995, 950, 810, 760, 700 cm^{-1}; NMR (CCl$_4$) δ 7.03 (d, J = 8 Hz, 1 H), 6.80–6.56 (m, 2 H), 3.77 (s, 3 H), 3.66 (s, 2 H), 2.86–2.68 (m, 2 H), 2.36–2.16 (m, 2 H), 2.0–1.6 (m, 4 H); exact mass m/e 204.115 (calcd for C$_{13}$H$_{16}$O$_2$, 204.116).

3-Methoxy-7,8,9,10-tetrahydro-6-vinyl-6(5H)-benzocyclooctenol (3b). Eight milliliters of 0.96 M vinylmagnesium bromide in THF was added dropwise with stirring to 1.00 g of 2b in 5 mL of THF while raising the temperature to 65 °C. After 1.25 h, the reaction was cooled and treated with 0.25 mL of methanol. This procedure[6,16] was repeated twice more and gave, after the usual workup,[2] 0.673 g (59% yield) of 3b: IR (neat) 3300 (br), 2920, 2850, 1600, 1580, 1500, 1460, 1320, 1295, 1260, 1200, 1160, 1040, 1000, 920, 810, 760, 780 cm^{-1}; NMR (CDCl$_3$) δ 7.14–7.04 (m, 1 H), 6.96–6.70 (m, 2 H), 6.14 (dd, J = 10, 17 Hz, 1 H), 5.34 (dd, J = 1, 17 Hz, 1 H), 5.14 (dd, J = 1 Hz, 1 H), 3.8 (s, 3 H), 3.0–2.6 (m, 4 H), 1.9–1.35 (m, 7 H); exact mass m/e 232.146 (calcd for C$_{15}$H$_{20}$O$_2$, 232.146).

3-Methoxy-5,6,9,10,11,12-hexahydro-8(7H)-benzocyclodecenone (4b) was prepared in 38% yield from 3b by the earlier procedures[2] using KH and HMPT at room temperature for 40 min: IR (neat) 2920, 2850, 1698, 1605, 1570, 1500, 1480, 1450, 1365, 1295, 1245, 1230, 1212, 1180, 1140, 1100, 1040, 1000, 995, 970, 930, 910, 880, 860, 850, 800, 750, 700 cm^{-1}; NMR (CCl$_4$) δ 7.02 (d, J = 8 Hz, 1 H), 6.6 (m, 2 H), 3.72 (s, 3 H), 2.7–1.5 (br m, 14 H); exact mass m/e 232.146 (calcd for C$_{15}$H$_{20}$O$_2$, 232.146).

Rate Measurements of 3a,b. A constant-temperature bath, maintained at 30.0 °C by a Bailey proportional controller, was equipped with a mechanical stirrer which had a strong magnetic bar in the bath. Three test tubes with magnetic stirrers were equilibrated under nitrogen in the bath with 0.1 g of 3a, 0.1 g of 3b, and 0.7 g of hexane-washed potassium hydride (KH) in 8 mL of HMPA, respectively. After 10 and 2 min, respectively, 5–9 aliquots (150 μL each) were taken sequentially to 2 half-lives of reaction. Each aliquot was quenched in ether–water, washed five times with water, dried over MgSO$_4$, and analyzed by GLC. An internal GLC standard indicated a 50–60% material balance. Duplicate, independent rate measurements by use of the logarithm of the peak-area ratio 3a,b/(3a,b + 4a,b) vs. time and with analysis by least-squares methods gave rate constants for 3a of 0.0227 and 0.0277 and for 3b of 0.798 and 0.728 with correlation coefficients of 0.8795, 0.9954, 0.9949, and 0.9968, respectively.

Attempted Rearrangement of 3c. Compound 3b was demethylated with sodium thiobutoxide by the method described earlier.[7] The resultant diol 3c (very broad IR band at 3300 cm^{-1} and OH peak at δ 5.6) was treated with KH/HMPA in the usual way for 2.3 h. The NMR spectrum of the recovered material strongly resembled starting 3c, and the IR spectrum showed no absorption in the carbonyl region.

2-Methyl-1-phenylbut-3-en-2-ol (8) was prepared in 86% yield from phenyl-2-propanone by reaction with vinylmagnesium bromide:[2] IR (neat) 3550, 3440, 3090, 3060, 3030, 2980, 2930, 1500, 1460, 1420, 1380, 1290, 1240, 1160, 1100, 1060, 1040, 1020, 1000, 920, 880, 770, 720, 700 cm^{-1}; NMR (CCl$_4$) δ 7.14 (s, 5 H), 5.90 (d of d, J = 18, 11 Hz, 1 H), 5.08 (dd, J = 2, 18 Hz, 1 H), 4.94 (dd, J = 2, 11 Hz, 1 H), 2.72 (s, 2 H), 2.18 (OH), 1.18 (s, 3 H); exact mass m/e 162.104 (calcd for C$_{11}$H$_{14}$O, 162.104).

Rearrangement of 8. Treatment of 8 with KH and HMPT as before[2] for 4 h at room temperature gave 2% recovered 8, 9% of toluene, and 21% of 5-phenyl-2-pentanone: IR (neat) 3090, 3060, 3030, 3000, 2940, 2860, 1710, 1670, 1600, 1500, 1460, 1370, 1360, 1250, 1220, 1180, 1160, 1080, 1030, 750, 700 cm^{-1}; NMR (CCl$_4$) δ 6.95–7.35 (m, 5 H), 2.55 (t, J = 7 Hz, 2 H), 2.31 (t, J = 7 Hz, 2 H), 1.98 (s, 3 H), 1.82 (pentet, J = 7 Hz, 2 H); the mass spectrum matched the published spectrum.[17]

Randall for capable NMR assistance and Richard Weilesec for mass spectra on the CDC 110B instrument at the University of Oregon.
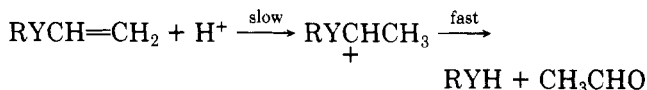

Mechanism of Hydrolysis of Aryl Vinyl Selenides. Selenium-Stabilized Carbonium Ions

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Recently there have been reported[1-8] several comparisons of the relative effect that oxygen and sulfur heteroatoms have on stabilizing an adjacent carbonium ion center. One such investigation[4] focused on a comparison of rate constants for the hydrolysis of vinyl ethers and vinyl sulfides, which are reactions with a rate-determining proton transfer to the olefinic bond, generating the α-heteroatom stabilized cation.

$$\text{RYCH=CH}_2 + \text{H}^+ \xrightarrow{\text{slow}} \underset{+}{\text{RYCHCH}_3} \xrightarrow{\text{fast}}$$
$$\text{RYH} + \text{CH}_3\text{CHO}$$

Organoselenium compounds have recently received considerable attention as reagents for organic syntheses,[9] and it is well established that, like sulfur, selenium has a pronounced effect of stabilizing an adjacent carbanion center. We felt it of interest to determine the extent to which selenium is also capable of stabilizing an adjacent carbonium ion center. Accordingly, we have prepared a series of aryl vinyl selenides and report here a study of their acid-catalyzed hydrolysis.

Experimental Section

Aryl vinyl ethers and aryl vinyl sulfides were the same as those used previously.[4] Benzene selenol was the gift of Dr. D. G. Garratt and was distilled immediately before use. Aryl vinyl selenides (XC$_6$H$_4$SeCH=CH$_2$) were prepared as follows. Ethylene was bubbled through a solution in methylene chloride of the aryl selenenyl chloride (ArSeCl) to produce a β-(arylseleno)ethyl chloride[10] (ArSeCH$_2$CH$_2$Cl). The solvent was removed, the adduct taken up in dimethyl sulfoxide, and potassium *tert*-butoxide added. After being stirred for 3 h, the solution was poured into an excess of water and extracted with ether. The ether was dried

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(1) Bernardi, F.; Csizmadia, I. G.; Schlegel, H. B.; Wolfe, S. *Can. J. Chem.* **1975**, *53*, 1144.
(2) McClelland, R. A. *Can. J. Chem.* **1975**, *53*, 2772.
(3) Bernardi, F.; Csizmadia, I. G.; Epiotis, N. D. *Tetrahedron* **1975**, *31*, 3085.
(4) McClelland, R. A. *Can. J. Chem.* **1977**, *55*, 548.
(5) Washtein, W.; Abeles, R. H. *Biochemistry* **1977**, *16*, 2485.
(6) Walter, W.; Meese, C. D. *Chem. Ber.* **1977**, 2463.
(7) Jensen, J. L.; Jencks, W. P. *J. Am. Chem. Soc.* **1979**, *101*, 1476.
(8) Modena, G.; Scorrano, G.; Venturello, P. *J. Chem. Soc., Perkin Trans. 2* **1979**, 1.
(9) Reich, H. J. *Acc. Chem. Res.* **1979**, *12*, 30.
(10) Garratt, D. G.; Schmid, G. *Can. J. Chem.* **1974**, *52*, 3599.

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(16) In later work, adding the ketone to excess vinyl Grignard reagent also gave nearly complete conversion.
(17) Dalton, J. C.; Chan, H. G. *Tetrahedron Lett.* **1973**, 3145.

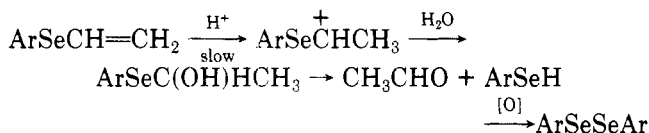**Table I. First-Order Rate Constants for the Hydrolysis of Phenyl Vinyl Selenide in 50% Dioxane-Water (25 °C)**

acid	k, s^{-1}	$k/[\text{H}^+]$
0.04 M HCl	7.4×10^{-5}	1.85×10^{-3}
0.07 M HCl	1.35×10^{-4}	1.93×10^{-3}
0.10 M HCl	1.84×10^{-4}	1.84×10^{-3}
0.20 M HCl	4.08×10^{-4}	2.04×10^{-3}
0.20 M DCl	1.40×10^{-4}	7.00×10^{-4}

(MgSO$_4$), and the vinyl selenides were obtained by distillation: X = 4-CH$_3$O, 90 °C (3 mmHg); X = 4-CH$_3$, 100 °C (3.5 mmHg), X = H, 70 °C (3.5 mmHg), X = 4-F, 88 °C (4 mmHg); X = 4-Br, 130 °C (3.5 mmHg); X = 4-Cl, 122 °C (4 mmHg); X = 4-CF$_3$, 90 °C (4 mmHg); X = 4-NO$_2$, 125 °C (0.5 mmHg). All compounds had satisfactory ^{1}H and ^{13}C NMR spectra; the ^{13}C NMR data have been discussed elsewhere.[11] Satisfactory analyses (C,H) were obtained in all cases.

Rate constants were obtained in acidic solutions in 50% dioxane-water, using standard UV spectroscopic techniques. First-order kinetic plots were excellently linear over several half-lives; first-order rate constants obtained from triplicate runs had a standard deviation of 1–3%. Products were identified in the case of phenyl vinyl selenide to be diphenyl diselenide and acetaldehyde by UV and NMR spectral analysis and by the quantitative isolation of the diselenide. Under our experimental conditions, benzene selenol was established to be rapidly converted to diphenyl diselenide. We were unable to prevent this from occurring, even with rigorous purification of the dioxane solvent or nitrogen purging beforehand.

Results and Discussion

The products of the aryl vinyl selenide hydrolysis are acetaldehyde and the diaryl diselenide; the latter product is presumably the result of a rapid oxidative dimerization of an initially formed aryl selenol. A control experiment demonstrated that, under the experimental conditions employed for the hydrolysis, benzene selenol is rapidly converted to the diselenide. Products therefore are consistent with the standard hydration mechanism.

$$\text{ArSeCH}=\text{CH}_2 \xrightarrow[\text{slow}]{\text{H}^+} \text{ArSeCHCH}_3 \xrightarrow{\text{H}_2\text{O}}$$

$$\text{ArSeC(OH)HCH}_3 \rightarrow \text{CH}_3\text{CHO} + \text{ArSeH}$$

$$\xrightarrow{[\text{O}]} \text{ArSeSeAr}$$

Further evidence is based on kinetic results and follows the same line of reasoning used to establish the mechanism for vinyl ether hydrolysis[12] and vinyl sulfide hydrolysis.[4] The hydrolysis of phenyl vinyl selenide is first order in hydronium ion concentration and shows a normal solvent isotope effect, $k_{\text{H}_3\text{O}^+}/k_{\text{D}_3\text{O}^+}$ = 2.9 (Table I). The latter value is similar to those found in the hydrolysis of vinyl ethers[12] and vinyl sulfides[4] and is indicative of the rate-determining proton transfer. The reaction is accelerated by electron-donating substituents in the aromatic ring (Table II), with a Hammett ρ value of −1.55. We have repeated our study on the series of aryl vinyl ethers and aryl vinyl sulfides under the same conditions (Table II) and find ρ values of −2.00 (ethers) and −1.84 (sulfides).

There therefore seems little doubt that the hydrolysis reactions of vinyl ethers, sulfides, and selenides follow a common mechanism, with rate-limiting formation of the α-heteroatom stabilized carbonium ion. As before,[4] we can use the relative rates of hydrolysis as a measure of the relative stabilizing effect of the heteroatom.[13] As seen in

Table II. First-Order Rate Constants for the Hydrolysis of ArXCH=CH$_2$ in 1.5 M HCl in 50% Dioxane-Water (25 °C)

Ar	rate constant, s^{-1}		
	X = O	X = S	X = Se
4-MeOC$_6$H$_4$	0.250	0.0428	0.00501
4-MeC$_6$H$_4$	0.172	0.0283	0.00365
C$_6$H$_5$	0.1061	0.0169	0.00232
4-FC$_6$H$_4$	0.0692	0.01362	0.00180
4-BrC$_6$H$_4$	0.0347	0.00633	0.000997
4-ClC$_6$H$_4$	0.0342	0.00674	0.00108
3-ClC$_6$H$_4$	0.0166		
4-CF$_3$C$_6$H$_4$		0.00163	0.000347
4-NO$_2$C$_6$H$_4$	0.00280	0.000672	0.000140

Table II, the order for a given aryl group is ArO > ArS > ArSe, with the exact numerical differences being somewhat dependent on the nature of the aromatic substituent. For Ar = Ph, the relative rates amount to PhO = 42:PhS = 7:PhSe = 1. We can further note that in aqueous solution phenyl vinyl ether is 130 times less reactive than methyl vinyl ether,[4] and if this same difference carries over to 50% dioxane, phenyl vinyl selenide undergoes hydrolysis 5 × 10^3 times more slowly than does methyl vinyl ether.

Although these differences in reactivity may seem significant, they are not really all that large when the enormous range of reactivities (10^{22}) now observed[14] for olefin hydration is considered. Tidwell and co-workers have shown[14,15] that hydration reactivities are reasonably well correlated by the equation log k_2 = −10.5$\sum \sigma_p^+$ − 8.92, where k_2 is the second-order rate constant for hydration in water, and σ_p^+ refers to the substituents on the carbocation center. Based on that equation, we obtain[16] σ_p^+(PhO) = −0.62, σ_p^+(PhS) = −0.54, and σ_p^+(PhSe) = −0.47.

We can conclude by pointing out that although the reactivities are quite similar, the mechanics of stabilization may be quite different for the three heteroatoms. Electron donation via the π system is likely to be best with oxygen, since its valence 2p orbital can overlap most effectively with the vacant carbon 2p orbital. On the other hand, electron donation via the σ framework is expected to be best for the largest and most polarizable heteroatom, selenium. Thus the conjugative stabilizing order is O > S > Se, while the inductive order is Se > S > O, and the two effects will tend to cancel.[17]

(11) Reynolds, W. F.; McClelland, R. A. Can. J. Chem. 1977, 55, 536.
(12) Kresge, A. J.; Chiang, Y. J. Chem. Soc. B 1967, 58. Kresge, A. J.; Sagatys, D. S.; Chen, H. L. J. Am. Chem. Soc. 1968, 90, 4174.
(13) (a) This requires that the energy of the transition state leading to the cation parallels the energy of the cation. Evidence that this is the case in S$_N$1 solvolysis reactions has recently been presented.[13b] (b) Arnett, E. M.; Petro, C.; Schleyer, P. v. R. J. Am. Chem. Soc. 1979, 101, 522.

(14) Koshy, K. M.; Roy, D.; Tidwell, T. T. J. Am. Chem. Soc. 1979, 101, 357.
(15) Nowlan, V. J.; Tidwell, T. T. Acc. Chem. Res. 1977, 10, 252.
(16) This is based on an estimate for k_2 in water for PhSeCH=CH$_2$, using the relative reactivity difference between this compound and PhOCH=CH$_2$.
(17) These opposing trends have in fact been suggested in a theoretical calculation of oxygen and sulfur stabilized cations.[1]

chloride, 71912-38-4; β-(4-bromophenylseleno)ethyl chloride, 57878-10-1; β-(4-chlorophenylseleno)ethyl chloride, 57878-09-8; β-(4-(trifluoromethyl)phenylseleno)ethyl chloride, 71912-39-5; β-(4-nitrophenylseleno)ethyl chloride, 57878-11-2; 4-methoxyphenyl vinyl ether, 4024-19-5; 4-methylphenyl vinyl ether, 1005-62-5; phenyl vinyl ether, 766-94-9; 4-fluorophenyl vinyl ether, 351-93-9; 4-bromophenyl vinyl ether, 1005-61-4; 4-chlorophenyl vinyl ether, 1074-56-2; 3-chlorophenyl vinyl ether, 1005-41-0; 4-nitrophenyl vinyl ether, 940-14-7; 4-methoxyphenyl vinyl sulfide, 16411-17-9; 4-methylphenyl vinyl sulfide, 16336-54-2; phenyl vinyl sulfide, 1822-73-7; 4-fluorophenyl vinyl sulfide, 64287-53-2; 4-bromophenyl vinyl sulfide, 16411-18-0; 4-chlorophenyl vinyl sulfide, 16411-16-8; 4-(trifluoromethyl)phenyl vinyl sulfide, 64287-55-4; 4-nitrophenyl vinyl sulfide, 42150-17-4.

A Nuclear Magnetic Resonance Study of Solvent Effects on the Conformational Preference of Thioxanthene S-Oxides

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Most stereochemical studies of thioxanthene S-oxides and related 6,6,6-tricyclic systems[1] have been conducted in weakly interacting or noninteracting solvents.[2] In general, it appears that the conformation favored in the solid state is also preferred in such solvents. For example, we have shown[3] that phenoxathiin S-oxide (1) possesses
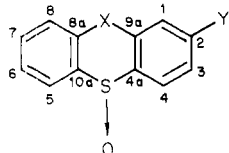
1, X = O; Y = H
2, X = CH(CH₃); Y = H
3, X = NH; Y = H
4, X = CH₂; Y = H
5, X = CH₂; Y = Cl

a pseudoaxial (a′) sulfinyl oxygen both in the solid state and in solution.[4] Also, *cis-* and *trans-*9-methylthioxanthene S-oxides (*cis-* and *trans-*2) have a similar conformations (i.e., e′ S–O) in the solid state and in solution.[5] Phenothiazine S-oxide (3) appears to have an a′ sulfinyl oxygen both in the solid and in solution.[6] We now report what appears to be the first observation of the solvent dependence of the preferred conformation of a thioxanthene S-oxide (i.e., a conformationally restricted diaryl sulfoxide) ascribed to a specific interaction between the

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(1) These structures may be thought of as conformationally restricted diaryl sulfoxides.

(2) Ternay, A. L., Jr.; Evans, S. A. *J. Org. Chem.* **1974**, *39*, 2941. Evans, S. A.; Ternay, A. L., Jr. *Ibid.* **1975**, *40*, 2993 and references cited therein.

(3) Chen, J. S.; Watson, W. H.; Austin, D.; Ternay, A. L., Jr. *J. Org. Chem.* **1979**, *44*, 1989.

(4) An earlier report, assigning phenoxathiin S-oxide the e′ conformation is apparently in error: Lumbroso, H.; Montando, G. *Bull. Soc. Chim. Fr.* **1964**, 2119.

(5) Ternay, A. L., Jr.; Ens, L.; Herrmann, J.; Evans, S. A. *J. Org. Chem.* **1969**, *34*, 940.

(6) Chu, S. S. C.; Ternay, A. L., Jr., to be submitted for publication. See, also: Vázquez, S.; Castrillon, J. *Spectrochim. Acta, Part A* **1974**, *30*, 2021.

Table I. ¹H NMR Chemical Shifts (ppm) of Thioxanthenes[a,f]

compd	C9-Ha′	C9-He′	R(a′/e′)[b,c]
4	4.70	4.21	1.5 (1.3)
6	4.73	4.27	1.8 (1.9)
7	4.53	4.82	1.4 (1.5)
8	1.55[d]	2.09[e]	

[a] CF₃CO₂H solvent. [b] Ratio of average bandwidth at half-height of a′ and e′ signals. [c] Value in parentheses for CDCl₃ as solvent. [d] a′ CH₃ (CDCl₃), 1.36 ppm. [e] e′ CH₃ (CDCl₃), 1.98 ppm. [f] From Me₄Si.

**Table II. ¹³C Chemical Shifts (ppm) of Phenoxathiin S-Oxide (1)**[a,b]

solvent	C1	C2	C3	C4	C4a	C9a
CDCl₃	124.6	133.5	118.5	130.6	123.5	149.1
CF₃CO₂H	127.2	137.7	120.9	132.6	118.4	151.9

[a] Carbon numbering used in this table is shown in the structure in the text. [b] From Me₄Si.

sulfinyl oxygen and the solvent.

In thioxanthene S-oxide (4), 2-chlorothioxanthene S-oxide (5), and related S-oxides lacking a substituent at both C4 and C5, the preferred conformation in weakly interacting solvents (e.g., CDCl₃, C₆D₆) is one in which the sulfinyl oxygen is pseudoequatorial (e′). In light of the results of our studies of 1 and 3 and of the greater hindrance in the e′ position, such results are somewhat surprising. Because of this difference between compounds such as 4 and 5 *and* 1 and 3, we have attempted to determine if 4, and related systems, can be forced to alter conformational preference by increasing the effective size of the sulfinyl oxygen.[7]

In the thioxanthene ring system C9-Ha′ is broadened (bandwidth at half-height) in comparison to C9-He′. This broadening, due to long-range coupling to aryl protons, permits ready distinction between e′ and a′ protons. In 4 and 5 the a′ proton appears upfield of the e′ proton. This

4a′   4e′
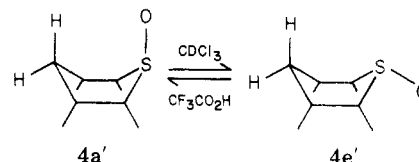
is the display expected when the sulfinyl oxygen is e′.[2] In compounds containing a substituent at C4 (which forces the sulfinyl oxygen into the a′ position), the (still-broadened) a′ C9-H is deshielded by the now pseudoaxial sulfinyl group. We now report a similar alteration in the spectra of 4 and 5 simply by changing the solvent from CDCl₃ or C₆D₆ to CF₃CO₂H, suggesting that the conformation is changed from e′ to a′.[8]

The view that association with the solvent (hydrogen bonding) alters the conformation of the sulfinyl oxygen is supported by the spectrum of 4-methylthioxanthene S-oxide (6), where S–O is a′ (in all solvents) by virtue of repulsions with C4-CH₃. In CF₃CO₂H the chemical shifts of C9-H in 6 are virtually identical with those of 4 in CF₃CO₂H (Table I). The ratio of the bandwidth at half-height of the C9-H's of 6 is nearly the same in CDCl₃

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(7) Complexation of sulfoxides with halogens can lead to altered conformation preferences: Ternay, A. L., Jr.; Herrmann, J.; Harris, M.; Hayes, B. R. *J. Org. Chem.* **1977**, *42*, 2010. However, the structural details of these complexes are unreported.

(8) We have observed that thioxanthenium bis(carbomethoxy)-methylide, like 4, exists in the e′ array in CDCl₃. Its C9-H signals resemble those of 4: Ternay, A. L., Jr.; Craig, D.; O'Neal, H. R., submitted for publication.