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The Kinetics and Mechanism of the Reaction of Tricoordinate Phosphorus Compounds with Diaryl Trisulfides

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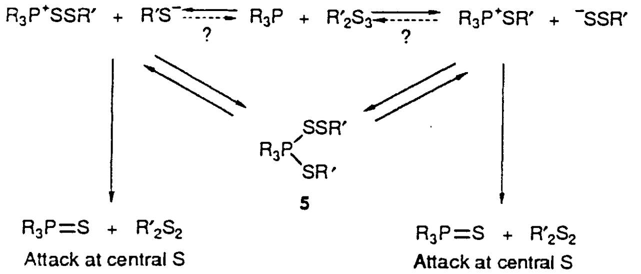
Kinetic data and activation parameters are reported for the reaction of a series of tricoordinate phosphorus compounds, $[\mathrm{Ar}_n\mathrm{P(OR)}_{3-n}]$, with diaryl trisulfides. The second-order rate coefficients for series of arylphosphines, phosphinites and phosphonites, correlate with the Hammett σ constants of the aryl substituents with ρ values of -1.1, -1.1 and -1.1 respectively and these results are discussed in terms of a biphilic mechanism analogous to that proposed for the reaction of tricoordinate phosphorus with S_8.

Tricoordinate phosphorus compounds are powerful nucleophiles[1] and their reactions with a wide variety of electrophilic substrates such as alkyl halides,[2] peroxides,[3] sulfenate esters[4] and S_8[5] have been investigated extensively over the past twenty years. The desulfurisation of dialkyl and diaryl trisulfides,[6] eqn. (1), have featured prominently in these studies and although the

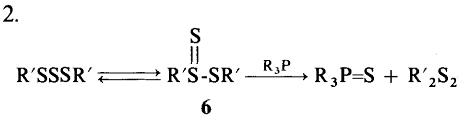
$$\underset{\mathbf{1}}{R_3P} + \underset{\mathbf{2}}{R'SSSR'} \longrightarrow \underset{\mathbf{3}}{R_3P{=}S} + \underset{\mathbf{4}}{R'SSR'} \qquad (1)$$

R = alkyl, aryl and dialkylamino; R^1 = alkyl or aryl.

reaction is in principle a simple extrusion of sulfur its mechanism is complicated by a number of features including (i) the site of initial attack by phosphorus at either central or terminal sulfur (Scheme 1); (ii) the possibility of pentacoordinate intermediates (**5**) containing two phosphorus–sulfur bonds; (iii) the potential reversibility of the first step and (iv) the possibility of reaction occurring through a thiosulfoxide intermediate (**6**),[7] Scheme 2.



Scheme 1



$$R'SSSR' \rightleftharpoons R'\overset{\overset{\displaystyle S}{\|}}{S}\text{-}SR' \xrightarrow{R_3P} R_3P{=}S + R'_2S_2$$

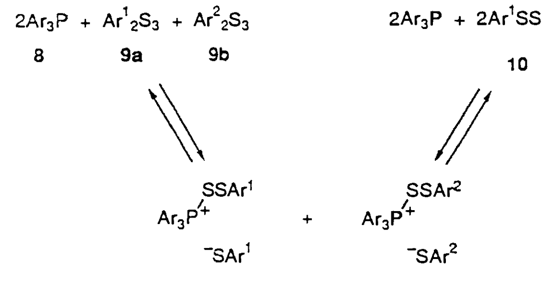
6

Scheme 2

Hence, in a continuation of earlier studies in this area, we undertook a kinetic investigation of the reaction of diphenyl trisulfide with a range of tricoordinate phosphorus compounds, $\mathrm{Ar}_n\mathrm{P(OR)}_{3-n}$(**7**), from phosphines (n = 3) to phosphites (n = 0). The objective was to assess the effect of structural variations within the nucleophile on (i) the reaction rate for n = 0–3 and (ii) the Hammett ρ values for reactions involving **7** with n = 1–3.

Results and Discussion

Reactions of Triaryl Phosphines with Ph_2S_3.—The reaction of triaryl phosphines (**1**; R = aryl) with diphenyl trisulfide (**2**; R′ = Ph) gives rise to the corresponding triarylphosphine sulfides (**3**; R = aryl) as the exclusive phosphorus-containing products with δ ^{31}P *ca.* +40 ppm. The use of radiochemically-labelled sulfur has already shown that with diaryltrisulfides attack occurs at the central S atom.[8] The kinetics were followed by observing the disappearance of (**2**; R′ = Ph) at λ = 350 nm and, as reported previously, were found to obey a second-order rate law consistent with rate-limiting attack by **1** on **2**. The second-order rate coefficient for R = Ph was in close agreement with that obtained by Feher[9] and there was no evidence for the formation of pentacoordinate species by ^{31}P NMR spectroscopy. The latter observation is not surprising in view of the known instability of acyclic arylthiophosphoranes which apparently fragment to generate tricoordinate phosphorus and disulfides.[10] In turn, however, this finding suggests that the initial reaction between tricoordinate phosphorus and diaryl trisulfides (and disulfides) is, at least in principle, a reversible process. In order to establish reversibility in the reaction with triarylphosphines it was necessary to detect unreacted mixed diaryl trisulfides in a reaction mixture containing an excess of two symmetrical trisulfides (Scheme 3). This experiment has now been accomplished using a 1:1:1 molar mixture of di-*p*-tolyl trisulfide (**9a**; Ar^1 = *p*-tolyl), di-β-naphthyl trisulfide (**9b**; Ar^2 = β-naphthyl) and triphenyl phosphine (**8**; Ar = Ph) in toluene at 0 °C for 2 h, then at ambient temperature for 30 min. Control experiments established that mixtures of the trisulfides in toluene did not disproportionate and that **8** reacted cleanly with **9a** or **9b** in toluene to form triphenylphosphine sulfide and the respective diaryl disulfides. A 1:1 molar mixture of **9a** and **9b** with 1 mol of **8** also gave triphenylphosphine sulfide by ^{31}P NMR spectroscopy but at the end of the reaction, examination of the mixture by HPLC revealed three peaks (A–C) in the region of the trisulfides. A combination of LC/MS then showed that peaks A and C corresponded to the original trisulfides **9a** and **9b**, respectively whereas peak B corresponded to the mixed



Scheme 3

Table 1 Data for the reaction of *p*-tolyl diphenylphosphinothioite (2 mol) with diphenyl trisulfide (1 mol) in toluene at 25 °C

Compound	δ^{31}P (ppm)	%[a]
Ph_2PS*p*-Tol	34.7	66
Ph_2PSPh	33.4	34
$Ph_2P(S)S$*p*-Tol	65.2	66
$Ph_2P(S)SPh$	65.3	34

[a] Estimated approximately from peak heights and integrals of the NMR signals.

Table 2 Second-order rate coefficients for the reactions of triarylphosphines with diphenyltrisulfide in toluene at 25 °C

$(XC_6H_4)_3P$	$k_2/10^{-3}$ dm^3 mol^{-1} s^{-1}	σ
3X = *p*-Me_2N	1698	−2.49
X = *p*-Me_2N, 2X = H	14.6	−0.83
3X = *p*-MeO	36.0	−0.81
2X = *p*-MeO, X = H	11.2	−0.54
3X = *p*-Me	6.04	−0.51
X = *p*-MeO, 2X = H	2.5	−0.27
3X = *m*-Me	6.72	−0.21
3X = H	6.0	0.00
3X = *p*-F	1.22	+0.19
3X = *p*-Cl	0.480	+0.69
3X = *m*-Cl	0.114	+1.10

trisulfide **10** ($Ar^1 = p\text{-}CH_3C_6H_5$, $Ar^2 = \beta\text{-}C_{10}H_7$) with a parent peak at 314 amu. These findings demonstrate that the initial nucleophilic attack of phosphorus on central (or terminal) sulfur *may* be reversible but there is an alternative explanation. If the initial attack of the tricoordinate phosphorus on the trisulfide produces a solvent-separated ion pair, the resultant thiol anion may attack unreacted trisulfide to generate a mixed trisulfide (Scheme 4). This hypothesis was checked by

$$Ar_3P + Ar^1{}_2S_3 \rightleftharpoons Ar_3P^+SSAr^1\ {}^-SAr^1$$

$$Ar^1S^- + Ar^2{}_2S_3 \longrightarrow Ar^1SSSAr^2 + {}^-SAr^2$$

Scheme 4

mixing a solution of benzyltriphenylphosphonium β-naphthyl thioate in toluene (generated as shown in Scheme 5) with

$$Ph_3P^+CH_2Ph\ Br^- + Bu^nLi \longrightarrow Ph_3\overset{+}{P}\text{–}\overset{-}{C}HPh$$

$$Ph_3\overset{+}{P}\text{–}\overset{-}{C}HPh + \beta\text{-}C_{10}H_7SH \longrightarrow Ph_3PCH_2Ph\ {}^-S\text{–}\beta\text{-}C_{10}H_7$$

Scheme 5

diphenyl trisulfide (molar ratio *ca.* 1:10) and recording the resultant LC/MS. The mixed β-naphthylphenyl trisulfide was observed at a parent mass of 300 amu and a molar concentration level of *ca.* 9%, thus demonstrating that this route could also afford the mixed trisulfide.

Further evidence of reversibility was obtained from the reaction of an aryl diphenylphosphinothioite (**11**) with a trisulfide (**2**; R′ = Ph) and the results of this study are shown in Table 1 and rationalized in Scheme 6. The observation of the anticipated statistical quantity of Ph_2PSPh in the unreacted portion of the tricoordinate phosphorus compound suggests that the initial reaction, whether attack on central or terminal sulfur, is reversible. This conclusion is reinforced by the observation that both $Ph_2P(S)SPh$ and $Ph_2P(S)S$-*p*-Tol, which probably originated as depicted in Scheme 6, are formed as products, It is again possible, however, that the reaction of thiophenate anion with unreacted *p*-tolyl diphenylphosphinothioite gives rise to the observed phenyl diphenylphosphinothioite. This was checked by reacting the *p*-toluenethiolate ion (generated from the ylide and *p*-tolSH as shown in Scheme 5) with phenyl diphenylphosphinothioite (δ = 33.7) in toluene when Ph_2PS-*p*-tol (δ = 34.7) was produced immediately.

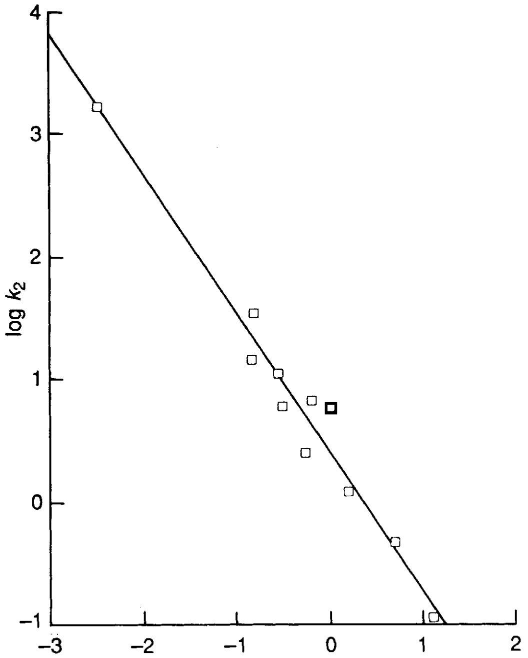
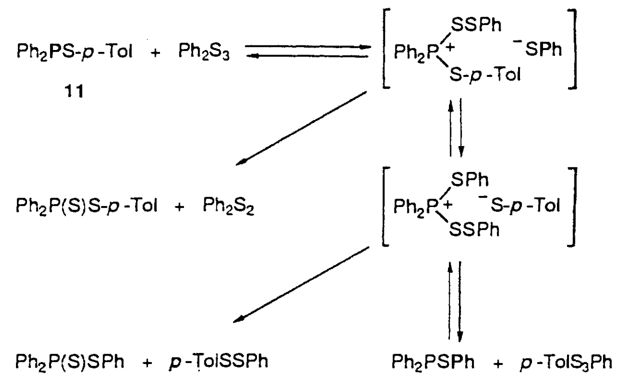


Fig. 1 The Hammett plot of log k_2 *vs.* σ for the reaction of triaryl phosphines with diphenyl trisulfide in toluene at 25 °C



Scheme 6

Thus, in summary, the data suggests, but does not prove, reversibility in the alkyl diarylphosphinite and dialkyl arylphosphonite series. Ultimately the reversibility would depend on the relative rates of the second step (formation of the thiophosphoryl or phosphoryl bonds) *vs.* the rate of the reverse of the initial nucleophilic attack.

The rates of reaction of a series of triaryl phosphines with diphenyl trisulfide were determined (Table 2) and a Hammett correlation with the σ-constants of the aryl substituents was established from which a ρ value of −1.1 (±0.1) was derived (Fig. 1). The negative ρ-value is indicative of a moderate degree of positive charge developing on phosphorus in the transition state (TS) and may be compared with the ρ values of +0.98 and +1.04 obtained for the reactions of *para*-substituted diaryl trisulfides with triphenylphosphine and tris(diethylamino) phosphine, respectively.[8,9] Assuming the transmission coefficients for phosphorus and sulfur are similar it is clear that, as one might anticipate, the same degree of (opposite) charge is developing on phosphorus and sulfur and that there must be a polar component to the reaction. It should be noted at this point that despite the similarity in ρ values (*i.e.* charge development in the transition states) the rates for $(Et_2N)_3P$ relative to Ph_3P

Table 3 Products of the reactions of phosphinites, phosphonites and phosphites with diphenyltrisulfide

PIII Compounds	Products	δ^{31}P	%[a]
Ph_2POPr^i	$Ph_2P(S)OPr^i$	+78.6	89
	$Ph_2P(O)OPr^i$	+28.2	11
$PhP(OPr^i)_2$	$PhP(S)(OPr^i)_2$	+84.2	94
	$PhP(O)(OPr^i)_2$	+16.9	6
$P(OPr^i)_3$	$(Pr^iO)_3P{=}S$	+66.1	87
	$(Pr^iO)_3P{=}O$	+4.5	13

[a] Estimated approximately from peak heights and integrals of the ^{31}P NMR signals.

Table 4 Second-order rate coefficients and activation parameters for the reactions of isopropyl diphenylphosphinite and diisopropyl phenylphosphonite with diphenyl trisulfide in toluene[a]

Ph_2POPr^i [b]		$PhP(OPr^i)_2$ [c]	
T/°C	k_2/dm^3 mol^{-1} s^{-1}	T/°C	k_2/dm^3 mol^{-1} s^{-1}
15.5	0.77	24.0	0.88
24.5	1.33	30.0	1.09
35.0	2.03	38.5	1.47
48.0	3.09	47.5	2.35

[a] k_2 (298 K) for $Ph_3P + Ph_2S_3 = 6 \times 10^{-3}$ dm^3 mol^{-1} s^{-1}; k_2 (298 K) for $P(OPr^i)_3 + Ph_2S_3 = 6 \times 10^{-4}$ dm^3 mol^{-1} s^{-1}. [b] $E_a = 7.8$ kcal mol^{-1}; $\Delta S^{\ddagger}_{298} = -34$ cal mol^{-1} K^{-1}; $\Delta G^{\ddagger}_{298} = 17.3$ kcal mol^{-1}; k_2 (298) = 1.26 dm^3 mol^{-1} s^{-1}. [c] $E_a = 7.7$ kcal mol^{-1} $\Delta S^{\ddagger}_{298} = -35$ cal mol^{-1} K^{-1}; $\Delta G^{\ddagger}_{298} = 17.5$ kcal mol^{-1}; k_2 (298) = 0.89 dm^3 mol^{-1} s^{-1}.

Table 5 Solvent sensitivity for the reaction of $PhP(OPr^i)_2$ with Ph_2S_3 at 25 °C

% CH_3CN in C_7H_8 (v/v)	k_2/dm^3 mol^{-1} s^{-1}
0	0.95
1	1.68
2	2.04
3	2.63
5	3.23
10	6.06
15	11.8
30	25.2

Table 6 Second-order rate coefficients for the reactions of diarylphosphinites and arylphosphonites with diphenyltrisulfide in toluene at 25 °C

Phosphinites

$(XC_6H_4)_2POPr^i$	$k_2/10^{-3}$ dm^3 mol^{-1} s^{-1}	σ[a]
2X = p-CF_3	136	+1.1
2X = H	1 350	0.00
2X = p-SMe	2 320	−0.1
2X = m-Me	1 885	−0.14
X = p-OMe, X = H	2 988	−0.27
X = p-OPr^i, X = H	3 510	−0.37[b]
2X = p-OMe	7 330	−0.54
2X = p-OPr^i	11 890	−0.74[b]

Gives: $\log k_2 = -1.06\sigma + 3.03$ $r = 0.99$

Phosphonites

$XC_6H_4P(OPr^i)_2$	$k_2/10^{-3}$ dm^3 mol^{-1} s^{-1}	σ
X = p-CF_3	251	+0.54
X = p-Cl	437	+0.23
X = H	1 072	0.00
X = p-Me	1 000	−0.17
X = p-OMe	2 291	−0.27
X = p-OPr^i	2 291	−0.37[b]
X = p-NMe_2	6 761	−0.83

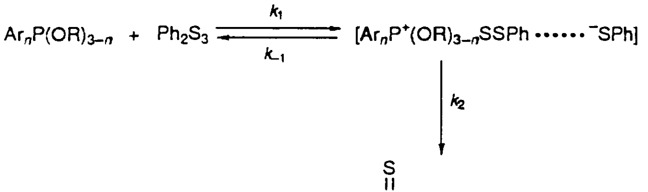
Gives: $\log k_2 = 1.07\sigma + 2.96$ $r = 0.98$

[a] Values from (i) D. H. McDaniel and H. C. Brown, *J. Org. Chem.*, 1958, **23**, 420 and (ii) V. A. Pal'm, *Russ. Chem. Rev.*, 1961, **30**, 471. [b] There is a considerable discrepancy in the values of σ quoted for p-OPr^i; the value used is an average of those quoted (−0.28 and −0.45).

with a given disulfide are in the range from 3.3–11, *i.e.* rate differences do not result in different ρ-values.

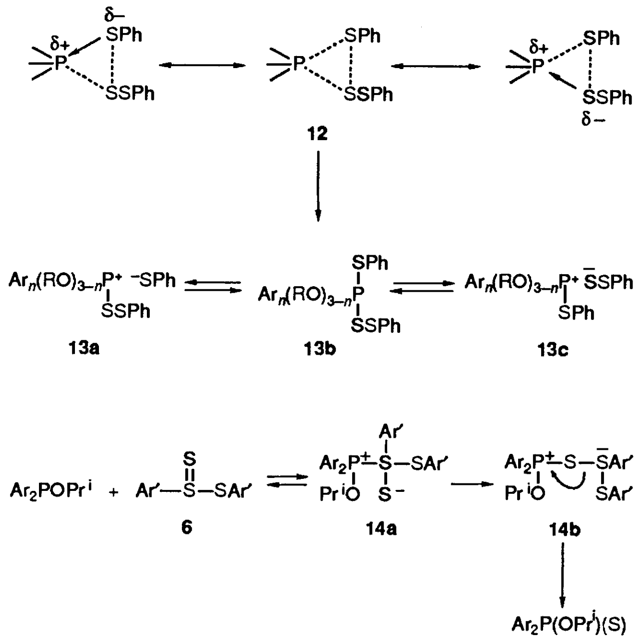
Reactions of Phosphinites, Phosphonites and Phosphites with Ph_2S_3.—In contrast to Harpp's findings for the reaction of phosphites with diaryl trisulfides[11] only one type of product (the thiophosphoryl compound) was observed by ^{31}P NMR spectroscopy when either Ph_2POPr^i, $PhP(OPr^i)_2$ or $P(OPr^i)_3$ was allowed to react with diphenyl trisulfide (Table 3) and there was no sign of the possible de-alkylation products [*e.g.*, $Ph_2P(O)SPh$ or $Ph_2P(O)SSPh$]. The difference between these results and those reported by Harpp may be due to the use of toluene rather than THF as solvent, which suggests that in toluene the reactions proceed within the solvent cage and without the solvent separation of arenethiol anions necessary to effect the de-alkylation. The LC/MS data on these systems, however, are analogous to those found with phosphines, *i.e.* some mixed trisulfide is formed, which is consistent with a degree of reversibility but may also be explained by reactions of the intermediate ions with Ph_2S_3. In any event, apart from a trace of adventitious oxidation of tricoordinate phosphorus, the reactions were very clean and therefore suitable for kinetic investigations.

The kinetic data for the reactions of Ph_2POPr^i, $PhP(OPr^i)_2$ and $P(OPr^i)_3$ with diphenyl trisulfide in toluene over a range of temperature are presented in Table 4 together with the derived activation energy data. The high negative entropies of activation denote a high degree of order in a bimolecular transition state and are very similar to those obtained for the reaction of triphenylphosphine with Ph_2S_3 and the reaction of trisdiethylaminophosphine with dialkyl and diaryl trisulfides. The solvent effect for the $PhP(OPr^i)_2/Ph_2S_3$ reaction is reported in Table 5 and is clearly between that observed for the reactions of tricoordinate phosphorus compounds with either dialkyl peroxide (virtually no rate enhancement in pure acetonitrile relative to toluene) or S_8 (25 fold rate enhancement in 15% v/v CH_3CN/C_7H_8). The results suggest a moderately polar transition state and in order to confirm this conclusion Hammett ρ values were obtained for a series of diarylphosphinites and a series of arylphosphonites (Table 6). Once again the correlations were with the σ values of the aromatic substituents and both types of tricoordinate phosphorus gave ρ values of −1.1 indicating a moderate degree of positive charge developing on phosphorus in the TS and entirely in accord with the moderate solvent effect. The crucial observation, however, is that once again, despite rate differences of *ca.* 200:1 (phosphinites:phosphines), the ρ-values for the three types of tricoordinate phosphorus remain the same. This is precisely analogous to the observations with diethyl peroxide and S_8 as substrates and in common with these latter two substrates the rate sequence of $Ar_2POPr^i > ArP(OPr^i)_2 \gg Ar_3P$ or $(Pr^iO)_3P$ is again observed which is quite different to the rate sequence observed for S_N2 attack at tetrahedral carbon for which $Ph_3P > Ph_2POR > PhP(OR)_2 > P(OR)_3$.[2] Once again the anomalous rate sequence and the constancy of the ρ values may be explained by a degree of back donation from sulfur to phosphorus in the TS so that irrespective of the degree of bond formation or cleavage in the TS the charge development on phosphorus and sulfur would remain the same. This would be equivalent to a biphilic mechanism with a moderate degree of polar character to the P–S bonds of the TS as represented by the resonance hybrid **12**. Furthermore, this could lead to an equilibrium mixture of three intermediates, as represented by **13** and hence to the thiophosphoryl products. It should be noted that this interpretation has been disputed recently for the desulfurisation of disulfides in aqueous alcoholic media.[12] The other explanation for the constant ρ values which deserves consideration is a mechanism involving reversible formation of a phosphonium ion-pair intermediate followed by rate limiting collapse of the ion-pair to products (Scheme 7). If $k_{-1} \gg k_2$, the observed second-order rate coefficient becomes a composite term ($k_{obs} = K_1k_2$) in which ρ for K_1 would be negative but ρ for k_2 positive (for variation of the substituents on P) so that ρ (observed) = ($\rho_1 + \rho_2$) is balanced over the range of phosphorus compounds for any substrate. We were unable to find any evidence for reversibility in the peroxide reaction, and there is no probe for reversibility in the S_8 reaction. In the trisulfide reaction however, evidence which is consistent with reversibility is available (*vide supra*). All the evidence available from the Arbusov reaction, however, indicates that with phosphinites, phosphonites and phosphites, the dealkylation step and therefore by analogy, the desulfurisation step, is much faster than the nucleophilic attack,[13] *i.e.* $k_2 \gg k_{-1}$.



Scheme 7

Finally, the intermediacy of **6** cannot be entirely discounted, although liquid chromatography was unable to detect an isomer being present in the starting trisulfides. Reaction with tricoordinate phosphorus (*e.g.* phosphinites) presumably would form either **14a** or **14b** neither of which would respond to the test for reversibility but would lead *via* **14b** to products (Scheme 8).



Scheme 8

Experimental

Routine ^{1}H and ^{31}P (^{1}H decoupled) NMR spectra were obtained on a Bruker WM 250 spectrometer with either CDCl$_3$ or C_7D_8 as solvents. UV spectra were recorded on Unicam SP800, SP6-400 or Unicam SP1700 instruments using a thermostatic water bath (±0.5 °C) to maintain constant temperature in the cells during kinetic studies.

HPLC analyses were carried out on a Perkin-Elmer dual pump system fitted with an auto-injector (ISS 100), UV detector (LC-75) and computing integrator (LC-100). The column (15 cm × 4.6 mm ID) was packed with Spherisorb S3CN and the analyses were performed at a flow rate of 1 cm^3 min^{-1} using 4% CH_2Cl_2 in n-hexane as eluent and a detector set at λ = 254 nm.

The HPLC/MS data were acquired using a Vestec VT201, dedicated LC/MS system and processed using a Tecnivent Model 1050 interface. The column and the conditions were identical to those used for the LC analyses described above. After the reaction of 1 mol of triphenyl phosphine with an equimolar mixture of *p*-tol$_2$S$_3$ and β-nap$_2$S$_3$ in toluene, the LC trace of the mixture showed three peaks with retention times of 2.7 min (peak A), 3.1 min (peak B) and 3.65 min (peak C). The mass spectrum of each of these peaks (from the LC/MS experiment) showed: for component A, a base peak at 246 (*p*-tol$_2$S$_2$) and a parent peak at 278 amu (*p*-tol$_2$S$_3$); for component B, a base peak at 282 (*p*-tolS$_2$β-nap) and a parent peak at 314 amu (*p*-tolS$_3$-β-nap); and for component C, a base peak at 318 (β-nap$_2$S$_2$) and a parent peak at 350 amu (β-nap$_2$S$_3$).

All the tricoordinate phosphorus compounds were prepared and purified as previously described[3] and all solvents were rigorously dried and deoxygenated before use. The diaryltrisulfides were prepared from sulfur dichloride and the appropriate arenethiol as described in the literature.[9] The aryl diphenylthiophosphinites (Ph$_2$PSAr, where Ar = *p*-tolyl or phenyl) were prepared by the condensation of the corresponding arenethiol with chlorodiphenylphosphine in the presence of triethylamine in ether at 0 °C. The products were recrystallised from diethyl ether to give the compounds with δ^{31}P NMR spectra (C_7D_8) = 33.4 (Ar = Ph) and 34.7 ppm (Ar = *p*-tol). A typical procedure for the reactions of tricoordinate phosphorus compounds with diaryl trisulfides is as follows.

A solution of isopropyl diphenylphosphinite (0.046 g, 0.19 mmol) in toluene (1 cm^3) was added to a solution of diphenyl trisulfide (0.047 g, 0.19 mmol) in C_7D_8 (1 cm^3). The mixture was allowed to stand at room temperature until the reaction was complete (in this case *ca.* 15 min) when ^{31}P NMR spectroscopy showed δ 78.6, [89% Ph$_2$P(S)(OPr^i)] and 21.5 ppm [11% Ph$_2$P(O)OPr^i] as the only detectable products of the reaction.

Reactions of Arylthiolate Anions with Diaryl Trisulfides or Thiophosphinites.—Benzyltriphenylphosphonium chloride (3.88 g, 0.01 mol) was suspended in dry toluene (10 cm^3) and 10 mol dm^{-3} Bu^{n}Li (1 cm^3) was added dropwise at 0–5 °C when the solution turned red. A solution of *p*-thiocresol (1.24 g, 0.01 mol) was added dropwise to the ylide solution and the mixture stirred for 1 h at 0 °C before the ^{31}P NMR spectra were checked. The resultant phosphonium thiocresolate was added to an equimolar quantity of a solution of phenyl diphenylphosphinothioite in toluene and the mixture was examined by ^{31}P NMR spectroscopy to detect any exchange between the ArS groups.

A similar experiment was performed for the exchange of β-naphthylthiolate anions with diphenyl trisulfide.

Kinetic Procedure.—The reactions were carried out in reagent grade toluene dried over LiAlH$_4$ and distilled (×2) under nitrogen. Stock solutions of the reactants (at 4 × 10^{-3} mol dm^{-3}) were thermostatted at the desired temperature and equal volumes of the reactants were mixed in a 10 mm cuvette and placed in the thermostatted cell holder of the spectrometer. The reaction was followed by observing the disappearance of the trisulfide absorbance at $\lambda = 350$ nm. Absorbance values were converted into the corresponding concentration data and plots of $1/[Ar_2S_3]$ *vs.* time gave good straight lines over 3 half lives. A least-mean squares programme was used to calculate the second order rate coefficients and each reaction was conducted in duplicate or triplicate to afford averaged rate constants.

Conclusions

The reactions of tricoordinate phosphorus compounds, $Ar_nP(OPr^i)_{3-n}$, with diphenyl trisulfide in toluene proceed with the formation of the expected thiophosphoryl compounds, $Ar_nP(S)(OPr^i)_{3-n}$ as the only products, with the second-order rate coefficients in the order $n = 2$ (2200) > $n = 1$ (1470) ≫ $n = 3$ (10) > $n = 0$ (1). The order is similar to that found for dialkyl peroxides and S_8 as substrates and is consistent with a biphilic mechanism with a moderate polar component in the transition state. This conclusion is reinforced by the observation of ρ-values of *ca.* -1.1 derived from variation in the aryl substituents on phosphorus for $n = 3$, 2 and 1.

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