exclusively, the α-substituted monosulfonic acids. The degree of sulfonation at the 2- and 7-position of **3** are about the same.

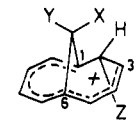
The effect of replacing the methylene hydrogens of **1** successively by fluorine on the rate of sulfonation has been studied by comparing the rate of substrate conversion under strictly comparable reaction conditions. The results are in Table III. The strong decrease in the annulene reactivity upon the introduction of the fluorine atoms in the bridge is notable and the reactivity of the [10]-annulenes is strikingly higher than that of naphthalene.

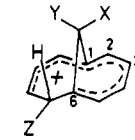
The fluoro derivatives **3** and **4** have been protonated in the HSO_3F–SO_2ClF (1:2, v/v) solvent system at −80 °C. The ^1H NMR data at the temperature of highest spectral resolution are given in Table IV (supplementary material), together with the data for protonated **1**, reported by Winstein.[12] The protonation appears to occur exclusively at one of the α-positions. The fluoro containing cations **7–9** are more stable than **6**. The latter cation slowly rearranges[12,13] irreversibly at temperatures ≥−60 °C to the 1,2-dihydro-1,2-methano-4-naphthalenium ion,[13] whereas, e.g., **9** was found to be stable up to at least −10 °C. The degree of protonation of **3** is significantly smaller at the 2-position (36% ± 3%) than the 7-position (64% ± 3%).

Table III. Sulfur Trioxide Sulfonation Reactivities in [$^2H_8$]Dioxane at 35 ± 1 °C

no.	10^{-5} (±5%), s^{-1}: overall $_{ps}k_1$	^2k	^7k	$\Delta\Delta G^{\ddagger}$ (35 °C),[a] ±0.5, kJ mol^{-1}
1	8500	2100		0
3	240	58		9.2
			62	9.0
4	8.8	2.2		17.5
$C_{10}H_8$	$<3 \times 10^{-4}$ [b]	$<0.6 \times 10^{-4}$ [c]		>44[c]

[a] Relative to the substitution of one α-position of **1**. [b] The conversion of naphthalene in 180 days was below the limit of the naphthalenesulfonic acid detection, i.e., <3%. [c] These data refer to the sulfonation at position 1.





6 X = Y = Z = H
7 X = F ; Y = Z = H
9 X = Y = F ; Z = H
12 X = F ; Y = H ; Z = SO_3^-

8 X = F ; Y = Z = H
13 X = F ; Y = H ; Z = SO_3^-

Discussion

The monosulfonation of the 1,6-methano[10]annulenes **1–5**, **10**, and **11**[14] leads only to α-sulfo deprotonation (cf. Table II and ref 15), whereas that of 2,5-dimethyl-**1** leads to both α-sulfo deprotonation and α-sulfo demethylation.[15] The very predominant α-substitution also occurs in bromination[16,17] and protiodetritiation [for **4** k_α/k_β (70 °C) = 24].[18] Sulfonation of the 2-sulfonic acid **10** leads to substitution at the 7-position as a result of electronic deac-

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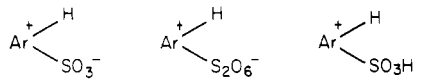
tivation of the 5-position by the sulfo group.[19] Sulfonation of the 5-sulfonic acid of **5** does not take place at the vacant α-positions in view of a prohibitive peri strain[12] that would occur between the 2-methoxy or 5-sulfo group, and the incoming sulfo group at the positions 10 and 7, respectively. Instead, sulfonation takes place at the β-positions 3, 8, and 9.

The reactivity of electrophilic sulfonation decreases upon replacing the two methylene hydrogens of **1** successively by fluorine (Table III). In fact, on going from **1** via **3** to **4** the increase in the free energy of activation is additive and the relative free energy of activation for substitution of the 2- and 7-positions of **3** is about the same. In view of Taylor's report[18] that the σ^+ for the 2-positions of **1** and **4** are −0.80 and −0.41, respectively, the present results imply that the σ^+ values for the 2- and 7-positions of **3** are −0.59 and −0.60, respectively. A photoelectron spectral and theoretical study on **1**, **3**, and **4** revealed that the introduction of fluorines in the methylene bridge leads to a roughly equal stabilization of the (four highest) π-MO's.[20]

The sulfonation reactivity is greater for 1,6-methano[10]annulene **1** than naphthalene,[21] the free energy of activation for the substitution of one of the α-positions being at least 44 kJ mol^{-1} smaller for the former substrate. The lower free energy of activation of **1** may be explained in part in terms of a lower resonance energy of the [10]annulene **1** than naphthalene, as a result of the noncoplanarity of the perimeter of **1**.

The formation of the sulfo products in the SO_3 sulfonation of the annulenes in dioxane is assumed to proceed similarly as established before for chlorobenzene and 1,4-dichlorobenzene.[25] The primary aprotic sulfonation proceeds via the 1-arenium-1-sulfonate (A) and 1-arenium-1-pyrosulfonate (B) as the subsequent σ-complexes, of which the latter rapidly rearranges to the arenepyrosulfonic acid.[25,26] With reactive substrates as the annulenes, the resulting pyrosulfonic acid acts again as sulfonating entity to effect the so-called secondary sulfonation via the 1-arenium-1-sulfonic acid (C) as σ-complex.[26]



A B C

The ratio in which the isomeric sulfo products will be formed thus depends on the relative rates of formation of the σ-complexes A–C for the isomeric routes. An estimate of the relative stability of a given set of isomeric σ-complexes may be obtained by determining the ratio of the protonation σ-complexes formed under stable ion solution conditions, although the steric requirements for adding the sulfonating entity(ies) or the proton may be different for the nonplanar bridged [10]annulenes under study. The electrophile may add to the nonplanar 1,6-methano[10]annulenes in two ways, viz., endo and exo. As to the HOMO of **1**, i.e., the $7a_2$ π-MO, shown in Figure 7 of ref 20, the sizes of the upward and downward lobes at the α-carbons are about the same and their direction relative to the molecular framework is such that a small electrophile like a proton may attack an α-carbon from both the endo and the exo side, yielding the same σ-complex in both cases. The far more bulky sulfonating entity(ies) will only attack from the endo side to yield the much less strained σ-complex. This interpretation is somewhat at variance with Vogel's observation that the reaction of **1** with bromine in chloroform at −60 °C leads to a relatively stable 1,4-cis addition product in which the two bromine atoms at the positions 2 and 5 are both syn to the methylene bridge.[17,27] However, it should be realized (i) that the bromo addition does not necessarily proceed via a cationic σ-complex intermediate and (ii) that the effective size of a sulfonate group is substantially greater than that of a bromine atom (cf. ref 28).

The sulfonation of the monofluoro compound **3** leads to the formation of 47% ± 2% 2-sulfonic acid and 53% ± 2% 7-sulfonic acid, whereas the protonation yields 36% ± 3% of the cation **7**, resulting from protonation at C(2), and 64% ± 3% of **8** as result of protonation at C(7). The smaller amount of **7** as compared with **8** may be explained in terms of strain as result of steric repulsion between the fluorine and the *exo*-methylene hydrogen of the protonated center in **7**.

Experimental Section

The 1,6-methano[10]annulenes **1** and **3**–**5** were obtained as a gift from Prof. E. Vogel.

Sulfonation Procedure and Analysis. The sulfonation was effected[12] by adding 0.25 mmol of the [10]annulene in [$^2H_8$]dioxane (0.40 mL) to a solution of SO_3 (in most cases 0.50 mmol = 2.0 equiv) in [$^2H_8$]dioxane (1.00 mL). The compositions of the reaction mixtures were determined by recording ^1H NMR spectra at appropriate time intervals. In some cases the products have been isolated as their potassium sulfonates, as described previously.[12] The ^1H NMR spectra were recorded with a Bruker WM-250 and a Varian XL-12 CW spectrometer. For [$^2H_8$]dioxane and [$^2H_3$]acetonitrile as solvent, the chemical shifts are relative to internal $SiMe_4$ and for ^2H_2O as solvent relative to external (neat) $SiMe_4$. It is of diagnostic interest that the $^4J_{H,H}$ between the bridge hydrogens and the α-hydrogens of the 1,6-methano[10]annulenes is greater when they are in the anti than in the syn orientation.[29,30] The sulfo product composition was determined by multicomponent ^1H NMR analysis.[34] The assignment of the signals of the mixture of the potassium salts of the 2- and 7-sulfonate of **3** was made by 250-MHz ^1H shift correlated 2D NMR in C^2H_3CN at 298 K (see, e.g., ref 35). The proton–proton shift correlation

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(21) The sulfonation reactivity of **1** also exceeds that of anthracene,[22] as appears from a comparison of the required reaction conditions.[12,23] It should be realized that the sulfonation of the 9-position of anthracene is far more retarded than that of the 2-position of **1**, due to the development of a greater peri strain on bringing the sulfo group between H(1) and H(8) of anthracene than peri to H(10) of **1**, the k_H/k_D of these sulfonations being 7 ± 1[22] and 3.8 ± 0.3,[24] respectively.
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(31) The relatively small peri sulfo shift of H(7) of the 5-sulfonic acid of **5** (0.28 ppm) is ascribed to the large mesomeric electron release from the methoxy to the sulfonic acid group, leading to shielding of H(7).
(32) The ortho sulfo shifts of the 1,6-methano[10]annulene-2-sulfonic acids in [$^2H_8$]dioxane are somewhat higher and the peri sulfo shifts smaller than those of the planar condensed polycyclic arenesulfonic acids in [$^2H_6$]dimethylsulfoxide for which the values are 0.27–0.67 and 0.93–1.25 ppm, respectively.[33]
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spectrum with the assignments is shown in Figure 1 (supplementary material).

Sulfonation Reactivities. The relative substrate reactivities have been determined from the initial slopes of graphs of log |ArH| vs. the reaction time, using $\ln \{|ArH|/|ArH|_0\} = -_{ps}k_1 t$, thus presuming pseudo first order kinetics. For 3 and 4 the plots of log $\{|ArH|/|ArH|_0\}$ vs. time were linear up to ca. 50% substrate conversion. The reactivity of 1 is so high that only the tail of the plot, >89% substrate conversion, could be measured. For the calculation of the $_{ps}k_1$ of 1 it was assumed that the relative curvature is the same for 1 and 3. The reaction mixtures were made up by adding a solution of 0.25 mmol of the [10]annulene in 0.40 mL dioxane-$^2H_8$ at 35 °C to a homogeneous solution of 0.50 mmol SO_3 in 1.00 mL of dioxane-$^2H_8$ and subsequent homogenization at 35 °C.

Preparation of Monocations. The method of preparation of the 1,6-methano[10]annulenium ions and the recording of their ^1H NMR spectra was similar as described for the monocations of the methylphenanthrenes.[36] The assignment of ^1H NMR signals of the cations of 3 and 4 were made by comparison with the fully assigned ^1H NMR spectrum of protonated 1.[13] The doublets at lowest and highest field in the vinylic part of the spectrum were taken to be the hydrogens para and peri to the protonated center, respectively. The triplet at 7.82 ppm in the spectrum of protonated 3 is ascribed to H(9) of 8 [and not to H(4) of 7], as its chemical shift is very similar to that of H(4) of 6. More important the difference between the chemical shifts of the low field parts of the AB absorptions of the protonated centers of the two annulenium ions is much greater (0.33 ppm) than that between the two corresponding high field parts (0.05 ppm, cf. Table IV). The highest shielded hydrogen, viz., that at 4.15 ppm, is therefore ascribed to the hydrogen in closest vicinity to the electronegative fluorine. Thus the 4.15 + 4.9[5] AB system is ascribed to $C(2)H_2$ of 7 and the 4.48 + 4.90 AB to $C(7)H_2$ of 8, and the 4.15 and 4.48 absorptions are ascribed to the *endo*-hydrogens and the 4.9 ppm absorptions to the *exo*-hydrogens.

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Registry No. 1, 2443-46-1; 2-MeO-5-HO_3S-1, 90913-12-5; 3, 71671-89-1; 3-SO_3H (isomer 1), 90913-13-6; 3-SO_3H (isomer 2), 91048-23-6; 4, 19026-91-6; 5, 58853-55-7; 8, 90900-68-8.

Supplementary Material Available: ^1H NMR spectral data of 1, 3-5 (in $[^2H_8]$dioxane) their sulfo products (in $[^2H_6]$acetonitrile) the cations 6-9 in HSO_3F/SO_2ClF, and the 250-MHz ^1H shift correlated 2D NMR spectrum of the mixture of the potassium salts of the 2- and 7-sulfonic acids of 3 (in $[^2H_6]$acetonitrile) (5 pages). Ordering information is given on any current masthead page.

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Mechanism of the Hydrolysis of *o*-Nitro- and *o*-Benzoylbenzeneselenenic Anhydrides[1]

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The hydrolyses (eq 1) of *o*-nitro- (**2a**) and *o*-benzoylbenzeneselenenic (**2b**) anhydrides to the corresponding selenenic acids (**1a** and **1b**) have been studied kinetically over a range of pH in a series of buffers in 60% dioxane. Both hydrolyses require acid catalysis. The hydrolysis of **2a** exhibits general-acid catalysis, with a *nonlinear* Brønsted plot where $\alpha = 0$ for catalyzing acids with a $pK_a \leq pK_a$ of trichloroacetic acid and $\alpha = 0.7$ for acids with $pK_a \geq pK_a$ of dichloroacetic acid. This behavior seems best accounted for by a preassociation mechanism (eq 8) in which addition of water to a selenium in the encounter complex **2a**·HA gives a highly unstable intermediate ($I^{\pm}$·HA) that then collapses to products (step k_p) via a proton transfer to the departing *o*-$O_2NC_6H_4SeO$- group that is coincident with the cleavage of the Se–OSe bond. With the stronger acid catalysts formation of $I^{\pm}$·HA from **2a**·HA plus water is rate determining and $\alpha = 0$. With weaker acids as catalysts the transfer of the proton within $I^{\pm}$·HA becomes rate determining, and $\alpha = 0.7$. The hydrolysis of the *o*-benzoyl compound (**2b**) is much faster than that of **2a** and exhibits specific-H^+ catalysis under most reaction conditions. The pH–rate profile for the H_3O^+-catalyzed hydrolysis of **2b** shows an inflection between pH 2.5 and 4. This pH–rate profile, and the other aspects of the behavior of the hydrolysis, can be best explained by a mechanism (eq 10) in which the reactive intermediate (**3**) is the carbonyl hydrate of **2b**. In buffers at higher pH's buffer-catalyzed establishment of the **2b** + $H_2O \rightleftarrows$ **3** equilibrium is rapid, and H_3O^+-catalyzed conversion of **3** to products is rate determining; but in dilute HCl or $HClO_4$ H_3O^+-catalyzed formation of **3** from **2b** becomes rate determining. The stabilization of **2a** (and **2b**) by direct interaction of the *o*-NO_2 (or PhC(O)) group with selenium is thought to prevent facile, one-step displacement of ArSeO by a nucleophile and to be the reason that the two hydrolyses are forced to adopt the more complex mechanisms outlined above.

Selenenic acids are generated as reactive intermediates in a considerable number of reactions in organoselenium chemistry. For example, the widely used, olefin-forming oxidative elimination of an arylseleno group gives an alkene plus an areneselenenic acid (ArSeOH), and the subsequent fate of the selenenic acid (determined by the specific reaction conditions employed) can have a significant effect on the yield of alkene that is obtained.[2] Areneselenenic acids are also thought to be formed as reactive intermediates during the reduction of areneseleninic acids (Ar-SeO_2H) by a wide variety of reagents.[3] In physiological

(1) This research supported by the National Science Foundation, Grant CHE-79-18877.

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