THE KINETICS AND MECHANISM OF THE REACTION OF TRICOORDINATE PHOSPHORUS COMPOUNDS WITH SULFENATE ESTERS

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THE KINETICS AND MECHANISM OF THE REACTION OF TRICOORDINATE PHOSPHORUS COMPOUNDS WITH SULFENATE ESTERS*

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The kinetics and mechanism of the reaction of tricoordinate phosphorus compounds, $Ar_nP(OCH_2CF_3)_{3-n}$ with arylsulfenate esters, $ArSOCH_2CF_3$, are reported. Product analysis, kinetic order, activation parameters, Hammett data and solvent effects are the criteria used to elucidate the two step mechanism involving arylthiophosphoranes as intermediates.

Keywords: tricoordinate phosphorus; sulfenate esters; thiophosphoranes; oxyphosphoranes; kinetics; mechanism

INTRODUCTION

The reaction of trivalent phosphorus compounds (**1**) with sulfenate esters (**2**) is now a well established route to oxyphosphoranes (**4**)[1–4]. The reaction proceeds in two steps *via* a thiophosphorane intermediate (**3**) and the reaction is a valuable route for the synthesis of both acyclic and cyclic phosphoranes.[2–4] Subsequent studies by Evans *et al.* underlined the synthetic utility of alkoxyphosphoranes by, for example, the cyclodehydration of diols to form cyclic ethers[5]. The relative rates of (**1**, Ar=Ph, R = Et) with (**2**, Ar′ = Ph, R′ = Et) followed the sequence $n = 1 > n = 2 > n = 0 > n = 3$[4] which contrasts with the sequence $n = 3 > 2 > 1 > 0$ for quaternisation of (**1**) with ethyl iodide[6]. This result was indicative of a biphilic mechanism as found with diethyl peroxide.[7] Subsequent work by Denney on the reaction of trimethyl phosphite with methyl arylsulphenates, XC_6H_4SOMe, showed that variation of X had virtually no effect on the rate, thus

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* Dedicated to Professor Robert Wolf in recognition of his outstanding contributions to Phosphorus Chemistry

supporting the proposal of a biphilic mechanism.[8] Furthermore, the reaction of excess $(EtO)_3P$ with PhSOMe gave rise to thiophosphorane, $PhSP(OEt)_3(OMe)$ but only a *single peak* in the P(III) region at 138.9 ppm due to $(EtO)_3P$ thus indicating that formation of the thiophosphorane was not reversible[8]. 2,2,2-Trifluoroethyl benzenesulfe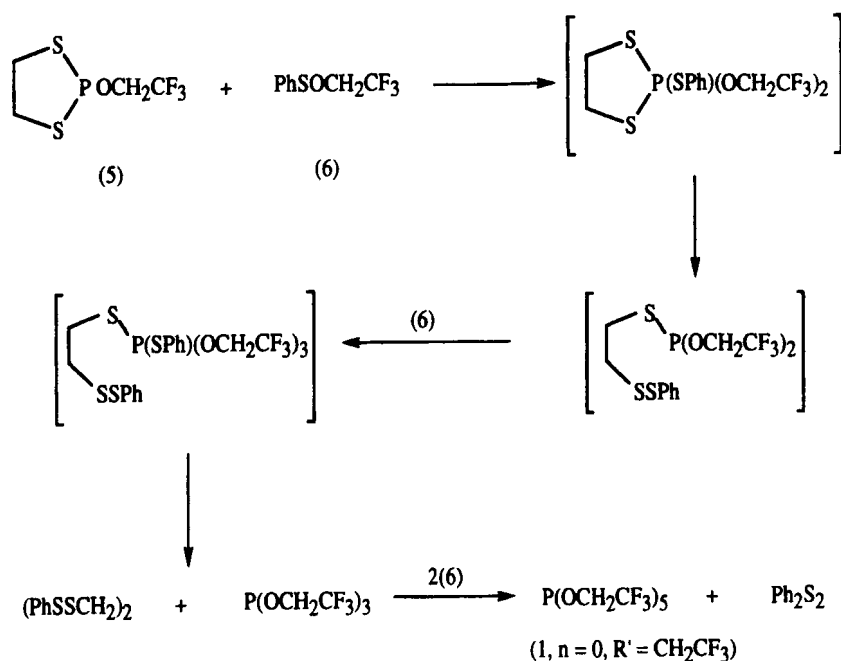nate (2, Ar' = Ph, R' = CH_2CF_3) and 1,1,1,3,3,3-hexafluoro–2-propylbenzene sulfenate {2, Ar' = Ph, R' = $CH(CF_3)_2$} also react with a range of P(III) compounds to form unusually stable phosphoranes which are often isolable in high yields[9-11]. In two cases using (1) with n = 0, R = CH_2CF_3 and n = 0, R = $CH(CF_3)_2$, the intermediate thiophosphorane was so stable that no further reaction was observed. Later work by Denney focused on the synthesis of a range of novel cyclic phosphoranes[12a-b] and interestingly, the use of a cyclic thiophosphite (5) led to the formation of (4, n = 0, R,R' = CH_2CF_3) through fragmentation of di- and trithio phosphorane intermediates (Scheme 1).

$$Ar_nP(OR)_{3-n} \ + \ Ar'SOR' \ \rightarrow \ \begin{bmatrix} OR' \\ | \\ Ar_nP(OR)_{3-n} \\ | \\ SAr' \end{bmatrix} \xrightarrow{(2)} \ Ar_nP(OR)_{3-n}(OR')_2$$

$$(1, n = 0 - 3) \qquad\qquad (2) \qquad\qquad\qquad (3) \qquad\qquad\qquad\qquad (4)$$
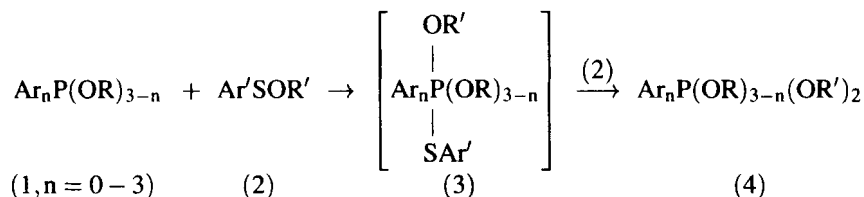
In view of the synthetic importance of the reaction and the relevance to the biphilic insertion of tricoordinate phosphorus into σ bonds[7,12-15] a detailed mechanistic study was desirable. Thus the work presented below seeks to enhance our understanding of the sulfenate ester reaction by a kinetic study including activation parameters and Hammett correlations.

RESULTS AND DISCUSSION

The initial phase of the project involved an examination by ^{31}P nmr of the products formed from reaction of equimolar quantities of (7a-d) with (6) in toluene at −78° and 30°C to form either (8a-d) or (9a-d) or a mixture of both. The results are shown in Table I and a number of conclusions may be drawn from the data. In all cases, except n = 3, thiooxyphosphoranes are observed and, as Denney found with n = 0, (8a) is stable even at room temperature. With n = 1, however (8b) is stable only at −78°and with n = 2 (8c) leads only a transient existence even at low temperature. The result for n = 1, however, illustrates that the thiophosphorane (formed in 95% yield at −78°C) *disproportionates* to (9b) and (7b)

$$\underset{(5)}{\text{[S, S]P—OCH}_2\text{CF}_3} + \underset{(6)}{\text{PhSOCH}_2\text{CF}_3} \longrightarrow \left[\text{[S, S]P(SPh)(OCH}_2\text{CF}_3)_2\right]$$

$$\left[\text{[S]P(SPh)(OCH}_2\text{CF}_3)_3 \atop \text{SSPh}\right] \overset{(6)}{\longleftarrow} \left[\text{[S]P(OCH}_2\text{CF}_3)_2 \atop \text{SSPh}\right]$$

$$(\text{PhSSCH}_2)_2 + \text{P(OCH}_2\text{CF}_3)_3 \overset{2(6)}{\longrightarrow} \text{P(OCH}_2\text{CF}_3)_5 + \text{Ph}_2\text{S}_2$$

$$(1, n = 0, R' = \text{CH}_2\text{CF}_3)$$

SCHEME 1

at 30°C. This delineates one mechanistic route to the oxyphosphorane which occurs even at −78°C for $n = 2$ and is complete for $n = 2$ on reaching 30 °C. For $n = 3$ no thiophosphorane could be detected even at −78° and so it is impossible to decide whether (9d) is formed by disproportionation of (8d) or by rapid reaction of (8d) with remaining sulfenate ester (vide infra). It should be noted that in all of these reactions there is always a small proportion of the corresponding oxide formed which could arise through ionisation of the intermediate thiophosphorane followed by dealkylation of the respective alkoxyphosphonium salt.* In conclusion, it seems likely that the potential for ionisation of the thiophosphorane $\{\text{P(V)} \rightleftharpoons \text{P}^{+-}\text{SPh}\}$ which increases in the order $n = 0 < 1 < 2 < 3$,[16] dictates the final composition of the product as either (8) or (9).

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* In support of this contention a peak at $\delta^{31}\text{P} = 6.8$ ppm was observed in the reaction with $n = 0$ which was tentatively assigned to $\text{PhS}^{-+}\text{P(OCH}_2\text{CF}_3)_4$ by analogy with Denney's findings.

TABLE I The reaction of tricoordinate phosphorus compounds $Ph_nP(OCH_2CF_3)_{3-n}$ with $PhSOCH_2CF_3$ (1:1 molar ratio in toluene)

n	Temperature ($^\circ C$)	Time (min)	$\delta 31P$ (ppm)	% (*)	Assignment ($R = CH_2CF_3$)
0	−78	5 and 10	−52.6	56	$PhSP(OR)_4$
			6.8	3	$PhS^- P^+(OR)_4$?
			136.0	42	$(RO)_3 P$
0	+30	25	−52.6	93	$PhSP(OR)_4$
			−2.2	7	$(RO)_3P(O)$
1	−78	5 and 25	−35.3	95	$PhP(SPh)(OR)_3$
			20.8	5	$PhP(O) (OR)_3$
1	+30	5	−61.5	52	$PhP(OR)_4$
			161.5	29	$PhP(OR)_2$
			20.4	19	$PhP(O)(OR)_2$
2	−78	5	−47.3	45	$Ph_2P(OR)_3$
			−44.7	14	$Ph_2 P(SPh)(OR)_2$
			128.2	35	$Ph_2P(OR)$
			34.2	6	$Ph_2P(O)(OR)$
2	−78	15	−47.3	46	$Ph_2P(OR)_3$
			−44.7	1	$Ph_2P(SPh)(OR)_2$
			+128.2	44	$Ph_2P(OR)$
			+34.2	10	$Ph_2P(O)(OR)$
2	+30	5	−45.6	44	$Ph_2P(OR)_3$
			+125.8	44	Ph_2POR
			+33.0	12	$Ph_2P(O)(OR)$
3	−78	5	−61.5	43	$Ph_3P (OR)_2$
			−3.2	50	Ph_3P
			30.3	7	$Ph_3P(O)$
3	30	5	−59.3	45	$Ph_3P (OR)_2$
			−5	46	Ph_3P
			+27.0	9	$Ph_3P(O)$

* Estimated from ^{31}P nmr assuming identical response factors for all the compounds.

TABLE II Activation parameters for the formation of thiophosphorane $PhSP(OCH_2CF_3)_4$ in toluene

	T (K)	195	190	185	180
	$10^4 k_2$ ($1mol^{-1}s^{-1}$)	4.69	2.53	1.66	0.91
Gives :	E_A	= 7.4 (+/− 0.4) k cal mol^{-1} (r = 0.997)			
	k_2 (298K)	= 0.259 $1mol^{-1}s^{-1}$			
	$\triangle G^\ddagger_{298}$	= 18.3 k cal mol^{-1}			
	$\triangle S^\ddagger_{298}$	= −38 (+/− 1) cal K^{-1}mol^{-1}			

TABLE III ^{31}P nmr δ values for $XC_6H_4SP(OCH_2CF_3)_4$ in C_7D_8

X	H	p-Cl	p-Me	p-MeO
$\delta^{31}P$ (ppm)	−52.5	−51.7	−52.9	−53.0

Kinetics and mechanism of thiophosphorane formation

A low temperature kinetic study of the reaction of (7a) with (6) was carried out with toluene as solvent and ^{31}P nmr as the monitor. Using equimolar quantities of each reactant, a plot of reciprocal concentration vs time gave excellent linearity up to 80% reaction (r > 0.99 throughout) indicating first-order behaviour in each reactant. The second-order rate coefficients at various temperatures are shown in Table II together with the resultant activation parameters which reveal an associative process $\{\Delta S^{\ddagger}(298) = -38$ e.u.$\}$ with a low Arrhenius activation energy $(E_A = 7.4$ kcal mol$^{-1})$ which is similar to the $\Delta S^{\ddagger}$ value (–39 e,u) reported for the quaternisation of tertiary phosphines.[17] Four sulfenate esters $(XC_6H_4SPOCH_2CF_3)$ with X=H, p-Cl, p-Me and p-MeO were than reacted with (7a) in a series of competitive experiments in toluene at 195K in order to evaluate a Hammett ρ value of 1.5 +/– 0.3 {Tables III (nmr data) and IV (rate data)}. This indicates that a moderate degree of negative charge develops on sulphur during the reaction which is consistent with nucleophilic attack by phosphorus on either O (to generate PhS$^-$) or on S (to form $^+$P-S$^-$(Ph)OCH$_2$CF$_3$). It should be noted that with X = p-NO$_2$, only oxyphosphorane (9a) and no thiophosphorane was observed, indicating that either the disproportionation of p-NO$_2$C$_6$H$_4$SP(OCH$_2$CF$_3$)$_4$ was much faster than its formation or that (8a) reacts with a second mole of (6) much faster than its formation *(vide infra)*. A repeat of this competitive rate study in toluene at 195K using the same series of sulfenate esters and PhP(OCH$_2$CF$_3$)$_2$ (7b) gave a ρ value of +1.3 +/– 0.2 (Tables V and VIa) again indicating a moderate degree of negative charge developing on S in reaching the T.S. Another interesting feature about these data is that even though the reaction of (6) with (7b) is ca. 100 times faster than the reaction with (7a) the ρ values remain the same. This emphasises once again that the p value depends on the *nature* of the reactants governing the charge development but as found in other systems,[7,13-15] does not depend upon the rate of the reaction under scrutiny.

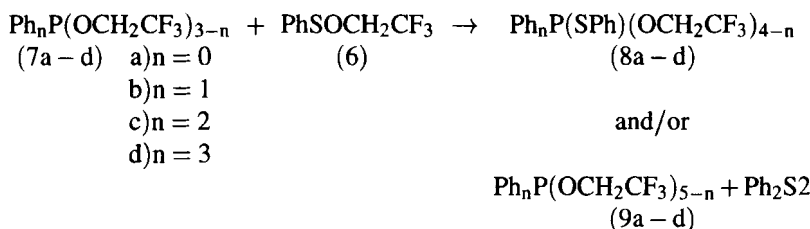$$Ph_nP(OCH_2CF_3)_{3-n} + PhSOCH_2CF_3 \rightarrow Ph_nP(SPh)(OCH_2CF_3)_{4-n}$$

| (7a – d) | a)n = 0 | (6) | (8a – d) |

           b)n = 1

           c)n = 2   and/or

           d)n = 3

$$Ph_nP(OCH_2CF_3)_{5-n} + Ph_2S_2$$
$$(9a - d)$$

TABLE IV Hammett data from a competitive study of the reactions of sulfenate $XC_6H_4SOCH_2CF_3$ and $X'C_6H_4SOCH_2CF_3$ with $P(OCH_2CF_3)_3$ in toluene at 195K[a]

X	X'	k/k'	log k/k'	Δσ	ρ
H	p-MeO	2.22	0.346	0.268	1.29
p-Cl	p-Me	3.15	0.498	0.397	1.25
p-Cl	H	2.72	0.434	0.227	1.91
H	p-Me	1.62	0.209	0.170	1.23
p-Me	p-MeO	1.53	0.184	0.098	1.88
p-Cl	p-MeO	4.71	0.673	0.495	1.36
Average ρ (195K) = +1.5±0.3					

[a] Estimated by ^{31}P nmr of reactants and products (see Table III).

TABLE V Hammett data from a competitive kinetic study of the reactions of sulfenate esters $XC_6H_4SOCH_2CF_3$ and $X'C_6H_4SOCH_2CF_3$ with $PhP(OCH_2CF_3)_2$ in toluene at 195K[a]

X	X'	k/k'	log k/k'	Δσ	ρ
p-Me	p-MeO	1.40	0.147	0.098	1.5
p-Cl	p-MeO	3.84	0.584	0.495	1.2
p-Cl	p-Me	4.13	0.615	0.397	1.6
H	p-Me	1.73	0.238	0.170	1.4
H	p-MeO	1.86	0.269	0.268	1.0
p-Cl	H	1.94	0.287	0.227	1.3
Average ρ (195K) = +1.3 ± 0.2					

[a] Estimated by ^{31}P nmr of reactants and products

TABLE VIab ^{31}P nmr δ values for $XC_6H_4(OCH_2CF_3)_3(SC_6H_4X')$ in C_7D_8

a) X = H					
X' :		H	p-Me	p-MeO	p-Cl
δ [31]P (ppm)		−35.3	−35.2	−35.3	−35.4
b) X' = H					
X :	p-Cl	p-MeO	m-Me	p-Me	p-Me₂N
δ^{31}P (ppm)	−36.1	−35.6	−35.8	−35.9	−35.0

The use of a phosphonite (**7b**) allows the evaluation of ρ from variation of the substituents, X, in the nucleophile, $XC_6H_4P(OCH_2F_3)_2$ again by a competitive kinetic study (Tables VIb and VII). The p value of −2 (+/− 0.4) although not very precise due to the nature of the experiment, indicates a moderate degree of positive charge development on phosphorus in reaching the T.S. and compares with values of −0.34 (Et_2O_2)[7], −0.6 $(PhN=NPh)$[14], −1.1 (Ph_2S_3)[15] and −3.0 (S_8).[13]

The ρ value of -2 for the sulfenate substrate was determined at 195K and although ρ decreases generally with increasing temperature,[18] it is highly unlikely to fall as far as -0.3 at 30° and hence the observed ρ value suggests attack of phosphorus on the sulphur rather than the oxygen of the sulfenate ester. Some additional support for this hypothesis appears from the observation that the reaction of diphenylphosphine (10) with ethyl, methyl or isopropyl benzenesulfenate (11a-c) gives a substantial amount of phenyl diphenylphosphinothioite (12), its oxide (13) and diphenylphosphine oxide (14) but none of the products (15) or (16) associated with displacement of the thiophenate ion followed by deprotonation and reaction with further sulfenate (Scheme 2).
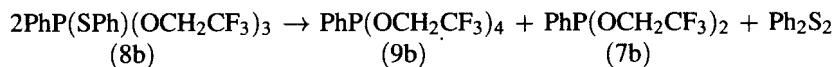
TABLE VII Hammett data from a competitive kinetic study of the reaction of phosphonites $XC_6H_4P(OCH_2CF_3)_2$ and $X'C_6H_4P(OCH_2CF_3)_2$ with $PhSOCH_2CF_3$ in toluene at 195K

X	X'	k/k'	Δσ	ρ
p-Me	m-Me	1.44	0.101	−1.6
p-Me	H	1.07	0.170	−1.9
m-Me	H	1.40	0.069	−2.1
H	p-Cl	3.56	0.227	−2.4
p-Me$_2$N	H	55.9	0.830	−2.1
p-MeO	p-Cl	6.39	0.495	−1.6
p-Me	p-Cl	6.38	0.397	−2.0
m-Me	p-Cl	4.01	0.296	−2.0
Average ρ (195K) = −1.96 ± 0.4				

Kinetics of oxyphosphorane formation.

a) Disproportionation of $PhP(SPh)OCH_2CF_3)_3$.

It proved possible to follow the disproportionation of (8b) to (7b) and (9b) at 40°C in toluene and the values of kobs at three different concentrations (0.23M, 0.32M and 0.45M)of (8b) were 3.6×10^{-4}, 3.7×10^{-4} and 3.6×10^{-4} s^{-1} respectively. Clearly the reaction is first-order in (8b) and therefore the T.S. is unimolecular and the r.l.s. is probably ionisation of the thiophosphorane to a tetraalkoxyphosphonium thiophenate. The subsequent fast reactions may be represented by Scheme 3.

$$2PhP(SPh)(OCH_2CF_3)_3 \rightarrow PhP(OCH_2CF_3)_4 + PhP(OCH_2CF_3)_2 + Ph_2S_2$$
$$(8b) \qquad\qquad\qquad (9b) \qquad\qquad (7b)$$

Ph$_2$PH   +   PhSOR $\longrightarrow$ $\begin{bmatrix} \overset{\displaystyle SPh}{\underset{\displaystyle OR}{Ph_2P-H}} \end{bmatrix}$

(10)   (11a-c)

R = Me, Et, Pr^i

$\begin{bmatrix} Ph_2\overset{+}{P}-H \\ \cdot OR \\ SPh \end{bmatrix}$ $\rightleftharpoons$ $\begin{bmatrix} Ph_2\overset{+}{P}\underset{OR}{\overset{H}{\,}} \quad ^-SPh \end{bmatrix}$

Ph$_2$PSPh   +   ROH   Ph$_2$P(O)H   Ph$_2$P(OR)

(12)   (14)   (15)

|2(11) |(11) |2(11)

Ph$_2$P(O)SPh   Ph$_2$P(O)SPh + ROH   Ph$_2$P(OR)$_3$

(13)   (16)

SCHEME 2

PhP(SPh)(OCH$_2$CF$_3$)$_3$ $\overset{rls}{\rightleftharpoons}$ $\overset{+}{PhP}(OCH_2CF_3)_3$ $^-$SPh

PhS$^-$

$\begin{array}{c} Ph \\ RO \end{array} \overset{SPh}{\underset{OR}{\overset{|}{P}}}$

$\begin{array}{c} Ph \\ RO \end{array} \overset{+}{\underset{OR}{\overset{OR}{\overset{|}{P}}-OR}}$ $\overset{fast}{\longrightarrow}$ PhP(OR)$_4$ +   Ph(OR)$_2$ +   Ph$_2$S$_2$

R = CH$_2$CF$_3$

SCHEME 3

b) Reaction of thiophosphorane (8a n=0) with sulfenate ester.

The rate coefficients for the reaction of the thiophosphorane (8a) with varying concentrations of (6) in toluene @ 30°C are shown in Table VIII. One concludes that the reaction is first-order in thiophosphorane but zero order in sulfenate ester and hence the rate-limiting step again appears to be ionisation of the thiophosphorane followed by rapid reaction with the sulfenate ester (Scheme 4).
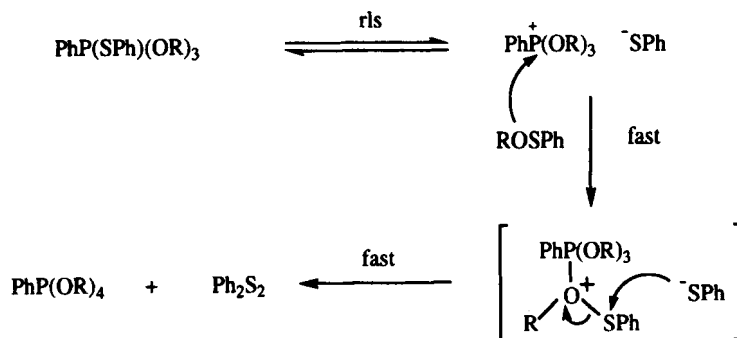
SCHEME 4

TABLE VIII Rate coefficients for the reaction of $PhSP(OCH_2CF_3)_4$ with $PhSOCH_2CF_3$ in toluene at 30°C

$[PhSP(OR)_4]/M$	0.262	0.256	0.235
$[PhSOR]/M$	0.252	0.524	1.17
10^4 kobs (s^{-1})	1.7 ± 0.2	1.7 ± 0.2	2.2 ± 0.3
$R = CH_2CF_3$			

The rates at various temperatures are shown in Table IX along with the resultant activation parameters. These data are not definitive, however, since a $\Delta S^{\ddagger}$ value of -17 +/$-$ 4 cal mol^{-1}K^{-1} could be consistent with an associative or dissociative process. Perhaps the dissociation occurs to an ion-pair rather than the dissociated ions (since the latter would not be supported by toluene) and this would limit the entropy increase from G.S. to T.S. The solvent effect (Table X) suggests a moderate degree of charge development from G.S. to T.S. and this is supported by the Hammett data of Table XI. Variation of the substituent in the thiophenate group showed a rate increase with electron-withdrawing substituents with a ρ value of +2.1 at 30°C. The rates, however, showed hardly any variation with substituents in the sulfenate ester (Table XII). Thus ionisation of the thiophosphorane again appears to be the rate-limiting step and finally this is substantiated by the relative rate of ca. 100 : 1 for $PhP(SPh)(OCH_2CF_3)_3$: $P(SPh)(OCH_2CF_3)_4$ with $PhSOCH_2CF_3$.

TABLE IX Activation parameters for the reaction of $PhSP(OCH_2CF_3)_4$, with $PhSOCH_2CF_3$ in toluene

		[PhSP(OR)₄ =[PhSOR] = 0.26M			
	T(K)	303	308	313	318
	10^4k (s⁻¹)	1.67	3.17	3.67	6.83
Gives :	E_A	$= 18 \pm 2$ kcal mol⁻¹ (r = 0.973)			
	$\triangle G^{\ddagger}_{298} = 22.7$ kcal mol⁻¹				
	$\triangle S^{\ddagger}_{298\ 8} = -17 \pm 4$ cal k-1 mol⁻¹				

TABLE X First-order rate coefficients for the reaction of $PhSP(OCH_2CF_3)_4$ with $PhSOCH_2CF_3$ in toluene/benzonitrile at 305K

% PhCN in PhMe (v/v)	ε (calc) μ	$10^4 k_{obs}$ (s⁻¹)
0	2.4	2.3
8	4.5	3.3
15	6.3	3.7

TABLE XI Hammett data for the reaction of $PhSOCH_2CF_3$ with $XC_6H_4SP(OCH_2CF_3)_4$ in toluene at 303K

X	$10^4 k_1$ (s⁻¹)	σ
p-Cl	3.70	0.227
H	1.57	0
p-Me	0.62	–0.170
p-MeO	0.33	–0.268
Gives : ρ (303) = 2.1 ± 0.2, r = 0.993		

TABLE XII Hammett data for the reaction of $PhSP(OCH_2CF_3)_4$ with $XC_6H_4SOCH_2CF_3$ in toluene at 303K

X	*p-MeO*	*p-Me*	*H*	*p-Cl*	*p-NO₂*
$10^4K_{obs(s^{-1})}$	1.53	1.58	1.57	1.23	1.03

Thus the overall picture for oxyphosphorane formation is of rate-limiting ionisation of the thiophosphorane giving a "phosphonium-like" T.S. which may resemble a tight ion pair rather than solvent separated ions. There follows a fast interaction with a mole of sulphenate ester to give the observed products of oxyphosphorane and disulphide (Scheme 4).

Because the rates of reaction of tricoordinate phosphorus compounds with sulfenate esters are fast and occur in two steps, it is difficult to use the data

reported above to comment on the possible biphilic insertion of P(III) into the S-O bond. A competitive rate study, however, has shown that reaction of a mixture of the tricoordinate phosphorus compounds (17a-d) with a limited quantity of iso-propyl benzenesulfenate (18) in toluene at -78°C shows consumption of the P(III) compounds in the order, $Ph_2POPr^i > PhP(OPr^i)_2 > P(OPr^i)_3 >> Ph_3P$.[19] Apart from the reversal of phosphinite and phosphonite rates this relative rate sequence agrees with that observed by Denney[8] which again suggests that the initial reaction of P(III) with the S-O bond involves a biphilic insertion mechanism.

$$P(OPr^i)_3 + PhP(OPr^i)_2 + Ph_2(OPr^i) + Ph_3P \xrightarrow{\quad PhSOPr^i \quad} \text{mixture of products}$$
$$\;\;(17a)\qquad\quad (17b)\qquad\quad (17c)\qquad\quad (17d)\quad (18)$$
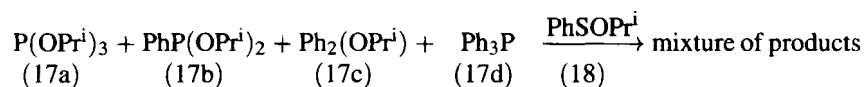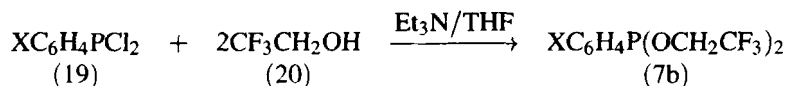
EXPERIMENTAL

^1H, ^{19}F and ^{31}Pnmr spectra were recorded on Bruker HFX90 and Bruker AM 360 instruments generally with C_7D_8 as solvent and either TMS, $CFCl_3$ (ext.) or H_3PO_4 (ext.) as reference. Mass spectra were obtained by the U.L.I.R.S. at the School of Pharmacy, London and elemental analyses were obtained at the School of Pharmacy or University College, London. All solvents were dried by standard methods[20] and stored under nitrogen over molecular sieves (4A) prior to use. Triphenylphosphine was available commercially from Aldrich and all the phosphines were either obtained or synthesised as described earlier.[16]

Preparation of 2,2,2-trifluoroethyl diphenylphosphinite (7c).

A solution of 2,2,2-trifluoroethanol (6.9g,m 69 mol) in THF (30ml) was added dropwise to a stirred solution of diphenylphosphinous chloride (15.0g, 68 mmol) and triethylamine (6.9g, 69 mol) in THF (120ml) under nitrogen at -15°C over a period of 1h. The reaction mixture was allowed to warm to ambient and was stirred for a further 6 h. The precipitated amine hydrochloride was removed by filtration and the volatiles were removed under reduced pressure leaving 15.0g (78%) of a pale yellow oil which was distilled through a 10 cm Vigreux to give the product as a colourless oil of b.p.97-98°C @ 0.7mm (lit[21] 130°C @ 2.5mm); $\delta^{31}P$ (C_6D_6) +125.9; ^1H ($CDCl_3$) 4.15 (dq, $^3J_{PH}$ = 8.0Hz, $^3J_{FH}$ = 8.0Hz, 2H) and 7.55 (m, 10H); ^{19}F ($CDCl_3/CFCl_3$) -75.4 (dt, $^3J_{FH}$ = 8.0Hz, $^4J_{PF}$ = 5.9 Hz).

Preparation of *m*-and *p*-substituted bis(2,2,2-trifluoroethyl) arylphosphonites (7b)

A series of substituted bis(2,2,2,-trifluoroethyl) arylphosphonites (7b) was prepared from the corresponding phosphonous dichloride (19) and trifluoroethanol (20). The general method is described for the parent phosphonite (X=H).

$$XC_6H_4PCl_2 \ + \ 2CF_3CH_2OH \ \xrightarrow{\ Et_3N/THF\ } \ XC_6H_4P(OCH_2CF_3)_2$$
$$(19) \qquad\qquad (20) \qquad\qquad\qquad\qquad (7b)$$

Preparation of bis(2,2,2-trifluoroethyl) phenylphosphonite

A solution of 2,2,2-trifluoroethanol (13.35g, 135 mmol) in THF (25 ml) was added, dropwise under nitrogen to a cooled (−10°C) stirred solution of phenylphosphonous dichloride (11.70g, 65mmol) and triethylamine (13.50g, 134mmol) in THF (100 ml). The mixture was allowed to warm to ambient and stirring was continued for a further 4 h. The precipitated triethylamine hydrochloride was removed by filtration and the volatiles were removed under reduced pressure from the filtrate leaving a yellow oil. This was distilled through a 20cm. Vigreux column to yield 12.9g (65%)of a colourless oil of b.p. 63–64°C @ 0.35mm (lit.[21] 48°C @ 0.1mm). $\delta^{31}P$ (C_6D_6) +166.0; δ^1H ($CDCl_3$) 4.13 (m, 4H) and 7.50 (m, 5H); $\delta^{19}F$ ($CDCl_3/CFCl_3$) − 75.6 (dt,$^3J_{FH}$ = 8.5 Hz, $^4J_{PF}$ = 3.5 Hz).

Preparation of *p*-dimethylaminophenylphosphonous dichloride

Aluminium trichloride (6.0g, 0.045 mol) was added in portions over 2 h at 0°C with stirring under nitrogen to a mixture of phosphorus trichloride (33.2g, 0.24 mol) and N,N-dimethylaniline (22.0g, 0.18 mol). The mixture was stirred at ambient for 3 h and was allowed to stand for a further 15 h. The thick green-brown semi-solid was extracted with boiling 100–120 petroleum ether (3 x 40 ml). After removal of the solvent under reduced pressure there remained 18.3g (46%) of a semi-crystalline yellow material. An analytical sample was prepared by distillation (Kugelrohr) giving, initially, a pale yellow liquid of b.p. 150–160°C @ 0.5mm which crystallised on standing to give a pale yellow solid of m.p. 63–65°C (lit[22] 65–66°C); $\delta^{31}P$ (C_6D_6) + 161.4; δ^1H (C_6D_6) 3.04 (s,6H) and 7.30 (m, 4H).

Preparation of *p*-anisylphosphonous dichloride

A solution of anisole (22.2g, 0.20 mol) and phosphorus trichloride (91.8g, 0.66 mol) containing stannic chloride (8.2g, 0.032 mol) was heated under reflux

for 136 h. At periodic intervals further increments (6g) of the Lewis acid were added (18 , 42, 54 and 64 h). The reaction was monitored by ^{1}H n.m.r. when the anisyl methyl resonance shifted from ca. 3.70 to 3.75 ppm. After 136 h under reflux ca 80% conversion had occurred. The mixture was concentrated under reduced pressure and was distilled through a 10cm. Vigreux column to give the product as a colourless oil of b.p. 99–101°C @ 1 mm (lit.[23] 74–78°C @ 0.05mm); δ^{31}P (CDCl$_3$) +161.8; δ^1H (CDCl$_3$) 3.75 (s,3H) and 7.35 (m, 4H).

All the phosphonous halides were condensed with 2,2,2-trifluoroethanol in an analogous manner to the parent phenylphosphonous dichloride to yield the desired phosphonites. Table XIII reports the yields, boiling points and ^{31}P n.m.r. chemical shifts of the phosphonites and the relative molecular mass of each material was verified by mass spectrometry.

TABLE XIII Yields, boiling points and ^{31}P nmr chemical shifts of the series of bis(2,2,2-trifluoroethyl)phosphonites. $XC_6H_4P(OCH_2CF_3)_2$

Phosphonite	Yield(%)	Boiling points	$\delta^{31}P(CDCl_3)$
X = H	65	63 - 64° @ 0.35 mm	+166.0[a]
X = p-Cl	69	71 - 72° @ 0.01 mm	+165.9
X = m-Me	64	55 - 56° @ 0.03 mm	+167.7[b]
X = p-Me	64	55 - 56° @ 0.03 mm	+167.9[b]
X = p-Me$_2$N	36	120 - 122° @ 0.9 mm	+170.4
X = p-MeO	59	95 - 99° @ 1 mm	+166.9[a]

a The solvent is C_6D_6

b Tentative assignments: the phosphonites were obtained as an equimolar mixture of the m-Me and p-Me isomers and it proved impossible to assign the nmr data unambiguously.

High field ^{1}H n.m.r. spectra of the phosphonites showed that the δ value of the CH$_2$ protons in the 2,2,2-trifluoroethyl groups did not vary with the substituent attached to the aryl ring. In each case a complex multiplet was observed between δ3.90 and δ4.40 in CDCl$_3$. When phosphorus-decoupled the resonances simplified in each case to the expected symmetrical 16-line pattern for an ABX$_3$ spin system. Phosphorus decoupling was also found to simplify the complex AA'BB'X aromatic splitting patterns to a symmetrical four-spin AA'BB'system for the para-disubstituted compounds. It is interesting to note that the splitting pattern virtually collapsed for the p-chloro material (a substituent with a high electron-withdrawing capacity).

The ^{19}F n.m.r. spectra of each phosphonite gave a simple six-line pattern (doublet of triplets) with no variation in δ^{19}F across the series. Pertinent ^{1}H and ^{19}F n.m.r. data are presented in Table XIV for reference.

TABLE XIV ^{1}H and ^{19}F nmr data of the series of bis(2,2,2-trifluoroethyl)-arylphosphonites XArP(OCH$_2$CF$_3$)$_2$

| Phophonite	$\delta^1 H(CDCl_3)$	$\delta^{19}F$ (CDCl$_3$/CFCl$_3$)
X = H	7.30 - 7.70 (*m*, 5H)	−75.6 (*dt*, $^3J_{FH}$= 8.5 Hz, $^4J_{PF}$ = 3.5 Hz)
X = *p*-Cl	7.40 - 7.60 (*m*, 4H)	−75.6 (*dt*, $^3J_{FH}$ = 8.4 Hz, $^4J_{PF}$ = 3.8 Hz)
X = *m*-Me	2.40 (*s*, 3H) and	−75.6 (*dt*, $^3J_{FH}$ = 8.5 Hz, $^4J_{PF}$ = 3.4 Hz)
	7.25 - 7.50 (*m*, 4H)	
X = *p*-Me	2.40 (*s*, 3H) and	−75.6 (*dt*, $^3J_{FH}$ = 8.5 Hz, $^4J_{PF}$ = 3.4 Hz)
	7.30 - 7.60 (*m*, 4H)	
X = *p*-MeO	3.21 (*s*, 3H) and	−75.6 (*dt*, $^3J_{FH}$ = 8.4 Hz, $^4J_{PF}$ = 3.5 Hz)
	7.20 - 7.60 (*m*, 4H)	
X = *p*-Me$_2$N	3.00 (*s*, 6H) and	−75.6 (*dt*, $^3J_{FH}$ = 8.5 Hz, $^4J_{PF}$ = 3.3 Hz)
	7.10 - 7.55 (*m*, 4H)	

Preparation of tris(2,2,2-trifluoroethyl) phosphite

A mixture of 2,2,2-trifluoroethanol (15.3g, 0.153 mol) and phosphorus trichloride (7.0g, 0.051 mol) was stirred under an atmosphere of nitrogen in a roundbottom flask fitted with a reflux condenser . Hydrogen chloride gas was expelled vigorously at the beginning. The reaction vessel was heated to 80–90°C for 4 h, cooled to ambient and allowed to stand for 14 h. The mixture was then distilled through a 20cm.Vigreux column to give 11.5g (71%) of a light, colourless oil of b.p. 65–67°C @ 16mm (lit.[21] 130–131°C @ 743mm). δ^{31}P (CDCl$_3$) + 139.1; δ^1H (CDCl$_3$) 4.24 (dq, $^3J_{PH}$ = 8.2 Hz, $^3J_{FH}$ = 8.2 Hz); δ^{19}F (CDCl$_3$) - 75.9 (dt, $^3J_{FH}$ = 8.2Hz, $^4J_{PF}$ = 4.5Hz).

Tri-isopropylphosphite, di-isopropyl phenylphosphonite and isopropyl diphenylphosphinite were prepared as described earlier.[15]

Preparation of 2,2,2-trifluoroethyl arylsulfenate esters (6)

In each case the sulfenate esters were prepared by the condensation of the corresponding sulfenyl chloride with 2,2,2-trifluoroethanol.

$$XC_6H_4SCl \quad + \quad CF_3CH_2OH \xrightarrow{Et_3N/THF} XC_6H_4SOCH_2CF_3$$
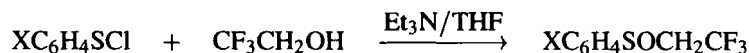
The sulfenyl chlorides were prepared by chlorination of the corresponding diaryl disulphides or arylthiols. Examples of each method are given below.
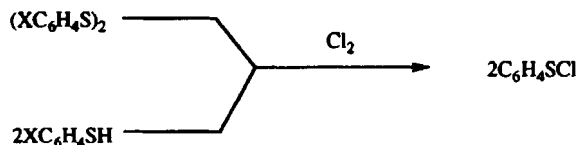
Preparation of benzenesulfenyl chloride

Chlorine gas was bubbled through a cooled (–20°C) solution of diphenyl disulphide (90g, 0.42 mol) in carbon tetrachloride (500 ml) in a vessel equipped with a cold (–78°C) finger. The progress of reaction was monitored by ^{1}H n.m.r. On completion of the reaction the volatiles were removed under reduced pressure and the residue was distilled to yield 113g(93%) of a deep red fuming liquid of b.p. 82–83°C @ 9mm (lit.[23] 50–54°C @ 2.5 mm); δ^1H (CDCl₃) 7.50 (m).

An analogous procedure was used to prepare p-tolylsulfenyl chloride (X = p-Me) in a 98% yield as a deep red liquid, δ^1H (CDCl₃) 2.33 (s, 3H) and 7.35 (m). The crude product was used without further purification.

p-Nitrophenylsulfenyl chloride (X=p-NO₂) was synthesised using the same method except that it was necessary to warm the reaction mixture to 60–70°C. The crude product was obtained as a low melting orange solid in an 85% yield, m.p 45–50°C(lit.[24] 52°C); δ^1H (CDCl₃) 7.85 (m). The material was used without any further purification.

Preparation of p-chlorophenylsulfenyl chloride

A solution of p-chlorothiophenol (10.0g, 69 mmol) in carbon tetrachloride (100 ml) was added, dropwise, to a cooled (0°C) saturated solution of chlorine in carbon tetrachloride (200ml). The solvent and excess chlorine were removed under reduced pressure and the residue was distilled to give 11.2g (90%) of a red liquid, b.p. 66–68°C @ 2mm (lit[25] 94°C @ 6mm); δ^1H (CDCl₃) 7.45 (m).

p-Anisylsulfenyl chloride (X=p-MeO) was prepared using an analogous method in a 98% yield as a deep red liquid, δ^1H (CDCl₃) 3.83 (s, 3H) and 7.31 (m, 4H). The crude product was used without further purification.

Preparation of 2,2,2-trifluoroethyl benzenesulfenate

Phenylsulfenyl chloride (60g, 0.414 mol) was added, dropwise over 2 h to a stirred solution of 2,2,2-trifluoroethanol (41.4g 0.414 mol) and triethylamine (41.9g, 0.415 mol) in THF (500 ml) at –30°C under an atmosphere of nitrogen. The reaction mixture was allowed to warm to ambient and stirring was continued for a further 30 mins. After filtration of the precipitated amine hydrochloride and removal of the remaining volatiles from the filtrate in vacuo, there remained a yellow oil. This was distilled through a 10cm Vigreux column to give 72.6g (84%) of the product as a pale yellow oil, b.p. 39–40°C @ 0.02mm (lit.[9] 47°C @ 0.05 mm).

The same experimental procedure was used in the synthesis of five substitued analogues. The corresponding boiling points, yields and spectroscopic data appear in Table XV. The molecular weight of each compound was verified by mass spectrometry.

Reaction of (6) with (7a-d)

a. For n=1–3 (**7b-d**)

To a solution of 2,2,2-trifluoroethyl benzenesulfenate (0.2g, 0.96 mmol) in deuteriotoluene (1.5ml) was added, dropwise with stirring at –78°C, a solution of the tricoordinated phosphorus nucleophile (0.48 mmol) in deuteriotoluene (1.5ml). The mixture was allowed to warm to ambient and ^1H, ^{31}P and ^{19}F n.m.r. spectra were recorded which were consistent with the formation of a single product (Table XVI).

b. For n =0 (**7a**)

i.   To a solution of 2,2,2-trifluoroethyl benzenesulfenate (0.1g, 0.48 mmol) in deuteriotoluene (1.5 ml) was added, dropwise with stirring at –78°C, a solution of tris(2,2,2-trifluoroethyl) phosphite (0.157g,0.48 mmol) in deuteriotoluene (1.5ml). The mixture was allowed to warm to ambient and ^1H,^{31}P and ^{19}F n.m.r. spectra were recorded which were consistent with the formation of a single thiophosphorane product (**8a**, Table 16).

ii. To a solution of 2,2,2-trifluoroethyl benzenesulfenate (0.2g, 0.96 mmol) in deuteriotoluene (1.5 ml) was added dropwise with stirring at –78°C, a solution of tris(2,2,2-trifluoroethyl) phosphite (0.157g,0.48mmol) in deuteriotoluene (1.5ml). The mixture was allowed to warm to ambient and was stirred for 12 h. ^1H,^{31}P and ^{19}F n.m.r. spectra were recorded which were consistent with the formation of a single pentaoxaphosphorane product (**9a**, Table 16).

Thiophenyltetrakis(2,2,2-trifluoroethoxy)phosphorane (**8a**) and penta(2,2,2 trifluoroethoxy)phosphorane (**9a**) were synthesised and isolated in 67 and 75% yields respectively using the method described by Denney[9], b.p. 101–2°C @ 1.1mm (lit.[9] 72°C @ 0.15mm) and 55–56°C @ 0.7mm (lit[9], 44°C @ 0.15mm) respectively.

Series of bis(2,2,2-trifluoroethoxy)trisarylphosphoranes (**9d**) and tetrakis(2,2,2-trifluoroethoxy)arylphosphoranes (**9b**) were prepared as described above and the ^{31}P nmr data of the products are reported in reference 16.

TABLE XV Yields, boiling points and spectroscopic data of the series of 2,2,2-trifluoroethyl-arylsulfenates $XArSOCH_2CF_3$

Sulphenate	% Yield	Boiling point	$\delta^1H(CDCl_3)$	$\delta^{19}F(C_6D_6/CFCl_3)$
X = H	84	39 - 40° 0.02 mm[a]	3.98 (q, $^3J_{HF}$ = 8.5 Hz, 2H) and 7.40 (m, 5H)	-74.5 (t, $^3J_{HF}$ = 8.5 Hz)
X = p-NO$_2$	48	140 - 150° 0.2 mm[b]	4.18 (q, $^3J_{HF}$ = 8.3 Hz, 2H) and 7.80 (m, 4H)	-74.6 (t, $^3J_{HF}$ = 8.3 Hz)
X = p-Cl	76	78-80° 2 mm[a]	4.06 (q, $^3J_{HF}$ = 8.4 Hz, 2H) and 7.40 (m 4H)	-74.5 (t, $^3J_{HF}$ = 8.4 Hz)
X = p-Me	64	78-80° 1.5 mm[a]	2.39 (s, 3H), 4.00 (q, $^3J_{HF}$ = 8.5 Hz) and 7.35 (m, 4H)	-74.5 (t, $^3J_{HF}$ = 8.5 Hz)
X = pMeO	60	72-72° 0.1 mm[a]	3.81 (s, 3H), 3.98 (q, $^3J_{HF}$ = 8.6 Hz, 2H) and 7.25 (m, 4H)	-74.4 (t, $^3J_{HF}$ = 8.6 Hz)

[a] Products obtained as pale yellow oils
[b] Kugelrohr distillation : product obtained as a low melting yellow solid

TABLE XVI Spectroscopic data of the phosphoranes resulting from the treatment of acyclic P(III) nucleophiles with $PhSOCH_2CF_3$

Phosphoranes	$\delta^{31}P(C_7D_8)$	$\delta^1H(C_7D_8)$	$\delta^{19}F(C_7D_8)$
Ph$_3$P(OCH$_2$CF$_3$)$_2$	-59.1	2.95 (dq^3J_{PH} = 4.5 Hz, $^3J_{FH}$ = 8.8 Hz 4H) and 7.10 - 8.35 (m, 15 H)	-75.3 (t)
Ph$_2$P(OCHCF$_3$)$_3$	-44.5	3.80 (mound[a], 6H) and 7.20 - 8.10 (m, 10H)	-74.4 (mound[a], 2F) -75.4 (mound[a], 1F)
PhP(OCH$_2$CF$_3$)$_4$	-61.3	4.10 (dq, $^3J_{PH}$ = 5.0 Hz, $^3J_{FH}$ = 8.4 HZ, 8H) and 7.20 - 7.85 (m, 5H)	-75.2 (t)
P(OCH$_2$CF$_3$)$_5$	-77.2	4.22 (dq, $^3J_{PH}$ = 8.2 Hz, $^3J_{FH}$ = 8.2 Hz)	-75.7 (t)
PhSP(OCH$_2$CF$_3$)$_5$	-52.6	4.15 (dq, $^3J_{PH}$ = 8.2 Hz, $^3J_{FH}$ = 8.2 Hz, 8H) and 7.40 - 7.75 (m, 5H)	-75.3 (t)

[a] Broad peaks due to slow ligand reorganisation on the nmr time scale

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