The Phenylseleno Neighboring Group. Solvolysis of 2-Phenylselenoethyl Chloride

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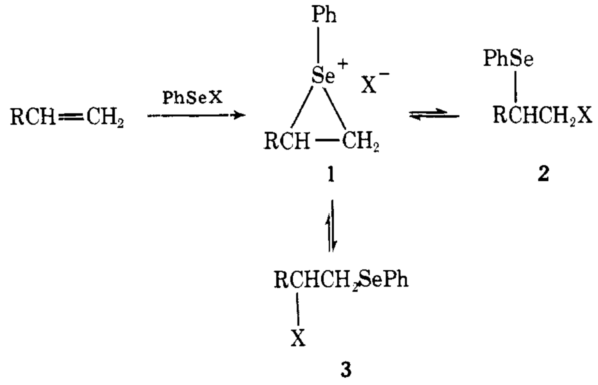
Solvolysis of 2-phenylselenoethyl chloride is an anchimerically assisted reaction in methanol and in aqueous ethanol. While the selenium compound is only some five times faster than the analogous sulfur derivative in methanol, selenium participation is extraordinarily efficient in aqueous ethanol. The Grunwald–Winstein *m* value for the aqueous ethanolysis of 2-phenylselenoethyl chloride was found to be 0.40, which is typical of nucleophilically assisted reactions. Furthermore, with decreasing solvent ionizing power the calculated enthalpy and entropy of activation become less positive and more negative, respectively. This is discussed.

The ease of formation[2–8] of β-phenylselenoalkyl halides, esters, alcohols, and ethers and the synthetic utility[6–13] of the intermediate selenides have attracted considerable recent interest. A semiquantitative study[13] of the ease of rearrangement of the kinetic addition products **2** to the thermodynamic products **3**, presumably via the seleniranium ions **1**,



R = H or alkyl
X = Cl, Br, acetate, or trifluoroacetate

has appeared, and the thermal and solvolytic instability of secondary β-phenylselenoalkyl halides has been noted.[7] We now present the results of the first quantitative study of the reactivity of such compounds and compare the neighboring group effects of sulfur and selenium.

First-order rate constants were measured conductometrically for the solvolysis in aqueous ethanol and in methanol of phenylselenoethyl chloride (**2**, R = H, X = Cl). The results of these studies are summarized in Table I and comparisons with analogous studies with sulfur compounds[14,15] are shown in Table II.[16,17]

Table I. Solvolysis Data for 2-Phenylselenoethyl Chloride

Solvent	$k \times 10^4$, s^{-1}	Temp., °C	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, eu
50E[a]	22.1 (±0.8)	25.6		
70E[a]	1.12 (±0.05)	0.0		
	8.13[b]	25.0	12.3	−31.4
	8.55 (±0.77)	25.6		
80E[a]	0.880 (±0.098)	0.0		
	5.52[b]	25.0	11.3	−35.6
	5.80[c]	25.0		
	7.14[c]	27.7		
	10.2 (±1.4)	35.0		
90E[a]	2.25 (±0.06)	25.2		
MeOH	0.670 (±0.011)	0.0		
	2.94[b]	25.0	8.98	−44.6
	4.54 (±0.11)	32.8		
	6.32 (±0.43)	40.3		

[a] Percent (v/v) aqueous ethanol; 80E = 80% EtOH. [b] Calculated using the experimentally determined $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$. [c] Only one kinetic determination at this temperature.

Table II. Relative Rates of Solvolysis at 25 °C

Substrate	Solvent	Relative rate
$PhSCH_2CH_2Cl$	MeOH	1.00[a,b]
$PhSeCH_2CH_2Cl$	MeOH	4.98[a]
p-$MeC_6H_4SCH_2$-CH_2Cl	80% EtOH (w/w)	1.00[a,c]
$PhSeCH_2CH_2Cl$	80% EtOH (w/w)	216[d]

[a] Calculated using extrapolated rates. [b] Using $\Delta H^{\ddagger} = 17.29$ kcal mol^{-1} and $\Delta S^{\ddagger} = -19.90$ eu, see ref 16; rate data from ref 14. [c] Using $\Delta H^{\ddagger} = 17.83$ kcal mol^{-1} and $\Delta S^{\ddagger} = -24.31$ eu, see ref 16; rate data from ref 15. [d] Rate data extrapolated from mY plot assuming 80% EtOH (w/w) = 83.4% EtOH (v/v).

Divalent sulfur groups are well known for their tendency to nucleophilically participate in solvolysis reactions.[18] Furthermore, sulfur neighboring group participation is especially facile when three-membered rings result.[18,19] Since intramolecular nucleophilicity parallels intermolecular nucleophilicity (e.g., I > Br > Cl and RS > RO[18,20,21]) one would predict that the phenylseleno group should be superior to the highly efficient phenylthio neighboring group.[23] In fact, this trend does indeed occur, and phenylselenoethyl chloride is found to be the most reactive primary chloride known when those which ionize with resonance stabilization are excluded. Obviously, this high degree of reactivity is the result of nucleophilic participation by selenium.

The solvolyses of **2** (R = H, X = Cl) are found to be mildly dependent on solvent. A plot of log *k* vs. Grunwald–Winstein *Y* values for the aqueous ethanolyses (25 °C) gives an *m* value of 0.40 (see Figure 1), which is typical of nucleophilically assisted reactions.[18] We also note that the enthalpy and entropy of activation are becoming less positive and more negative, respectively, with decreasing ionizing power. Thus, in poorly ionizing solvents, such as methanol, solvolysis rates are not greatly affected by a temperature change. Furthermore, since the same trend does not occur with the sulfur compounds,[24] there is a great difference in relative reactivities as the solvent is changed (see Table II).

Although strongly anchimerically assisted reactions are generally assumed not be nucleophilically solvent assisted,[25] a recent theory by McEwen et al.[22,25] explaining enhanced nucleophilicity of certain organophosphorus and organoarsenic compounds suggests a possible explanation for the observed trends in these solvolyses. According to the McEwen theory, solvent could nucleophilically assist the neighboring group as shown in Figure 2. If this type of solvent participation occurs, the reactions would be sensitive to solvent ionizing

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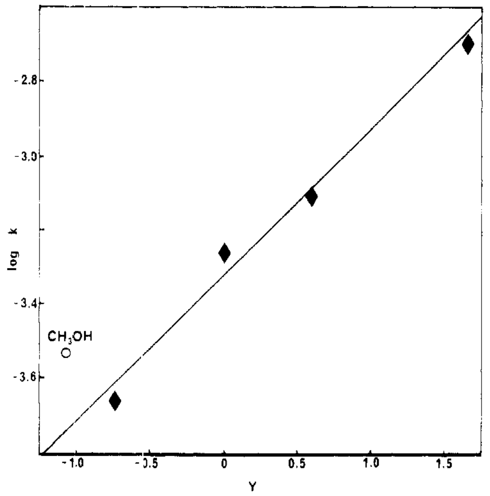

Figure 1. Grunwald–Winstein plot for the aqueous ethanolysis of 2-phenylselenoethyl chloride at 25 °C. The open circle (○), for the methanolysis reaction, is not included in the least-squares plot.

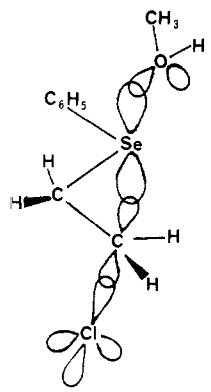

Figure 2. A possible transition state for the anchimerically assisted methanolysis of 2-phenylselenoethyl chloride with nucleophilic solvent assistance. Other geometries are possible.

power *and* solvent nucleophilicity instead of ionizing power alone.[27] That the methanol rate is significantly faster than that which is predicted from the Grunwald–Winstein plot (see Figure 1) seems to suggest that some factor other than ionizing power may be important. Furthermore, one would expect that the involvement of solvent as shown in Figure 2 would be accompanied by a substantial negative entropy of activation. As the solvent is changed toward the highly nucleophilic and poorly ionizing end of the spectrum, one would expect a trend toward more negative $\Delta S^{\ddagger}$ values; this is observed in the solvolyses of phenylselenoethyl chloride. The interesting proposal of solvent assistance of the type shown in Figure 2 is a subject on which we hope to comment at a later date.

Because the measured rates and the comparisons reported in Table II are probably affected by ion pairing phenomena, we have initiated studies of derivatives which will allow for the measurement of ionization rates corrected for ion pair return.

Experimental Section

Preparation and Purification of Chemicals. Methanol. Absolute methanol was distilled from magnesium methoxide as described by Lund and Bjerrum.[28]

Ethanol. Absolute ethanol was distilled from magnesium ethoxide as described by Lund and Bjerrum.[28] Aqueous ethanol for the kinetic measurements was prepared by mixing volume quantities of freshly distilled absolute ethanol with deionized water.

2-Phenylselenoethyl Chloride. Phenylselenenyl chloride (Aldrich) was reacted with ethylene according to the procedure of Kataev et al.[2] giving a quantitative yield of 2-phenylselenoethyl chloride which, after distillation, had physical properties and spectral properties consistent with those reported.[2]

Kinetic Method. Rates were determined conductometrically with a Beckman Model PC-18A impedence bridge capable of 0.1% accuracy. The conductivity cells had platinized electrodes, cell constants of 0.2–0.4, and a solution capacity of approximately 25 mL. Typically, solutions of 10^{-3} M were used for kinetic measurements. When temperatures other than ambient were employed, the solvent was preconditioned to the desired temperature for at least 0.1 h and, after addition of the substrate, the solutions were conditioned at the desired temperature for at least 5 min prior to recording the conductance. The raw conductance data, consisting of approximately 12 readings at intervals, were fitted to the first-order rate equation by means of the least-squares computer program (LSKIN) developed by Professor D. F. DeTar.

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References and Notes

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