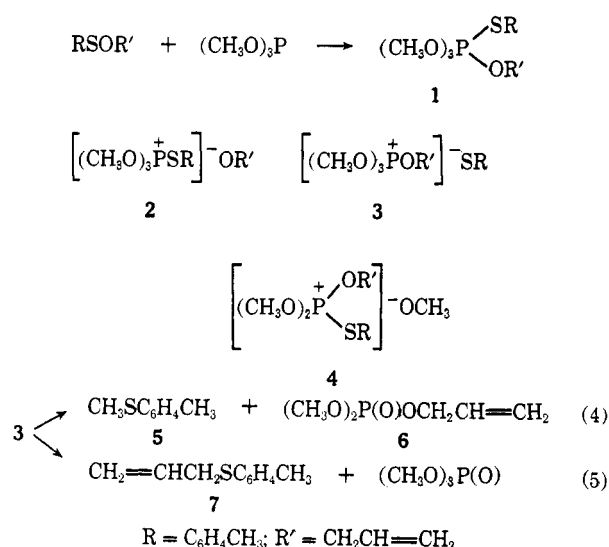


Although little mechanistic work has been carried out on the nucleophilic cleavage of sulfenate esters,⁶ closely analogous reactions of trivalent phosphorus with both disulfides⁷ and peroxides⁸ have been demonstrated to follow a mechanistically similar pathway. In direct analogy with these systems, the 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



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 phosphite.¹² These products, as well as their relative yields, are readily explained by attack of mercaptide on the tetravalent phosphonium intermediate **3** (R' = C₃H₅; R = C₆H₄CH₃) at methyl and allyl positions; the relative proportions of **5** and **7** correlate well with the known SN₂ 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).

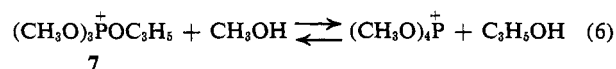
(10) J. Cheymol, P. Chabrier, M. Selim, and P. Leduc, *C. R. Acad. Sci.*, **247**, 1014 (1958).

(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. Streitwieser, 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' = C₃H₅) (eq 6) prior to attack by mercaptide. Such



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°

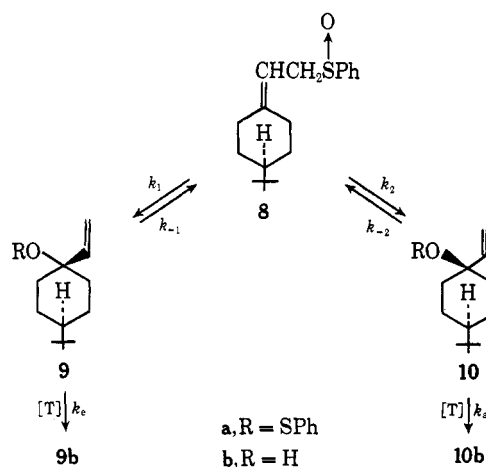
Run	$k_{\text{obsd}} \times 10^4 \text{ sec}^{-1b}$	$\mathbf{8}:(\text{CH}_3\text{O})_3\text{P}$	$[(\text{CH}_3\text{O})_3\text{P}], M$
1	4.2 ± 1.2	1:50	2.00
2	3.8 ± 0.3	1:5.0	2.0 × 10 ⁻¹
3	2.4 ± 0.3	1:2.8	1.1 × 10 ⁻¹
4	2.2 ± 0.6	1:1.2	4.67 × 10 ⁻²
5	3.1 ± 0.3	1:0.5	2.18 × 10 ⁻²

^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 medium¹⁵ 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. Ouellette, 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 cyclohexylidene 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 sulfenates **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 ₃ CN	58:42	24
Piperidine	66:34	90
C ₆ H ₅ S ⁻	88:12	99
[(C ₂ H ₅) ₂ N] ₃ P	92:8	99
(CH ₃ O) ₃ P	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.

D. A. Evans,*¹⁹ G. C. Andrews

Contribution No. 2945, Department of Chemistry
University of California, Los Angeles
Los Angeles, California 90024

Received January 24, 1972

Medium Activity Coefficient of Silver Cation between Acetonitrile and Water

Sir:

We have drawn attention¹ to some of the problems in estimating a number which is important to chemists, the medium activity coefficient, $\log \text{An}\gamma^{\text{W}}_{\text{Ag}^+}$ for transfer of silver cation from acetonitrile to water at 25°. Kolthoff and Chantooni² 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 $\log \text{An}\gamma^{\text{W}}_{\text{Ag}^+}$ is between 3 and 4.

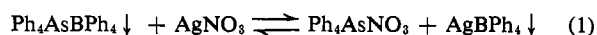
The solubility (S , moles liter⁻¹) of tetraphenylmethane is $10^{-7.8}$ in water and $10^{-8.2}$ in acetonitrile.¹ The new value for water was found by ether-extracting 1 l. of a saturated solution of tetraphenylmethane in water containing triphenylmethane, added as internal standard after saturation and filtering. The ether ex-

(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).

tract 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, $pK_s^{\text{W}}(\text{Ph}_4\text{AsBPh}_4)$, of tetraphenylarsonium tetraphenylboride in water at 25° is 17.4³ (molar scale). In acetonitrile, $pK_s^{\text{An}}(\text{Ph}_4\text{AsBPh}_4)$ 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



0.01 *M* silver nitrate with 1 g of **Ph₄AsBPh₄** containing a trace of **AgBPh₄** as seed and (b) by equilibrating 50 ml of 0.01 *M* **Ph₄AsNO₃** with 1 g of **AgBPh₄** containing a trace of **Ph₄AsBPh₄** as seed. Methods a and b both gave 6.0 for $pK_s^{\text{An}}(\text{Ph}_4\text{AsBPh}_4)$.⁴ Equilibration was in CO₂-free water or anhydrous acetonitrile, under nitrogen by shaking in lightproof vessels. The solutions were analyzed for silver by atomic absorption and for **Ph₄As⁺** by its uv absorption at 265 μ . Equation 2 gave $pK_s(\text{Ph}_4\text{AsBPh}_4)$ using $pK_s^{\text{W}}(\text{AgBPh}_4) = 17.2^2$

$$pK_s(\text{Ph}_4\text{AsBPh}_4) =$$

$$[\text{Ph}_4\text{As}^+]/[\text{Ag}^+] + pK_s(\text{AgBPh}_4) \quad (2)$$

and $pK_s^{\text{An}}(\text{AgBPh}_4) = 7.6$,⁵ respectively. Equation 2 also gave $pK_s^{\text{W}}(\text{AgBPh}_4) - pK_s^{\text{W}}(\text{Ph}_4\text{AsBPh}_4) = -0.2$ and $pK_s^{\text{An}}(\text{AgBPh}_4) - pK_s^{\text{An}}(\text{Ph}_4\text{AsBPh}_4) = 1.6$.

The latter value compares favorably with 1.7 calculated from our previously reported $pK_s^{\text{An}}(\text{Ph}_4\text{AsBPh}_4) = 5.8$ and $pK_s^{\text{An}}(\text{AgBPh}_4) = 7.5$ at zero ionic strength.

Values of $\log \text{An}\gamma^{\text{W}}_{\text{Ag}^+}$ are in Table I. Four of them

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

Assumption ^a	$\log \text{An}\gamma^{\text{W}}_{\text{Ag}^+}$	Assumption ^a	$\log \text{An}\gamma^{\text{W}}_{\text{Ag}^+}$
$\text{An}\gamma^{\text{W}}_{\text{Ph}_4\text{As}^+} = \text{An}\gamma^{\text{W}}_{\text{Ph}_4\text{B}^-}$	3.9 ^b	Negligible E_{1j}	3.1 ^c
$\text{An}\gamma^{\text{W}}_{\text{Ph}_4\text{As}^+} = \text{An}\gamma^{\text{W}}_{\text{Ph}_4\text{C}}$	2.8 ^b	$\text{An}\gamma^{\text{W}}_{\ddagger^-}$	3.2 ^c
$\text{An}\gamma^{\text{W}}_{\text{Ph}_4\text{B}^-} = \text{An}\gamma^{\text{W}}_{\text{Ph}_4\text{C}}$	5.0 ^b	$\text{An}\gamma^{\text{W}}_{\text{ArF}} = \text{An}\gamma^{\text{W}}_{\ddagger^*}$	2.8 ^c
		$\text{An}\gamma^{\text{W}}_{\text{Fc}^+} = \text{An}\gamma^{\text{W}}_{\text{Fc}^+}$	6.1 ^c

^a Abbreviations: Ar = 4-nitrophenyl; \ddagger^- is the transition state anion for the S_N2 reaction of SCN⁻ with CH₃I; \ddagger^* is the transition state anion for the S_NAr reaction of N₃⁻ with ArF; Fc is ferrocene; Fc⁺ is ferricinium cation. ^b This work. ^c Reference 1.

are from other assumptions, as reported previously.¹ They are compared with the three new values calculated from the solubility products of **AgBPh₄**, **Ph₄AsBPh₄**, and **Ph₄C** in water and acetonitrile by assuming (i) that $\text{An}\gamma^{\text{W}}_{\text{Ph}_4\text{As}^+} = \text{An}\gamma^{\text{W}}_{\text{Ph}_4\text{B}^-}$; (ii) that $\text{An}\gamma^{\text{W}}_{\text{Ph}_4\text{B}^-} = \text{An}\gamma^{\text{W}}_{\text{Ph}_4\text{C}}$; and (iii) that $\text{An}\gamma^{\text{W}}_{\text{Ph}_4\text{As}^+} = \text{An}\gamma^{\text{W}}_{\text{Ph}_4\text{C}}$ in eq 3. In eq 3 the concentrations of **Ag⁺**

$$\log \text{An}\gamma^{\text{W}}_{\text{Ag}^+} = \log \frac{[\text{Ag}^+]^{\text{W}}}{[\text{Ph}_4\text{As}^+]^{\text{W}}} - \log \frac{[\text{Ag}^+]^{\text{An}}}{[\text{Ph}_4\text{As}^+]^{\text{An}}} + pS^{\text{W}}\text{Ph}_4\text{C} - pS^{\text{An}}\text{Ph}_4\text{C} \quad (3)$$

and **Ph₄As⁺** in water and acetonitrile are those prevailing at equilibrium in reaction 1 and thus the first two

(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 measurement¹ on a saturated solution of **Ph₄AsBPh₄** in acetonitrile gave $pK_s^{\text{An}} = 5.8$.

(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.