Although it is quite clear that in 96% H_2SO_4 isomerization occurs *via* a π,π^* excited state of **2a**, the nature of the excited states of neutral 4-pyrones has not been established. It seems likely, however, that the similar photoreactivity of **1a** and **2a** also reflects a similarity of their respective excited states. In order to test such a suggestion we have irradiated neutral 4-pyrones **1a** and **1b** in 2,2,2-trifluoroethanol, a highly polar solvent that would be expected to stabilize π,π^* excited states relative to n,π^* excited states.[15]

The relative quantum efficiencies of photoisomerization of **1a** and **1b** in acetonitrile and trifluoroethanol tend to support the suggestion that the isomerization of neutral 4-pyrones also occurs *via* their π,π^* excited states. Thus irradiation of equimolar solutions of **1a** in acetonitrile and in trifluoroethanol in a merry-go-round apparatus resulted in a 30% greater conversion of **1a** in the latter, more polar solvent. This dependence on solvent polarity was particularly notable in the case of **1b**. Although photostable in acetonitrile,[4] we observe that in trifluoroethanol **1b** is converted to **3b**. These results are inconsistent with the suggestion that the efficiency of the photoisomerization is sterically controlled by the large phenyl groups at positions 3 and 5 of the 4-pyrone ring.[4] Indeed, our observation that tetramethyl-4-pyrone (**1c**) undergoes efficient photoisomerization to **3c** in either acetonitrile or trifluoroethanol clearly shows that phenyl groups in these positions are not a prerequisite to photoisomerization. Rather, these results suggest that the nature of the excited states and hence the reactivity of 4-pyrones is sensitive to the extent of substitution in the 4-pyrone ring.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

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[16] ACS-PRF Undergraduate Research Participant, 1972–1973.

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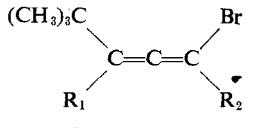
Isotope Effects in the Solvolysis of Haloallenes[1]

Sir:

We wish to report the first measurement of an α-secondary isotope effect for an sp^2 to sp hybridization change in a solvolysis reaction. We have been examining the behavior of tri- and disubstituted haloallenes under solvolytic conditions.[2] As a mechanistic probe we have measured the α- and β-secondary isotope effects associated with the solvolysis of **1a–e** in aqueous ethanol and trifluoroethanol. These data are collected in Table I.



1a, $R_1 = CH_3$; $R_2 = (CH_3)_3C$
b, $R_1 = CD_3$; $R_2 = (CH_3)_3C$
c, $R_1 = CH_3$; $R_2 = H$
d, $R_1 = CD_3$; $R_2 = H$
e, $R_1 = CH_3$; $R_2 = D$

Table I. Conductometric Rate Constants for Solvolysis of **1**

Compd	T, °C	Solvent[a]	10^4k, sec^{-1} [b]
1a	24.62 ± 0.01	60E	3.64 ± 0.06
		70E	1.14 ± 0.02
	34.68 ± 0.01	60E	12.1 ± 0.1
		70E	4.28 ± 0.03
		80E	1.47 ± 0.02
	45.30 ± 0.02	80E	5.15 ± 0.04
		90E	1.49 ± 0.03
1b	24.62 ± 0.01	60E	3.10 ± 0.04
		70E	0.98 ± 0.004
	45.30 ± 0.02	80E	4.31 ± 0.04
		90E	1.22 ± 0.07
1c	50.08 ± 0.01	70T	0.674 ± 0.003
	60.22 ± 0.01		2.44 ± 0.02
	70.13 ± 0.01		5.21 ± 0.01
1d	60.24 ± 0.01	70T	2.05 ± 0.002
1e	60.22 ± 0.01	70T	2.03 ± 0.01

[a] 60E represents 60:40 (v/v) ethanol–water, etc.; 70T represents 70:30 (w/w) trifluoroethanol–water. [b] Average of triplicate determinations.

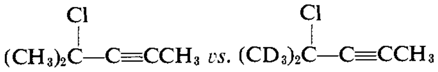
Table II. Isotope Effects for Solvolysis of **1**

	T_1, °C	Solvent	k_H/k_D (obsd)	$\Delta\Delta F^{\ddagger}$/D[a]	k_H/k_D (calcd)[b]
1a/1b	24.62	60E	1.17	37	1.21 ± 0.03
		70E	1.16	35	1.19 ± 0.02
	45.30	80E	1.19	44	1.23 ± 0.02
		90E	1.22	50	1.27 ± 0.04
1c/1d	60.2	70T	1.19	44	1.23 ± 0.01
1c/1e	60.2	70T	1.20	129	1.22 ± 0.01

[a] Corrected to 100% deuteration at the temperature of the measurement. (The authors are indebted to Professor Donald Hunt, University of Virginia, for the mass spectral analysis of **1b**, **d**, and **e**.) [b] Calculated from $\Delta\Delta F^{\ddagger}$.

Data derived from Table I support the proposal that these compounds all react *via* a carbonium ion mechanism.[3] The enhanced reactivity of these haloallenes compared to their vinyl analogs allows the convenient measurement of these rates even though the developing cation is not stabilized by a substituent at the reaction center in **1c**, **d**, and **e**.[4] The solvent dependence of **1a** yields $m = 0.72 \pm 0.05$ at 45°. The temperature dependence data yield the following activation parameters: for **1a** in 70E $\Delta H^{\ddagger} = 22.1$ kcal/mol and $\Delta S^{\ddagger}(25°) = -2.3$ eu, and for **1c** in 70T $\Delta H^{\ddagger} = 21.9$ kcal/mol and $\Delta S^{\ddagger}(25°) = -9.9$ eu. Table II presents the isotope effects observed.

The β-secondary isotope effect observed upon CD_3 substitution at the 3 position of a trisubstituted haloallene (**1a/1b**) is found to be $k_H/k_D = 1.23$ (44 cal/D) in 80% ethanol at 45°. This is to be compared with that reported by Shiner and Kriz for solvolysis of **2** where



$$(CH_3)_2\overset{\displaystyle Cl}{\overset{|}{C}}—C{\equiv}CCH_3 \textit{ vs. } (CD_3)_2\overset{\displaystyle Cl}{\overset{|}{C}}—C{\equiv}CCH_3$$

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[1] Submitted in partial fulfillment for the degree of Master of Arts in Chemistry, College of William and Mary, 1973.
[2] (a) M. D. Schiavelli, S. C. Hixon, H. W. Moran, and C. J. Boswell, *J. Amer. Chem. Soc.*, 93, 6989 (1971); (b) M. D. Schiavelli, R. P. Gilbert, W. A. Boynton, and C. J. Boswell, *ibid.*, 94, 5061 (1972); (c) M. D. Schiavelli and P. L. Timpanaro, *J. Org. Chem.*, 38, 3054 (1973).
[3] It is understood throughout that ion pairs are the most likely candidates for intermediates in these solvolyses. Preliminary results appear to confirm this.
[4] It should be noted that these haloallenes exhibit relative reactivity about one order of magnitude lower than *tert*-butyl chloride and α-phenylethyl chloride and are about as reactive as benzyl halides.

$k_H/k_D = 1.65$ (50 cal/D).[5] In the case of the terminal bromoallene, **1d**, $k_H/k_D = 1.23$ (44 cal/D) for CD_3 substitution at C-3 in 70T at 60°. These data strongly support the proposal that terminal haloallenes as well as trisubstituted haloallenes react *via* charge-delocalized cationic intermediates under initially neutral conditions.

The α-secondary isotope effect observed upon deuterium substitution at the reaction center $k_H/k_D = 1.22$ represents one of the largest α-secondary isotope effects yet reported. For saturated chlorides, such as 1-phenylethyl chloride, Shiner has suggested that values of $k_H/k_D = 1.15$ (83 cal/D) are to be considered a maximum for limiting solvolysis.[6] Shiner has also noted that these "limiting" maxima vary with the leaving group. Thus, the α effect reported here is to be compared with that for bromide as the leaving group, $k_H/k_D = 1.125$ (70 cal/D).[7] Larger α effects are observed in the solvolysis of secondary propargyl brosylates[6] and furylmethylcarbinyl *p*-nitrobenzoate.[8] Shiner has suggested that $k_H/k_D \simeq 1.23$ for oxygen leaving groups in saturated systems be considered comparable to the lower maximum effects observed with the halides.[7]

We are unable to assess the magnitude of the limiting α effect to be expected for an $sp^2 \rightarrow sp$ hybridization change from the data reported here. However, it is possible to estimate this maximum from a consideration of the exchange equilibrium constants for the reactions shown below.[9] These calculations imply that the iso-

$$CH_3CH_3 + CH_2{=}CHD \rightleftharpoons CH_3CH_2D + CH_2{=}CH_2 \qquad K = 1.075$$

$$CH_2{=}CH_2 + DC{\equiv}CH \rightleftharpoons CH_2{=}CHD + HC{\equiv}CH \qquad K = 1.257$$

tope effect for $sp^2 \rightarrow sp$ hybridization is $1.257/1.075 = 1.17$ times that for an $sp^3 \rightarrow sp^2$ change. Assuming a maximum $k_H/k_D = 1.125$ for Br^- leaving from a saturated halide, this predicts that the maximum α-isotope effect to be expected for solvolysis of a vinyl or allenyl bromide is 1.32.[10] Thus it appears that larger α-isotope effects may be observed for systems on which digonal cations are implicated.

We are continuing work in this area by varying solvent, temperature, and structure in order to assess the degree of limiting character in these solvolyses as well as to test the prediction that digonal cations assume a linear geometry.[11]

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[5] V. J. Shiner, Jr., and G. S. Kriz, Jr., *J. Amer. Chem. Soc.*, **86**, 2643 (1964).

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[8] D. S. Noyce and G. V. Kaiser, *J. Org. Chem.*, **34**, 1008 (1969).

[9] S. R. Hartshorn and V. J. Shiner, Jr., *J. Amer. Chem. Soc.*, **94**, 9002 (1972).

[10] In fact, a more appropriate exchange equilibrium constant required for prediction of this maximum is that for the reaction $CH_2{=}C{=}CHBr + DC{\equiv}CH \rightleftharpoons CH_2{=}C{=}CDBr + HC{\equiv}CH$. The calculations on this system are being attempted.

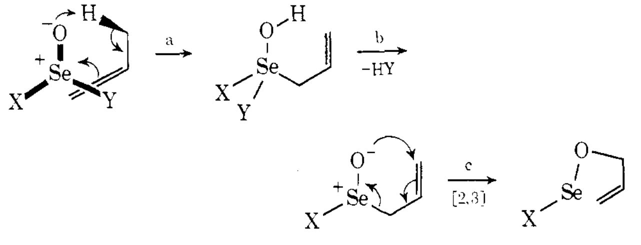
[11] J. E. Williams, R. Sustmann, L. C. Allen, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **91**, 1037 (1969).

Selenium Dioxide Oxidations of Olefins. Trapping of the Allylic Seleninic Acid Intermediate as a Seleninolactone

Sir:

A recently proposed mechanism (Scheme I) for the oxidation of olefins by selenium dioxide suggested an initial ene addition of an >Se⁺–O⁻ moiety (step a) followed by dehydration, or its equivalent (step b), and a [2,3] sigmatropic shift (step c) of the resulting allylseleninic acid.[1]

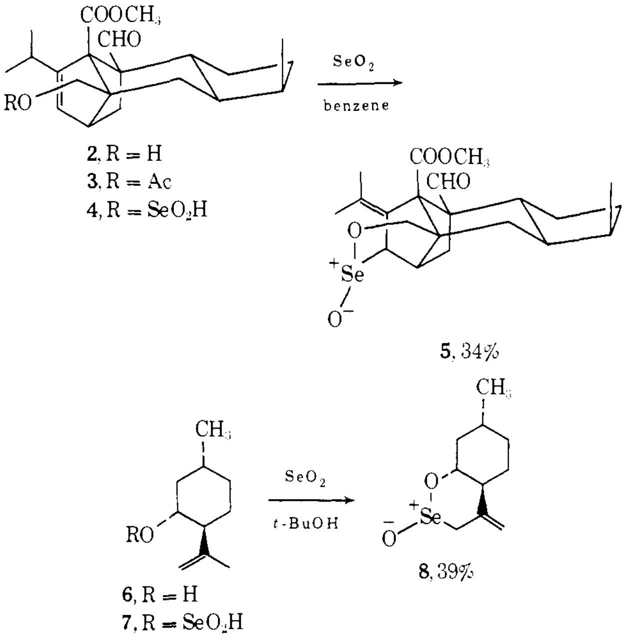
Scheme I



X, Y = OH, OAc, or OR

Having previously[1] provided support for the [2,3] shift, we now report evidence in favor of the initial ene reaction by demonstrating that with appropriate substrates, such as **2** and **6**, the intermediates can be trapped as seleninolactones (Scheme II).

Scheme II



Treatment of sordaricin methyl ester **2**[2,3] with sele-

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[2] D. Hauser and H. P. Sigg, *Helv. Chim. Acta*, **54**, 1178 (1971).

[3] A. Vasella, Ph.D. Thesis, ETH Zürich, No. 4814, 1972. Independent evidence for the structure **2** is available from X-ray analysis of a degradation compound carried out in the group of Professor O. S. Mills, Manchester.