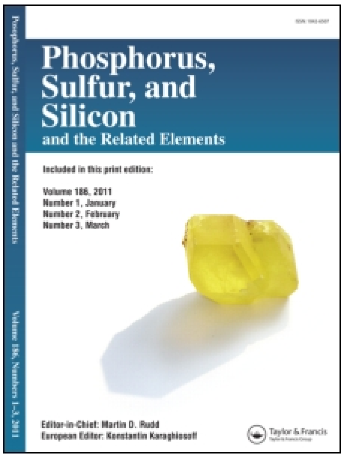

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TERNARY ADDUCTS OF SOME P(III) COMPOUNDS WITH ELEMENTAL SULFUR AND CARBON DISULFIDE

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Solutions of trialkylphosphites develop a yellow tint (life time: several hours) when reacted with sulfur in the presence of carbon disulfide. Similar phenomena occur with alkyl phosphonites or phosphinites and with trialkylphosphines, although not with triarylphosphines. The curves absorbance/time for $(EtO)_3P$ at 400 nm indicate a 3rd order kinetic law: $d\mathcal{A}_{400}/dt = \mathbf{k}_3 \epsilon[(RO)_3P][S_8][CS_2]$, where ϵ is the (unknown) absorptivity of the adduct and $\mathcal{A}_{400}$ is taken at 1 cm path length. Formulae $X_3P^+ - S_n - CS_2^-$ (**A**) or $X_3P^+\text{-}C(S)S\text{-}S_n^-$ (**B**) are considered, with more evidence in favour of **A**. A mechanism is proposed.

Keywords: Triethylphosphite; tributylphosphine; sulfur; carbon disulfide; triethylphosphite adducts

The research work reported below has its source in a qualitative observation: triethylphosphite, when treated with elemental sulfur (S_8) in carbon disulfide, progressively develops a bright yellow colour, which later fades out slowly and vanishes after several hours, when the conversion of $(EtO)_3P$ into $(EtO)_3PS$ has reached completion. That $(EtO)_3P$ itself is involved in this process follows from the fact that no similar phenomenon occurs with $HPO(OEt)_2$, $EtPO(OEt)_2$, $(EtO)_3PO$ (potential impurities in triethylphosphite), or with $(EtO)_3PS$ or $(EtO)_2(EtS)PO$.

While the presence of CS_2 is absolutely required for the production of the yellow tint, the latter withstands dilution by solvents such as hexane, toluene,

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carbon tetrachloride, acetonitrile or addition of moderate amounts of alcohols, phenol, acetic acid, pyridine, triphenylphosphine or excess triethylphosphite.

On the other hand, yellow colours are similarly developed by phosphonites $RP(OAlk)_2$ or phosphinites R_2POAlk ($R = Ph, Bu$) as well as by trialkylphosphines—although not by triarylphosphines.

At this early stage of the research, two hypotheses naturally come to mind, namely the production of ternary adducts **A** or **B**:

$$\mathbf{A}\quad X_3P^+\text{-}S_n\text{-}CS_2^- \qquad \mathbf{B}\quad X_3P^+\text{-}C(S)S\text{-}S_n^-$$

with $n = 8$ at the onset of the reaction and possibly <8 later on.

Formula **A** is in line with: (a) the general opinion that X_3P compounds react with sulfur *via* a transient zwitterion $X_3P^+\text{-}S_n^-$ (C);[1-5] (b) the ability of RS^- anions to yield trithiocarbonates $RSCS_2^-$ with carbon disulfide.[6]

On the other hand, **B** would be consistent with the property of many X_3P derivatives to yield red $X_3P^+\text{-}CS_2^-$ adducts with carbon disulfide[7-13]. With $(EtO)_3P$ however, only a pale pink tint is observable, even at high concentrations. With trialkylphosphines, the red colour is so strong that it appears transiently (2–3 s) at the onset of the reaction $Alk_3P + S_8 + CS_2$, prior to the development of the yellow tint.

RESULTS

Electronic Spectra.—Visible-near UV spectra were recorded at $\lambda \geq 375$ nm (cut off point imposed by the tail of the strong band of CS_2 at 316 nm). In the visible, the pale pink (concentrated) solutions of $(EtO)_3P$ in CS_2 exhibit absorption up to *ca.* 620 nm, with a peak at 515 nm and a steep rise below a minimum at 444 nm (Fig. 1a).

The yellow diluted solutions of $(EtO)_3P + S_8$ in CS_2 display growing absorption from *ca.* 500 down to the limit at 375 nm, with no apparent maximum (Fig. 1b).

In a similar way, the red diluted solutions of Bu_3P in CS_2 show strong absorption, culminating at 490 nm and steeply growing below a minimum at 438 nm (Fig. 2a). Taking into account the difference in X_3P concentrations in Fig. 1a and 2a (1:360), the peak at 490 nm for Bu_3P turns out to be intrinsically about 6000 times as strong as the peak at 515 nm for $(EtO)_3P$; on the basis of data in[11], and assuming similar absorptivities for both adducts $Bu_3P{\cdot}CS_2$ and $(EtO)_3P{\cdot}CS_2$, the formation constant of the latter may then be estimated at $\lesssim 2 \times 10^{-7}$ lmol $^{-1}$.

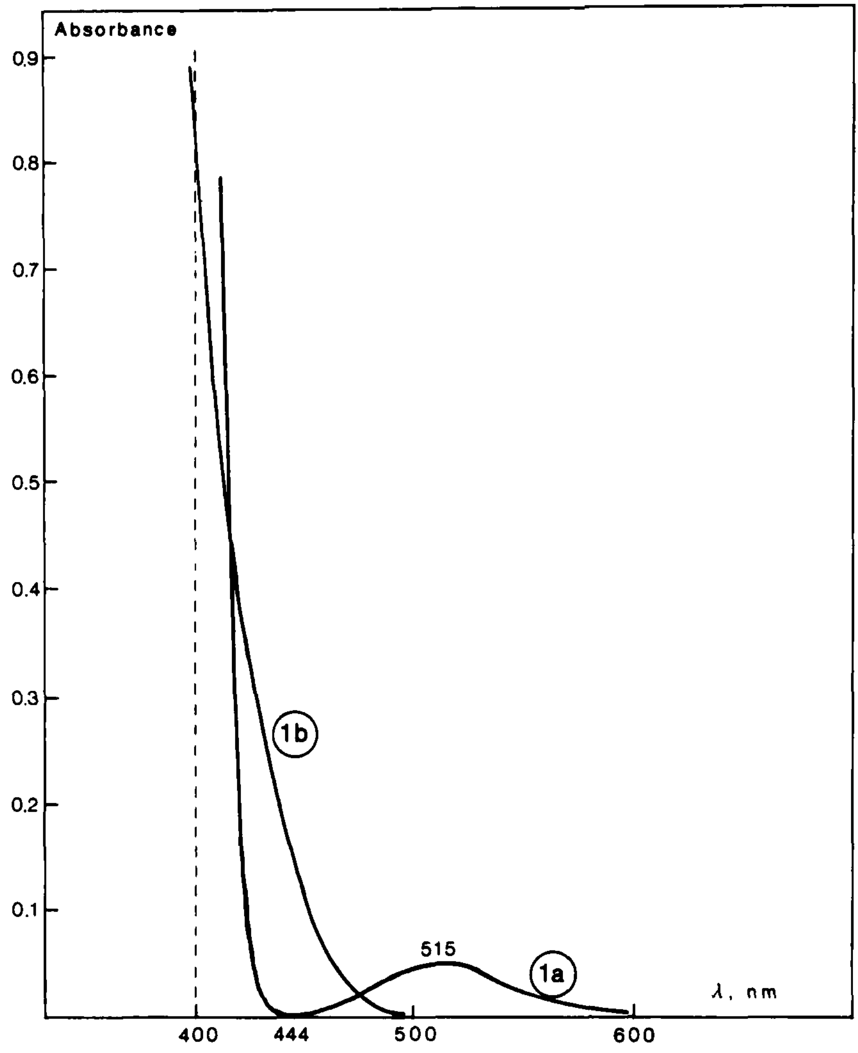


FIGURE 1 Electronic spectra (1 cm cells) for: (1a) Solution of $(EtO)_3P$ (2.25 mol l^{-1}) in CS_2; (1b) Solution of $(EtO)_3P$ (0.029 mol l^{-1}) + S_8 (0.0074 mol l^{-1}) in CS_2, spectrum recorded after 29 min.

The spectrum of the yellow solutions of $Bu_3P + S_8$ in CS_2 resembles that of $(EtO)_3P + S_8$ in the same solvent, though with a shoulder at 399 nm (Fig. 2b).

Kinetic Studies.—The formation of the yellow adduct from $(EtO)_3P$ (footnote[14]) was monitored by taking the absorbance ($\mathcal{A}_{400}$) at 400 nm (path length = 1 cm) as a measure of the extent of the process, after correction for a small absorbance at zero time, probably caused by traces of $(EtO)_3P{\cdot}CS_2$ (Fig. 1a);

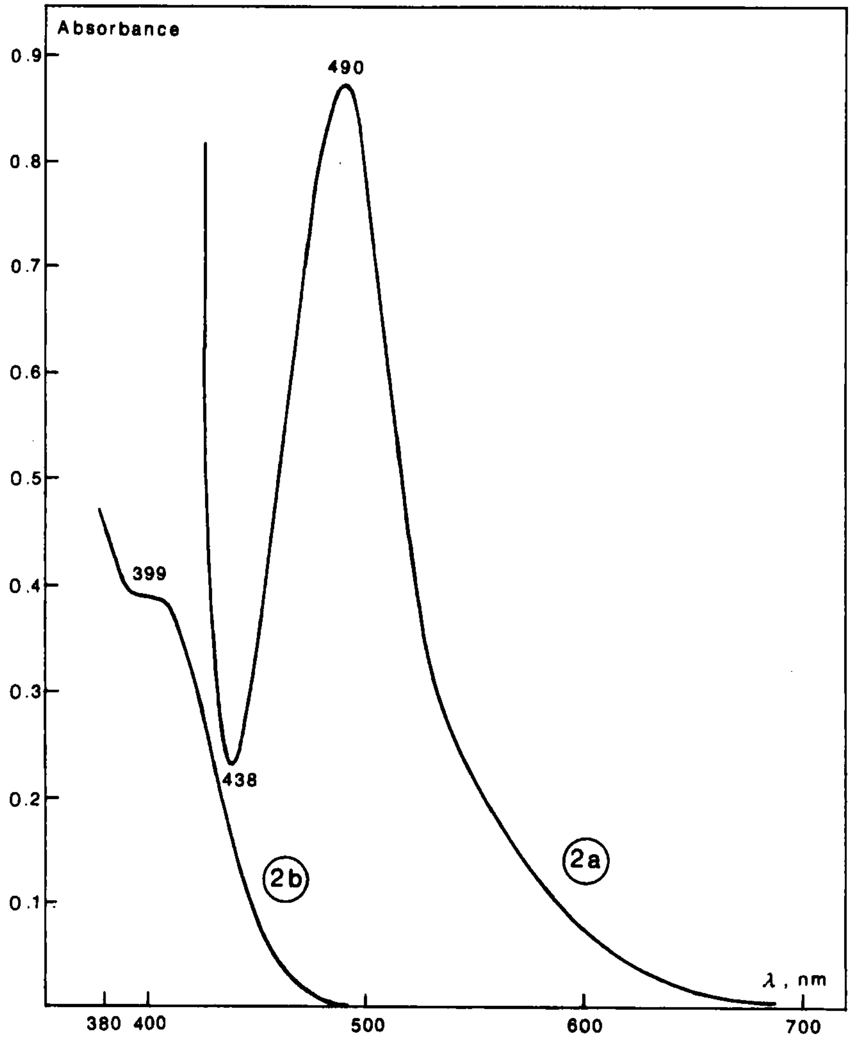


FIGURE 2 Electronic spectra (1 cm cells) for: (2a) Solution of Bu_3P (0.0062 mol l^{-1}) in CS_2; (2b) Solution of Bu_3P (0.0062 mol l^{-1}) + S_8 (0.00164 mol l^{-1}) in CS_2, spectrum recorded after 5 min.

neither S_8 in CS_2, nor $(EtO)_3P + S_8$ in other solvents absorb substantially at 400 nm. All $\mathcal{A}_{400}$/time plots are straight lines as long as the conversion to $(EtO)_3PS$ is not too extensive; remarkably, the slope of such linear sections is proportional to the concentrations of each reactant—*i.e.* the reaction is (pseudo) third order at this early stage:

$$\epsilon^{-1}\, d\mathcal{A}_{400}/dt = d[\text{yellow adduct}]/dt = \mathbf{k}_3[(RO)_3P][S_8][CS_2]$$

where ϵ is the (unknown) absorptivity of the adduct. It follows that the yellow complex obeys the stoicheiometry $X_3P:S_8:CS_2 = 1:1:1$, in accord with either formula **A** or **B**. Values of $\mathbf{k}_3$ are recorded in Table I.

Rate constants for the formation of X_3PS (X = EtO, Pr^{i}O, Ph) from X_3P and sulfur, also shown in Table I, were obtained by an iodometric method adapted from that of Bartlett and Meguerian.[1] Our data fully agree with those of Bartlett *et al.*,[1,18] Davis,[19] Goetz *et al.*,[20] or Schenk *et al.*[17] (X = Ph), whatever the technique used (iodometry, spectrophotometry at 345 nm or dielectric method); the agreement with the results of Hall *et al.*[2] is still acceptable for phosphites (spectrometry at 345 nm) but, oddly enough, very poor for triphenylphosphine (spectrometry at 300 nm).

NMR Analysis.—^{31}P NMR spectra were obtained from a solution of $(EtO)_3P + S_8$ (both 0.1 M) in carbon disulfide. A small peak at δ 38.1 p.p.m., possibly pertaining to the ternary adduct, becomes discernible in less than 5 min; it reaches its maximum (*ca.* 2% of total P) after about 20 min (when *ca.* 78 % of the phosphite has been converted into thiophosphate) and has totally vanished, with the last traces of phosphite, after about 16 h (the solution has become nearly colourless). Alternative assignments to either binary adducts $X_3P{\cdot}CS_2$ or $X_3P{\cdot}S_n$ are less plausible: as regards the former, because no NMR signal at 38.1 p.p.m. is visible as long as sulfur is omitted; as regards the latter, because such species have hitherto escaped NMR diagnosis in other solvents,[21] with the exception of a research work (following an indirect path), in which NMR peaks at δ 30 and 20 p.p.m. were tentatively assigned to $(RO)_3P^+\text{-}S_n^-$ species (R = Me and Ph respectively)[3–4]; however, the latter were unstable at room temperature, in contrast to the above signal at 38.1 p.p.m..

On prolonged standing, 1:1 (v/v) mixtures of $(EtO)_3P$ and CS_2 only afford negligible amounts (*ca.* 0.05 % in 39 days, r.t.) of insertion product $(EtOCS_2)_3P$ [^{31}P NMR: δ 8.7 p.p.m. (lit.,[22] 8.7 p.p.m.)], in keeping with the poor stability reported for such compounds.[23] $(EtO)_3PS$ (*ca.* 0.2 %) (δ 68.9 p.p.m.) and, possibly, traces of an intramolecular transalkylation product, $(EtO)_2P(O)CS_2Et$, δ −3.7 p.p.m. (lit. for $(Pr^iO)_2P(O)CS_2Me$,[24] −4.2 p.p.m.), were also detected.

The chemical shift of $Bu_3P{\cdot}CS_2$ was measured at 22.9 p.p.m. in MeCN.

Effect of Solvents.—The rate of formation of the adduct $(EtO)_3P/S_8/CS_2$ in various solvents, as shown in Table I, roughly parallels the reaction rates of X_3P (X = EtO, Pr^{i}O, Ph) with S_8, except for the benzene *vs.* toluene ordering. No comparison could be made with the pink tint given by $(EtO)_3P$ with CS_2, due to the extreme faintness of the latter.

Comparison with other X_3P Compounds.—The failure of certain X_3P compounds to give a yellow adduct with S_8 in carbon disulfide (X = Ph, PhO, RS) was found to be associated with both a failure to form red $X_3P{\cdot}CS_2$ adducts and a relative slowness of their reaction with sulfur (Table I and ref.[2,16]).

E I Solvent effects on: (i) the rate of development of the yellow tint in ternary solutions of $(EtO)_3P + S_8 + CS_2$; (ii) the rate of the reactio
→ X_3PS.

t	*$(EtO)_3P + S_8 + CS_2 \rightarrow$ yellow adduct*	*$X_3P + 1/8\ S_8 \rightarrow X_3PS$*		
	$\epsilon \mathbf{k}_3$ *(see text)* (298 K) [a] $l^3\ mol^{-3}\ s^{-1}\ cm^{-1}$	$10^3 \times \mathbf{k}_2$ (298 K) [b] $l^1\ mol^{-1}\ s^{-1}$ this work *vs. [literature data]*[ref]		
		X = EtO	X = Pr^iO	X = P
	0.092 ± 0.005[c]	2.7 ± 0.4 [d]		1.3 ± 0.
			[49, 299 K][e]	*[0.83, 29*
luene 1:2 (v/v)	0.46 ± 0.02[c]			
e	1.33 ± 0.02	7.03 ± 0.2	118 ± 2	2.7 ± 0
		[6.2 ± 0.5][2]	*[96 ± 8]*[2]	*[0.423*
ne	1.17 ± 0.02	14.9 ± 0.2	245 ± 4	4.45 ± 0
				[4.58]
				[4.36]
				[4.40]
				[~4.5]
	0.34 ± 0.01	1.59 ± 0.04	33.8 ± 1.7	0.92 ± 0.
				[0.93]
e	no yellow tint	0.054 ± 0.002	1.05 ± 0.02	0.047 ± 0

osorptivity of the ternary adduct. Range of concentrations: $[(EtO)_3P]$: 7.5 to 37 × 10^{-3} M; $[S_8]$: 2.75 to 11.4 × 10^{-3} M; $[CS_2]$: 0.4 to 17 M. [b]Sequential reactions te-limited by the production of the first molecule of X_3PS;[1,2,15] the overall pseudo-2nd order rate constant $\mathbf{k}_2$ is defined by: $d[X_3P]/dt = -\mathbf{k}_2[X_3P][S]$. [c]Data i rated CS_2 are biased ($\mathbf{k}_3$ lowered) by departure from ideality. [d]The remaining yellow tint of the ternary adduct makes iodometric titrations rather imprecise. [e]Recalcul e basis of the equation in footnote [b]. [f]From a curve published in [17]. [g]Intrapolated from data in [20]. [h]As proved by a blank test, no oxidation of X_3 P by CCl_4 took pl ental conditions.

Comparison with other Nucleophiles.—Table II presents the results of comparative tests on adducts afforded by nucleophiles RS^-, RCS_2^-, RO^-, $(EtO)_3P$ and Bu_3P with CS_2 and/or S_8:

(a) As for binary adducts ZCS_2^- (Z = RS, R, RO; entries 1, 3, 5), the yellow tint of ternary adducts $X_3P/S_n/CS_2$ (entries 9 and 12) is insensitive to excess triethylphosphite, despite their content of catena-sulfur.

(b) The colour of adducts ZCS_2^- (Z = RS, RO, Bu_3P^+; entries 1, 5, 10) is totally discharged by strong acids, due to their cleavage to ZH + CS_2 (note[25]); note the similitude with lines 9 and 12. In contrast, dithiocarboxylates RCS_2^- (entry 3), for which such a process is excluded, largely retain their colour in acid medium.

(c) The colour of adducts ZS_8^- (Z = RS, RO; entries 2, 6) is strongly sensitive to phosphite or toluenesulfonic acid; the former evidently acts as a desulfurising agent, the latter by producing unstable ZS_8H.

(d) No colour was observed for adducts $X_3P{\cdot}S_8$ (entries 8, 11), a confirmation of their very short life.

Ellman's Test for Thiolate Anions.—The use of Ellman's reagent $\Psi SS\Psi$ (Ψ = 3-Carboxy-4-nitrophenyl) to detect thiolates RS^-[4,26] is based on the characteristic red colour of the anion ΨS^- afforded by anion exchange with RS^-. We further found that the red tint of ΨS^-—produced in toluene from n-$C_{12}H_{25}SH,Et_3N$ + $\Psi SS\Psi$—is markedly deepened by adding elemental sulfur, due presumably to the formation of ΨS_n^- (a blank test $\Psi SS\Psi$ + sulfur + Et_3N was negative). In contrast, no colour change was noticed when Ellman's reagent was added to yellow solutions of $(EtO)_3P$ + S_8 + CS_2 in toluene.

DISCUSSION

Configuration of Ternary Adducts $X_3P/S_n/CS_2$.—While no definite conclusion can be drawn, the above results are in better accord with formula **A** than with **B**.

Thus, the insensitivity of the yellow colour to excess phosphite (Table II: entries 9, 12) suggests that polysulfide chains in the ternary adducts are not "open" (as in formula **B** and in runs 2, 6) but rather "capped" by a protective CS_2^- end group.

More evidence in favour of **A** stems from the negative result of Ellman's test. In actual fact, the ability of ZCS_2^- species to add terminal catena sulfur appears thermodynamically unfavourable, inasmuch as this would substitute a relatively basic polysulfide end group (estd $pK_a \geq 8$; lit.[27], $PhCH_2SSH$: 8.7, n-PrSSH: 10.3) for a weakly basic one (pK_a, lit.[28], $MeCS_2H$: 2.55, $EtOCS_2H$: 1.52,

TABLE II Reactions of various nucleophiles with sulfur and carbon disulfide

Reactions of nucleophiles (N) with S_8 and/or CS_2						*Colour change of the solu upon further addition o*	
N	*S_8 (mol/mol N)*	*CS_2 (mol/mol N)*	*Solvent*[a] *(ml/mmol N)*	*Adduct*	*Colour of the soln*[b]	*4-$CH_3C_6H_4$-SO_3H*[c]	*$(EtO)_3P$ (excess)*
RS^{-}[d]	none	11	E (1.5)	$RS\text{-}CS_2^{-}$	YELLOW *inst*	→colourless ~ *1 h*	unchang
ibid	0.4	none	E (2)	$RS\text{-}S_8^{-}$	Red *inst*	→colourless *inst*	→colour
RCS_2^{-}[e]	none	none	F (12)	RCS_2^{-}	Orange	Yellow	unchang
ibid	1.2	none	F (12)	none ?	Orange (*id.* Run 3)	Yellow	unchang
RO^{-}[f]	none	60	acetone (8)	$RO\text{-}CS_2^{-}$	yellow *inst*	→colourless *a few seconds*	unchang
ibid	0.5 partly dissolved	none	G (10)	$RO\text{-}S_8^{-}$?[g]	ORANGE/RED	→pale yellow *inst*	→yellow
$(EtO)_3P$	none	*ca.* 6	none	$(EtO)_3P^{+}\text{-}CS_2^{-}$	very pale pink *inst*	→almost colourless *not inst*	
ibid	0.3	none	toluene (10)	$(EtO)_3PS$ (slow, *via* $(EtO)_3P^{+}\text{-}S_n^{-}$)	colourless		
ibid	0.3	60	E (10)	$(EtO)_3P/S_n/CS_2$	YELLOW *inst*	→colourless *inst*[h]	unchang
Bu_3P	none	90	E (14)	$Bu_3P^{+}\text{-}CS_2^{-}$	RED *inst*	→colourless *a few minutes*	
ibid	1	none	E (14)	Bu_3PS (fast, *via* $Bu_3P^{+}\text{-}S_n^{-}$)	colourless		
ibid	1	90	E (14)	$Bu_3P/S_n/CS_2$	YELLOW	→colourless *inst*[h]	unchang

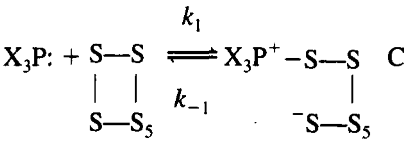
tonitrile-Dichloromethane 1:1 (v/v); F: Methanol-Dichloromethane 5:2 (v/v); G: Toluene-Acetone-Methanol 1:1:1 (v/v). [b]Colour scale of intensity: *e.g.* YELLOW
w > pale yellow; *inst* stands for instantaneous. [c]Solution in MeOH-CH_2Cl_2 1:1 (v/v), added dropwise until acid to pH test paper. [d]*n*-$C_{12}H_{25}SH$,Et_3N. Control so
$_3$N alone or of RSH or Et_3N separately (both with CS_2 and/or S_8) were colourless. [e]*n*-$C_{12}H_{25}$-CS_2MgBr (reddish solution ~ N in Et_2O), obtained by reaction of CS
onding Grignard reagent. [f]2N solution of KOH in alsolute EtOH. [g]Postulated first-stage sulfenyl derivative, subsequently rearranging to more stable species, such as p
de R-S(O)-S_7 . [h]The yellow colour is insensitive to acetic acid.

$EtSCS_2H$: 1.55); this viewpoint is borne out by the absence of colour change between runs 3 and 4 in Table II. On the contrary, **A** could be readily produced by insertion of S_n into $X_3P{\cdot}CS_2$, since the formation of the latter from X_3P and CS_2 is strongly reversible.[11,12,29]

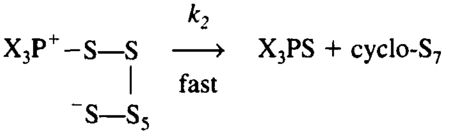
Further support to **A** comes from the observation that (even more rapidly than with binary adducts ZCS_2; Table II, entries 1, 5, 10), solutions of adducts $X_3P/S_n/CS_2$ are fully decolorised by strong acids (Table II, entries 9, 12). This is likely to take place through prototropic dissociation of $X_3P^+\text{-}S_n\text{-}CS_2H$ to CS_2 + $X_3P^+\text{-}S_nH$—the latter being unstable, especially in the presence of excess X_3P; it is significant that acetic acid—a weak acid ($pK_a = 4.8$), able to protonise S_n^- but not CS_2^- end groups (see above)—is ineffective (Table II, footnote[h]).

Note also that formula **B** could hardly be reconciled with the fact that, at identical concentrations, Bu_3P and $(EtO)_3P$ afford ternary adducts solutions with comparable absorbances, whilst the red tint of the binary adduct $X_3P{\cdot}CS_2$ is overwhelmingly more intense for Bu_3P.

Mechanism.—The reaction of X_3P compounds with octasulfur is a stepwise process, which is generally described as rate limited by the production of the first molecule of X_3PS, this step starting by the formation of a transient zwitterion **C** (equation 1).[1,2,5] Ultimately, **C** decays to X_3PS, either through bimolecular attack by a second molecule of X_3P[1] or, rather, as recently proposed,[15] by an intramolecular process (equations 2, 3):



(1)



(2)

$$\text{followed by:}\quad \text{cyclo-}S_7 + 7\,X_3P \xrightarrow{\text{very fast}} 7\,X_3PS \qquad (3)$$

A steady-state treatment gives:

$$[C] = k_1[X_3P][S_8]/(k_{-1} + k_2)$$

and the overall rate is pseudo 2nd-order, in accord with experiment:[1,2]

$$d[X_3PS]/dt = 8\,k_2[C] = \mathbf{k}_2[X_3P][S] \quad \text{with} \quad \mathbf{k}_2 = k_1k_2/(k_{-1} + k_2)$$

On the other hand, adduct **A** would result from the concomitant reaction of **C** with CS_2 (see note [30]):

$$\mathbf{C}\quad X_3P^+\text{-}S_8^- + CS_2 \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} X_3P^+\text{-}S_8\text{-}CS_2^- \quad \mathbf{A} \tag{4}$$

$$d[A]/dt = k_3[C][CS_2] - k_{-3}[A]$$

Since $k_{-3}[A]$ is negligible at the onset of the reaction, the initial kinetic law is 3rd order, in accord with experiment:

$$d[A]/dt = \mathbf{k}_3[X_3P][S_8][CS_2] \text{ with } \mathbf{k}_3 = k_1k_3/(k_{-1} + k_2) \text{ (see note }^{31}\text{)}$$

or:

$$d[A]/d[X_3PS] \approx k_3[CS_2]/8k_2.$$

EXPERIMENTAL

Electronic spectra were recorded with a Perkin Elmer 552 spectrophotometer; errors due to the evolution of the solutions were negligible. N.M.R. spectra were obtained at 121.5 MHz with a Bruker AC 300 apparatus.

X_3P compounds were commercial products, either redistilled (X = RO) or recrystallised from 95% ethanol (X = Ph) before use. Their purity was checked periodically by iodometry and taken into account in the calculation of rate constants. Elemental sulfur was an analytical grade, further recrystallised from toluene.

All solvents (analytical grades) were redistilled and dried over molecular sieve 4 Å; carbon disulfide, benzene, toluene and hexane were treated by 1 to 2 % triphenylphosphine prior to redistillation, in order to eliminate possible traces of reactive sulfur impurities.

Solutions for kinetic experiments were extemporaneously prepared and protected from direct sunlight. Most reactions $X_3P + S_8$ were carried out in glass stoppered *ca.* 30 ml flasks, ≥99 % filled (in order to minimise risks of air oxidation), immersed in a thermostat and gently magnetically stirred. Typically, a sample containing *ca.* 0.25 mmol $(EtO)_3P$ was syringed into a toluene solution containing 2 to 3 equivalents of sulfur and kept at 25°C; after 30 to 60 min, the content of the flask was quantitatively transferred into a mixture of methanol (*ca.* 10 ml) and standard iodine solution (10 ml, *ca.* 0.05 N in toluene-isopropanol-pyridine 36:13:1, v/v), rinsing the flask with 3 ml of toluene. The excess of iodine was immediately back-titrated in half light with a solution of triphenylphosphine (*ca.* 0.025 M in toluene-isopropanol 1:1, v/v)—both solutions of iodine and triphenylphosphine being freshly standardised. Moderate amounts of dialkylphosphites in trialkylphosphites do not introduce any error.

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[30] A yellow colour also develops when triethylphosphite is treated by a polysulfide RS_nR [R = Ph, $PhCH_2$, $4\text{-}MeC_6H_4$, $(EtO)_2P(S)$-; $n = 2$–4] in carbon disulfide. A plausible mechanism, analogous to (1) + (4) (see text), would involve the primary formation of a ion pair $X_3P^+\text{-}RS, RS_{n-1}^-$, followed by reaction of the anion with CS_2 to give $RS_{n-1}\text{-}CS_2^-$; the postulated site of attack on RS_nR, consistent with the fact that RS_{n-1}^- is a weaker base (better leaving group) than RS^- [D. N. Harpp and R. A. Smith, *J. Am. Chem. Soc.* **104**, 6045 (1982)], is borne out by the observation that the intensity of the yellow tint grows with n.

[31] Strictly, [C] should write: $[C] = \{k_1[X_3P][S_8] + k_{-3}[A]\}/\{k_{-1} + k_2 + k_3[CS_2]\}$. The change is immaterial however, because: (a) $k_{-3}[A]$ is negligible (see main text); (b) $k_3[CS_2]$ is much smaller than k_2, since only trivial amounts of ternary adduct are generated.