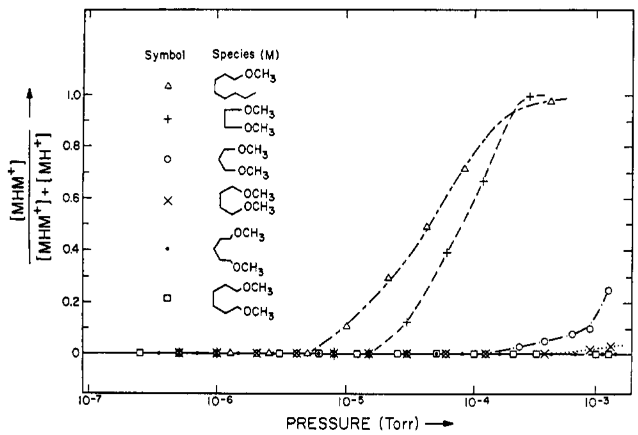
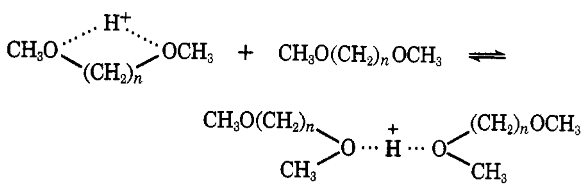


Figure 1. Fractional abundances of proton-bound dimers as a function of pressure.

been studied in detail by Kebarle, *et al.*, who have determined that, for reaction 1, $\Delta H = -36$ kcal/mol and $\Delta S = -33.3$ eu.[12] The negative entropy change represents mainly the loss of translational degrees of freedom of the system when two molecules aggregate,[12,13] and it is the enthalpy term which produces a large negative ΔG for reaction 1.

The aggregation of monofunctional ethers should parallel the example of reaction 1. However, if the proton is already bound to two sites in the protonated parent ion, then the *enthalpy* change for proton-bound dimer formation should be much smaller. The aggregation of bifunctional ethers, reaction 2, demonstrates


(2)

this phenomenon. From our results, it appears that the intramolecular proton bridge prefers an 8 member ($n = 5$) or larger ring structure.[14] Our inference is that the intramolecular strong hydrogen bond maintains a strong preference for linear geometry.[15]

Availability of other protonic binding sites in a proton-bridged bifunctional molecule permits proton-bound dimer formation to occur without rupture of the intramolecular strong hydrogen bond.[16,17] For instance, among the series of methoxyalkanols, X = $-OCH_3$, Y = -OH, n = 2–4, proton-bound dimer is observed in the pressure range 10^{-5}–10^{-4} Torr.

We consider that the applicability of these observations is very general and that such investigations of bifunctional compounds may serve as a general basis for detection of intramolecular strong hydrogen bonds. In addition, our examination of the mass spectra and ion–molecule reactions of bifunctional compounds has revealed a large number of processes in which remote functional groups may interact with one another in the same molecule.

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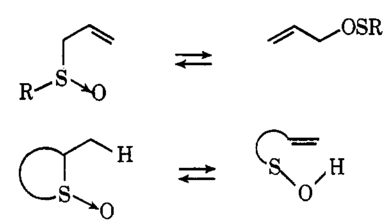
(12) P. Kebarle, S. K. Searles, A. Zolla, J. Scarborough, and M. Arshadi, *J. Amer. Chem. Soc.*, **89**, 6393 (1967).
(13) S. K. Searles and P. Kebarle, *Can. J. Chem.*, **47**, 2619 (1969).
(14) For a discussion of the structural preferences for weak hydrogen bonds, see S. N. Vinogradov and R. H. Linell, "Hydrogen Bonding," Van Nostrand, Princeton, N. J., 1971, pp 134–146, and references cited therein.
(15) For calculations describing the geometry of the proton-bound dimer of water, see P. A. Kollman and L. C. Allen, *J. Amer. Chem. Soc.*, **92**, 6101 (1970).
(16) Related systems have been examined by I. Dzidic and J. A. McCloskey, *ibid.*, **93**, 4955 (1971).
(17) The case $n = 4$ has been examined in solution by F. Klages, J. E. Gordon, and H. A. Jung, *Chem. Ber.*, **98**, 3748 (1965).

Nucleophilic Cleavage of Allylic Sulfenate Esters. Mechanistic Observations

Sir:

The role of both sulfenate esters and acids in sulfoxide chemistry has become increasingly apparent. Examples involving sulfur–oxygen scission from these reactive species generated as a consequence of the rearrangement of allylic sulfoxides[1] (eq 1) and the thermal fragmentation of certain cyclic sulfoxides[2,3] (eq 2) have been reported. In addition, the mechanistically interesting ether synthesis involving the desulfurization of sulfenate esters (eq 3) has been demonstrated by Barton and coworkers.[4]


(1)

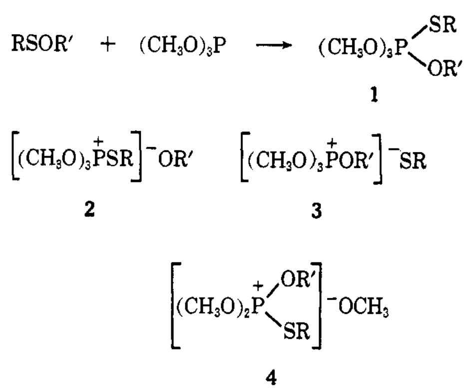
(2)

$$R{-}S{-}O{-}R' \longrightarrow R{-}O{-}R' \qquad (3)$$

As has been shown in each of these cases, trivalent phosphorus derivatives appear to be effective cleavage reagents. The purpose of this communication is to report our observations on the fate of allylic sulfenate esters produced by [2,3]-sigmatropic rearrangement (eq 1) in the presence of trimethyl phosphite and to suggest that the products derived from this reaction are consistent with a general Michaelis–Arbuzov[5] cleavage process.

(1) (a) D. A. Evans, G. C. Andrews, and C. L. Sims, *J. Amer. Chem. Soc.*, **93**, 4956 (1971); (b) D. A. Evans, C. A. Bryan, and C. L. Sims, *ibid.*, in press; (c) D. J. Abbott and C. J. M. Stirling, *J. Chem. Soc. C*, 818 (1969).
(2) (a) R. D. G. Cooper and F. L. José, *J. Amer. Chem. Soc.*, **92**, 2575 (1970); (b) D. H. R. Barton, D. G. T. Grieg, G. Lucente, P. G. Sammes, M. V. Taylor, C. M. Cooper, G. Hewitt, and W. G. E. Underwood, *J. Chem. Soc. D*, 1683 (1970).
(3) J. E. Baldwin, G. Höfle, and Se Chun Choi, *J. Amer. Chem. Soc.*, **93**, 2810 (1971).
(4) D. H. R. Barton, G. Page, and D. A. Widdowson, *J. Chem. Soc. D*, 1466 (1970).
(5) R. G. Harvey and E. R. DeSombre, *Top. Phosphorus Chem.*, **1**, 57 (1964).

Although little mechanistic work has been carried out on the nucleophilic cleavage of sulfenate esters,[6] closely analogous reactions of trivalent phosphorus with both disulfides[7] and peroxides[8] have been demonstrated to follow a mechanistically similar pathway. In direct analogy with these systems, the reaction of trimethyl phosphite with a sulfenate ester could, *a priori*, lead to the pentacoordinate phosphorane **1** and (or) the phosphonium salts **2**–**4** which in turn may lead to either sulfides (collapse of **3**) or ethers (collapse of **2** or **4**).[9] *However, we have found that only products which appear to be formed from decomposition of the tetraalkoxyphosphonium salt* **3** *are observed.* These results are interesting in light of Barton's recent observations on the cleavage of sulfenate esters with tributylphosphine (eq 3).[4]



$$3 \rightarrow CH_3SC_6H_4CH_3\ (\mathbf{5}) + (CH_3O)_2P(O)OCH_2CH{=}CH_2\ (\mathbf{6}) \quad (4)$$

$$3 \rightarrow CH_2{=}CHCH_2SC_6H_4CH_3\ (\mathbf{7}) + (CH_3O)_3P(O) \quad (5)$$

$R = C_6H_4CH_3$; $R' = CH_2CH{=}CH_2$

Allyl *p*-tolyl sulfoxide and trimethyl phosphite (4 equiv) when heated at reflux in THF for 12 hr afforded the allylic phosphate **6** (80%),[10] sulfide **5** (80%),[11] as well as smaller amounts of the alternate cleavage products **7** (16%) and trimethyl phosphate.[12] These products, as well as their relative yields, are readily explained by attack of mercaptide on the tetravalent phosphonium intermediate **3** ($R' = C_3H_5$; $R = C_6H_4CH_3$) at methyl and allyl positions; the relative proportions of **5** and **7** correlate well with the known S_N2 substrate reactivity in methyl and allyl systems.[13] The same reaction carried out in refluxing methanol (12 hr) afforded allyl alcohol (75%) and sulfide **5** (80%).

(6) C. Brown and D. R. Hogg, *J. Chem. Soc. D*, 38 (1967). These workers conclude that alkaline hydrolysis of sulfenate esters occurs by direct substitution on sulfur.
(7) D. N. Harpp and J. G. Gleason, *J. Amer. Chem. Soc.*, **93**, 2437 (1971), and references cited therein.
(8) D. B. Denney and D. H. Jones, *ibid.*, **91**, 5821 (1969), and references cited therein.
(9) Sulfides should not be expected to be derived from **2** or **4**: *cf.* H. I. Jacobson, R. G. Harvey, and E. V. Jenson, *ibid.*, **77**, 6064 (1955); G. Hilgetag and H. Teichmann, *Chem. Ber.*, **96**, 1465 (1963).
(10) J. Cheymol, P. Chabrier, M. Selim, and P. Leduc, *C. R. Acad. Sci.*, **247**, 1014 (1958).
(11) Since dibenzyl sulfoxide undergoes less than 1% reduction under these conditions even after 60 hr, it is concluded that sulfide **7** is *not* being produced by direct reduction of the corresponding sulfoxide.
(12) Product analysis was carried out by nmr and glpc based upon comparison with authentic samples.
(13) A. Streitweiser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill, New York, N. Y., 1962, p 13.

Since the allyl phosphate **6** is stable under these conditions, allyl alcohol is probably liberated by solvent exchange with the alkoxyphosphonium salt **3** ($R' = C_3H_5$) (eq 6) prior to attack by mercaptide. Such

$$\underset{\mathbf{7}}{(CH_3O)_3\overset{+}{P}OC_3H_5} + CH_3OH \rightleftarrows (CH_3O)_4\overset{+}{P} + C_3H_5OH \quad (6)$$

exchange processes have been documented in other systems.[14] A kinetic study of the rearrangement and cleavage of allylic sulfoxide **8**[1a] was undertaken to assess the trapping efficiency of trimethyl phosphite with allylic sulfenate esters and, concomitantly, to gain insight into the stereochemical course of [2,3]-sigmatropic processes in a sterically biased system.

As summarized in Table I, the values of k_{obsd} increase

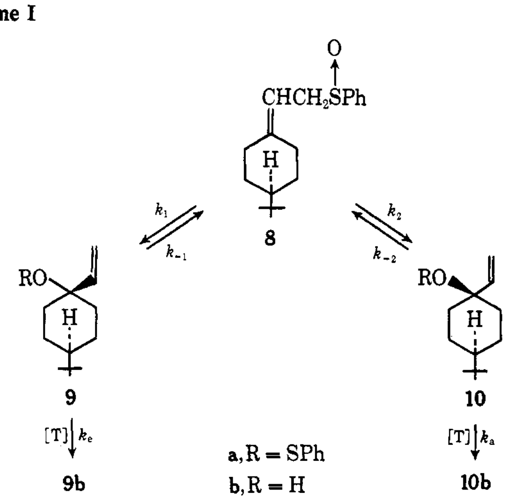
Table I. Rate Constants for the Rearrangement–Cleavage of Allylic Sulfoxide[a] **8** in Methanol at 60.3°

Run	$k_{obsd} \times 10^4$ sec^{-1} [b]	**8**:$(CH_3O)_3P$	$[(CH_3O)_3P]$, *M*
1	4.2 ± 1.2	1:50	2.00
2	3.8 ± 0.3	1:5.0	2.0×10^{-1}
3	2.4 ± 0.3	1:2.8	1.1×10^{-1}
4	2.2 ± 0.6	1:1.2	4.67×10^{-2}
5	3.1 ± 0.3	1:0.5	2.18×10^{-2}

[a] Sulfoxide concentration was 4.0×10^{-2} *M* for all runs. [b] Progress of the reaction was followed by glc using an internal standard for a period of 2–3 half-lives.

by a factor of 2 over a 100-fold increase in phosphite concentration. Even this small rate enhancement is most likely due to a decrease in polarity of the reaction medium[15] with added phosphite, the effect being most pronounced at high phosphite concentration (run 1). These results are consistent with the rate-determining step in the reaction scheme (Scheme I) being the pro-

Scheme I



duction of sulfenate esters **9a** and **10a** from **8** followed by rapid cleavage to the alcohols **9b** and **10b**.[16] Since the reaction is zero order in phosphite and the ratio of **9b**:**10b** (82%:18%) was found to be independent of phosphite concentration, both k_e and k_a are $\gg k_{-1}$

(14) J. H. Finley, D. Z. Denney, and D. B. Denney, *J. Amer. Chem. Soc.*, **91**, 5826 (1969).
(15) D. Bickart, F. W. Carson, J. Jacobus, E. G. Miller, and K. Mislow, *ibid.*, **90**, 4869 (1968).
(16) Alcohols **9b** and **10b** have been prepared by R. J. Ouelette, K. Liptak, and G. E. Booth, *J. Org. Chem.*, **31**, 546 (1966).

and k_{-2} and the $k_1:k_2$ ratio of 4.6 may be calculated from the proportions of the two alcohols produced in the cleavage process. These results indicate a clear preference for the [2,3]-sigmatropic process to proceed across the equatorial face of the cyclohexylidine ring system producing predominately the less stable equatorial alcohol **9b**.[17] This stereochemical outcome is consistent with a reactant-like transition state where steric effects are the major factors governing product geometry.[18]

The use of less efficient thiophiles for the interception of sulfenate esters **9a** and **10a** results in a change in the ratio of allylic alcohols produced when k_e and k_a approach the values of k_{-1} and k_{-2}. The results in Table II confirm this prediction.

Table II. Effect of Thiophile on **9b**:**10b** Ratio at 25° in Methanol[a]

Thiophile [T]	**9b**:**10b**	% conversion
$LiBH_3CN$	58:42	24
Piperidine	66:34	90
$C_6H_5S^-$	88:12	99
$[(C_2H_5)_2N]_3P$	92:8	99
$(CH_3O)_3P$	92:8	99

[a] All reactions were carried out with a 10:1 excess of thiophile for 14 days at 25°.

Acknowledgment. This investigation was supported by the National Institutes of Health, the National Science Foundation, and funds provided by Eli Lilly.

(17) From ref 13, **10b** is calculated to be 0.64 kcal/mol more stable than **9b** at 38°.
(18) M. Chérest and H. Felkin, *Tetrahedron Lett.*, 2205 (1968).
(19) Camille and Henry Dreyfus Teacher-Scholar recipient, 1971–1976.

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Medium Activity Coefficient of Silver Cation between Acetonitrile and Water

Sir:

We have drawn attention[1] to some of the problems in estimating a number which is important to chemists, the medium activity coefficient, log $^{An}\gamma^{W}_{Ag^+}$ for transfer of silver cation from acetonitrile to water at 25°. Kolthoff and Chantooni[2] have removed one of these problems by measuring the solubility product (pK_s = 17.2) of silver tetraphenylboride in water at 25°. We have measured some solubilities and equilibrium constants which give us confidence that log $^{An}\gamma^{W}_{Ag^+}$ is between 3 and 4.

The solubility (S, moles liter^{-1}) of tetraphenylmethane is $10^{-7.8}$ in water and $10^{-3.2}$ in acetonitrile.[1] The new value for water was found by ether-extracting 1 l. of a saturated solution of tetraphenylmethane in water containing triphenylmethane, added as internal standard after saturation and filtering. The ether extract was evaporated to 0.5 ml and analyzed by gas chromatography on a SE-30 column at 250° using a flame ionization detector.

The solubility product, $pK_s^W(Ph_4AsBPh_4)$, of tetraphenylarsonium tetraphenylboride in water at 25° is 17.4[3] (molar scale). In acetonitrile, $pK_s^{An}(Ph_4AsBPh_4)$ is 6.0. The new value for water is the mean of 17.3 and 17.5 measured (a) by equilibrating (eq 1) 50 ml of

$$Ph_4AsBPh_4\downarrow + AgNO_3 \rightleftharpoons Ph_4AsNO_3 + AgBPh_4\downarrow \quad (1)$$

0.01 M silver nitrate with 1 g of Ph_4AsBPh_4 containing a trace of $AgBPh_4$ as seed and (b) by equilibrating 50 ml of 0.01 M Ph_4AsNO_3 with 1 g of $AgBPh_4$ containing a trace of Ph_4AsBPh_4 as seed. Methods a and b both gave 6.0 for $pK_s^{An}(Ph_4AsBPh_4)$.[4] Equilibration was in CO_2-free water or anhydrous acetonitrile, under nitrogen by shaking in lightproof vessels. The solutions were analyzed for silver by atomic absorption and for Ph_4As^+ by its uv absorption at 265 mμ. Equation 2 gave $pK_s(Ph_4AsBPh_4)$ using $pK_s^W(AgBPh_4)$ = 17.2[2]

$$pK_s(Ph_4AsBPh_4) = [Ph_4As^+]/[Ag^+] + pK_s(AgBPh_4) \quad (2)$$

and $pK_s^{An}(AgBPh_4)$ = 7.6,[5] respectively. Equation 2 also gave $pK_s^W(AgBPh_4) - pK_s^W(Ph_4AsBPh_4) = -0.2$ and $pK_s^{An}(AgBPh_4) - pK_s^{An}(Ph_4AsBPh_4) = 1.6$.

The latter value compares favorably with 1.7 calculated from our previously reported $pK^{An}(Ph_4AsBPh_4)$ = 5.8 and $pK_s^{An}(AgBPh_4)$ = 7.5 at zero ionic strength.

Values of log $^{An}\gamma^{W}_{Ag^+}$ are in Table I. Four of them are from other assumptions, as reported previously.[1] They are compared with the three new values calculated from the solubility products of $AgBPh_4$, Ph_4AsBPh_4, and Ph_4C in water and acetonitrile by assuming (i) that $^{An}\gamma^{W}_{Ph_4As^+} = {}^{An}\gamma^{W}_{Ph_4B^-}$; (ii) that $^{An}\gamma^{W}_{Ph_4B^-} = {}^{An}\gamma^{W}_{Ph_4C}$; and (iii) that $^{An}\gamma^{W}_{Ph_4As^+} = {}^{An}\gamma^{W}_{Ph_4C}$ in eq 3. In eq 3 the concentrations of Ag^+

Table I. Values of Log $^{An}\gamma^{W}_{Ag^+}$ (Molar Scale) at 25°

Assumption[a]	Log $^{An}\gamma^{W}_{Ag^+}$	Assumption[a]	Log $^{An}\gamma^{W}_{Ag^+}$
$^{An}\gamma^{W}_{Ph_4As^+} = {}^{An}\gamma^{W}_{Ph_4B^-}$	3.9[b]	Negligible E_{1j}	3.1[c]
$^{An}\gamma^{W}_{Ph_4As^+} = {}^{An}\gamma^{W}_{Ph_4C}$	2.8[b]	$^{An}\gamma^{W}_{\ddagger^-}$	3.2[c]
$^{An}\gamma^{W}_{Ph_4B^-} = {}^{An}\gamma^{W}_{Ph_4C}$	5.0[b]	$^{An}\gamma^{W}_{ArF} = {}^{An}\gamma^{W}_{\ddagger*-}$	2.8[c]
		$^{An}\gamma^{W}_{Fc} = {}^{An}\gamma^{W}_{Fc^+}$	6.1[c]

[a] Abbreviations: Ar = 4-nitrophenyl; $\ddagger^-$ is the transition state anion for the SN2 reaction of SCN^- with CH_3I; $\ddagger*^-$ is the transition state anion for the SNAr reaction of N_3^- with ArF; Fc is ferrocene; Fc^+ is ferricinium cation. [b] This work. [c] Reference 1.

$$\log {}^{An}\gamma^{W}_{Ag^+} = \log \frac{[Ag^+]^W}{[Ph_4As^+]^W} - \log \frac{[Ag^+]^{An}}{[Ph_4As^+]^{An}} + pS^W Ph_4C - pS^{An} Ph_4C \quad (3)$$

and Ph_4As^+ in water and acetonitrile are those prevailing at equilibrium in reaction 1 and thus the first two

(1) R. Alexander, A. J. Parker, J. H. Sharp, and W. E. Waghorne, *J. Amer. Chem. Soc.*, **94**, 1143 (1972).
(2) I. M. Kolthoff and M. K. Chantooni, *Anal. Chem.*, **44**, 194 (1972).
(3) I. M. Kolthoff and M. K. Chantooni, *J. Amer. Chem. Soc.*, **93**, 7104 (1971), calculated a value of 17.3 from solubility products of a variety of salts.
(4) A direct measurement[1] on a saturated solution of Ph_4AsBPh_4 in acetonitrile gave pK_s^{An} = 5.8.
(5) This is a mean value between 7.5 from ref 1 and 7.7 from I. M. Kolthoff and M. K. Chantooni, private communication.