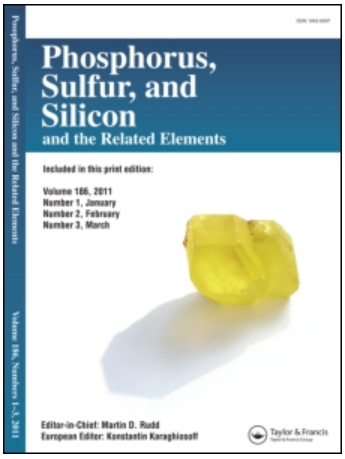

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

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To cite this Article Démarcq, Michel C.(1998) 'Reactivity of X_3P Compounds with Elemental Sulfur, Carbon Disulfide or Both, to Yield X_3PS, $X_3P.CS_2$ or $X_3P.S_n.CS_2$ Adducts', Phosphorus, Sulfur, and Silicon and the Related Elements, 134: 1, 307 — 320
To link to this Article: DOI: 10.1080/10426509808545471
URL: http://dx.doi.org/10.1080/10426509808545471

Phosphorus, Sulfur and Silicon, 1998, Vol. 134/135, pp. 307-320
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REACTIVITY OF X_3P COMPOUNDS WITH ELEMENTAL SULFUR, CARBON DISULFIDE OR BOTH, TO YIELD X_3PS, $X_3P.CS_2$ OR $X_3P.S_n.CS_2$ ADDUCTS

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(Received 23 December, 1997)

Kinetic constants $\mathbf{k_2}$ have been obtained for the reaction of sulfur with 25 P^{III} compounds in toluene or hexane. In the series $Ph_nMe_{3-n}P$ (n = 1–3) or $Ph_nBu_{3-n}P$ (n = 0–3), log $\mathbf{k_2}$ decreases linearly with $\Sigma\chi_i$ (χ_i=Tolman's electronic parameter of each ligand on P), taken as a gauge for the donor strength of P. Dramatic deviations from additivity are observed for the series $Ph_nP(OEt)_{3-n}$, $Ph_nP(OPh)_{3-n}$ and $Bu_nP(OEt)_{3-n}$(n = 0–3); the deviation is smaller for Ph_nPCl_{3-n} and even smaller for $Ph_nP(NEt_2)_{3-n}$. The results are discussed in terms of P-coordination (P^{IV} vs. P^V), stability and geometry of the intermediate $X_3P.S_8$ or of the transition state leading to this adduct, emphasis being laid on the donor/acceptor character of the P site. A similar dependence on X governs the reactivity of X_3P with S_8 , CS_2 or both, to give X_3PS, $X_3P.CS_2$ (binary red adduct) or $X_3P.S_n.CS_2$ (ternary yellow adduct) respectively; an explanation for this parallelism is proposed.

Keywords: Triphenylphosphine; tributylphosphine; phosphorous triesters; phosphonous diesters; phosphinous esters; sulfur; carbon disulfide; kinetics

On the basis of substituent parameters such as Taft's σ^*, Kabachnik's σ^{Φ} [1] or Tolman's χ [2], the electron donating power of X_3P compounds is expected to decrease in the order:

$$Alk_3P > Ph_3P > Ph_2POAlk > PhP(OAlk)_2 > P(OAlk)^3 > P(OPh)^3$$

This "regular" scale actually governs a number of acid-base or nucleophilic reactions of P^{III} derivatives, especially in polar solvents (note [3]). In contrast, the relative reactivity of Ph_3P is markedly depressed (notably in apolar solvents) for reactions involving attack at O or S (Table I, entries 1–5). Entry 6 further reveals that the low relative affinity of Ph_3P for S is not

only kinetic but thermodynamic as well. These observations agree with an earlier classification by Parker and Kharash,[11] who ranked Ph_3P as less nucleophilic than $P(OR)_3$ towards S-electrophiles.

An analogous situation was found for the reactions of X_3P with CS_2 or with $S_8 + CS_2$ (Table I, entries 7,8).[9]

In the case of O-O and S-S substrats (Table I, entries 2,3,4), the kinetic anomalies have been ascribed to a more or less biphilic character of the nucleophilic attack by P^{III}.[5,6,8,12,13] While this approach appears sound, a deeper insight into the role of substituents on P was felt desirable. This prompted us to investigate the reactions of elemental sulfur with a greater variety of P^{III} species, taking into account the multistep character of such processes.

RESULTS

Kinetic constants $\mathbf{k_2}$, involving the reaction of sulfur with 25 various P^{III} compounds, were obtained, either in toluene or hexane (Table II), by using the same iodometric method as in [9]. Figures 1 and 2 show plots of log $\mathbf{k_2}$ *versus* $\Sigma\chi_i$, where χ_i is the Tolman's electronic parameter [2] for each X ligand in $X^1X^2X^3P$ (note [15]). The correlations between log $\mathbf{k_2}$ in toluene and log $\mathbf{k_2}$ in hexane, benzene or carbon disulfide are illustrated in Figure 3. For the sake of comparison, log $\mathbf{k_2}$ / $\Sigma\chi_i$ plots are shown in Figure 4 for the reactions of $Ph_nP(OR)_{3-n}$ (R = Et, Pr^i) with PhSSSPh, EtOOEt and EtI.

A few salient features emerge clearly from these results:

i. The additivity rule is plainly fulfilled for the series $Ph_nMe_{3-n}P$ and $Ph_nBu_{3-n}P$, as attested by the straight lines (negative slopes) D/Fig.1 and I,J/Fig.2. The same remark applies to $Ph_n(4\text{-}YC^6H^4)_{3-n}P$ (Y = Cl or Me indistinctly) (line F/Fig.1) in benzene;[14] the latter data are consistent with our single result for $(4\text{-}MeC_6H_4)_3P$ in toluene, while, oddly enough, $(4\text{-}MeOC_6H_4)_3P$ falls out of line (note [23]);

ii. A gross departure from linearity is noticed for the series $Ph_n P(OR)_{3-n}$ (R = Et, Ph), as shown by broken lines (partly with positive slopes) A,B/Fig.1 and G/Fig 2; a similar effect is observed for $Bu_nP(OEt)_{3-n}$ (line K/Fig.2);

TABLE I Anomalous affinities of P^{III} compounds towards various substrats

Entry N°	*Substrat (solvent/ temperature °C)*	*Reaction product*	*Rate order[a] for the formation of the reaction product*	*Ref.*
1	$Bu^tO^{\cdot}$ *(neat/130)*	$X^3P^{\cdot}$-OBu^t	$Bu_3P > P(OEt)_3 > P(OPh)_3 > Ph_3P$	4
2	EtOOEt *(benzene/ 35)*	$X_3P(OEt)_2$ [b]	$Ph_2POR > PhP(OR)_2 > Ph_3P >> P(OR)_3$ ($R = Pr^i$)[c]	5
3	PhSSSPh *(toluene/ 25)*	X_3P^+-SSPh,PhS^- [b]	$Ph_2POR > PhP(OR)_2 > Ph_3P > P(OR)_3$ ($R = Pr^i$)[c]	6,7
4	S_8 *(toluene/25)*	X_3P^+-S_7-S^- [b]	$Ph_2POR > PhP(OR)_2 > P(OR)_3 > Ph_3P$ ($R = Et, Pr^i$)	8,9
5	*n*-$BuS^{\cdot}$ *(neat/ 70)*	$X_3P^{\cdot}$-SBu	$Bu_3P > P(OEt)_3 > Ph_3P > P(OPh)_3$	4
6	S exchange between Ph_3PS and $P(OEt)_3$ *(neat, boiling)*		$P(OEt)_3 > Ph_3P$ (Ph_3PS quasi totally reduced to Ph_3P after 3 hours [d])	10
7	CS_2 *(neat/ r.t.)*	X_3P^+-CS_2^-	$Ph_2P(OEt) > PhP(OEt)_2 > P(OEt)_3 >> Ph_3P$ [e]	9
8	$S_8 + CS_2$ *(neat/ r.t.)*	X_3P^+-S_8-CS_2^- [f]	*ibid* [g]	9

[a]Except for entries 6 and 7, for which the sequence shown is that of the formation constants of the adducts. [b]Alleged (rate-limiting ?) first step. [c]See also Figure 4. [d] No S exchange observed by ^{31}P NMR at room temperature after 22 days (this work). [e] Intensity order of the red colour at equilibrium, for identical concentrations of the reactants. [f]Assumed configuration.[9] [g]Based on the rate of development of the yellow tint at identical concentrations.

TABLE II Effect of X_i's on the reactivity of $X^1X^2X^3P$ with S_8 and/or CS_2

Entry	X_3P	*Reaction* $X_3P + S_8$ *Rate constant at 298K* k_2 (l^1 $mol^{-1}s^{-1}$) [a] × 10^3		*Coloured Reactions*	
		in toluene	*in hexane*	$X_3P + CS_2 \rightarrow$ *red binary adduct* [b]	$X_3P + S_8 + CS_2 \rightarrow$ *yellow ternary adduct* [b]
1	$P(OEt)_3$	7.03 ± 0.1	0.054 ± 0.002	1	3
2	$P(OPr^i)_3$	118 ± 2	1.05 ± 0.02	1	3–4
3	$P(OC_2H_4Cl)^3$			0	1
4	$P(OPh)_3$	$< 10^{-4}$		0[c]	0[c]
5	$P(NEt_2)_3$			3[d]	2
6	$P(SC_{12}H_{25}^n)_3$	very slow,[16]		0	0
7	Pr^i_3P		26200 ± 3000	4	4
8	Bu_3P		4060 ± 200	4	4
9	$PhBu_2P$		62 ± 2	3	3
10	Ph_2BuP		2.7 ± 0.2	1	3
11	$PhMe_2P$	5910 ± 100	51 ± 1	3	3
12	Ph_2MeP	163 ± 3	0.95 ± 0.04	1	3
13	Ph_3P	2.7 ± 0.15	0.047 ± 0.002	0[e]	0
14	$(4\text{-}MeC_6H_4)_3P$	39.2 ± 1.3	1.5 ± 0.1	0–1	0–1

Entry	X_3P	*Reaction* $X_3P + S_8$ *Rate constant at 298K* k_2 (l^1 $mol^{-1}s^{-1}$) [a] $\times 10^3$		*Coloured Reactions*	
		in toluene	*in hexane*	$X_3P + CS_2 \rightarrow$ *red binary adduct* [b]	$X_3P + S_8 + CS_2 \rightarrow$ *yellow ternary adduct* [b]
15	$(4\text{-}MeOC_6H_4)_3P$	542 ± 22	too poorly soluble	0 MeCN added	1 MeCN added
16	Bu_2POEt		12000 ± 2500	4	3
17	$BuP(OEt)_2$		45.9 ± 2.7	3	2
18	Ph_2POEt	3160 ± 60	25.4 ± 0.6	2–3	3
19	$PhP(OEt)_2$	1100 ± 15	7.3 ± 0.3	2	3
20	Ph_2POPh	33 ± 10		1	1
21	$PhP(OPh)_2$	0.066 ± 0.01		0	0
22	Ph_2PNEt_2		21.5 ± 1	0–1	1–2
23	$PhP(NEt_2)_2$		2160 ± 50	2	3
24	Ph_2PCl	0.333 ± 0.035		0	0–1
25	$PhPCl_2$	$(5.2 \pm 0.2) \times 10^{-4}$		0	0

[a]Overall rate constant defined by: $d[X_3P]/dt = -k_2[X_3P][S]$. [b]Neat reactants ; colour scale (after ca. 1 min) : 0 = no colour ; 1 = very pale (only at high concentrations of X_3P) ; 2 = weak ; 3 = medium ; 4 = intense. [c]Negative results were also obtained with $P(O\text{-}4\text{-}nonylphényl)_3$ and $P(OCH_2)_3CEt$. [d]The red tint later vanishes due to the conversion of the zwitterion $(R_2N)_3P^+\text{-}CS_2^-$ into insertion products such as $(R_2N\text{-}CS_2)_3P$.[17,18] [e]Likewise, no red adduct is given by $(2, 4, 6\text{-}Me_3C_6H_2)_3P$,[19] PH_3,[20] or trifluoromethyl phosphines,[21] and only slowly by $(CH_2{=}CH)_3P$.[22]

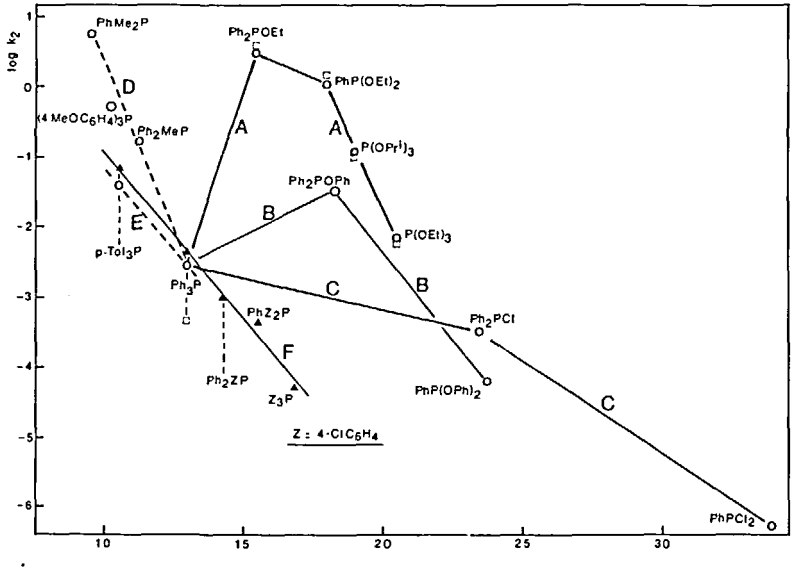


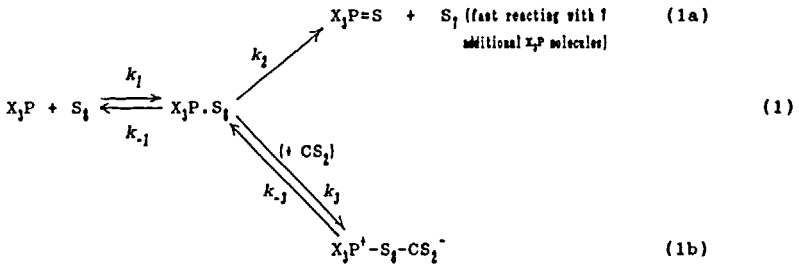
FIGURE 1 Plot of log k_2 *versus* $\Sigma\chi_i$ for the reaction of $X^1X^2X^3P$ with S_8 at 25°C. Lines A to E: this work, in toluene; small squares close to line A refer to earlier data for $Ph_nP(OEt)_{3-n}$.[8] Line F: literature data in benzene.[14] The χ values used in Fig. 1, 2, and 4 are Tolman's original ones;[2a] that for NEt_2(1.5) was estimated from the published value (1.9) for NMe_2

iii. The regular behaviour of $Ph_nMe_{3-n}P$, together with the recognition that Ph_2POEt is much more reactive than Ph_2MeP (Fig.1), are indications that the above deviations owe little to steric effects by the bulky phenyl groups. They rather point to a reactivity enhancement by electronegative ligands OAlk, OAr, or Cl (lines A,B,C/Fig.1); the enhancement is much smaller for Et_2N groups (line H/Fig. 2);

iv. Table II provides qualitative evidence that the ability of P^{III} compounds to afford either red binary adducts with CS_2, or yellow ternary adducts with $S_8 + CS_2$,[9] parallels their reactivity with sulfur alone.

DISCUSSION

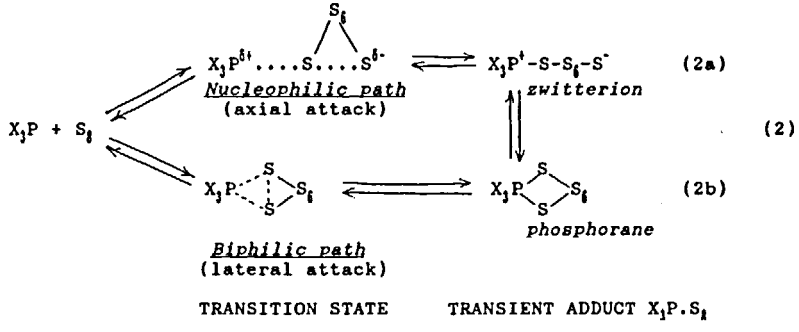
The stepwise reactions of X_3P with S_8, either in the presence or not of CS_2, are schematised in (1) (note [25]):



The overall kinetic law for the production of X_3PS (path 1a) is:

$$d[X_3P]/dt = -8k_2\,[X_3P][S_8] \quad \text{with } k_2 = k_1k_2/(k_{-1} + k_2)$$

The mechanism for the formation of the transient adduct $X_3P.S_8$ may be regarded as nucleophilic or biphilic (equation 2); a mixed mechanism was also considered;[8] this adduct itself may be a phosphonium zwitterion, a phosphorane, or a hybrid of both structures, in rapid tautomeric equilibrium.



The recognition that no racemisation takes place during the reaction of sulfur with chiral $MeBu(PhCH_2)P$ in benzene has led to the conclusion that the phosphonium character totally dominates in the intermediate $R_3P.S_8$ (R = alkyl);[26] we believe it to be true for the aryl analogs too. On the other hand, remembering that ion pairs Ph_3P^+-SR,RS^- dissociate quantitatively to Ph_3P + RSSR,[27,28] it is further postulated, by analogy, that the formation of adducts $R_3P.S_8$ will be strongly reversible, notably in apolar solvents.

In contrast, the increased stability reported for several dithiophosphoranes $X_3P(SR)_2$ containing electronegative X substituents, [29] suggests that adducts $X_3P.S_8$ derived from R_nPZ_{3-n}(R = Alk, Ar; Z = OAlk, OAr, Cl;

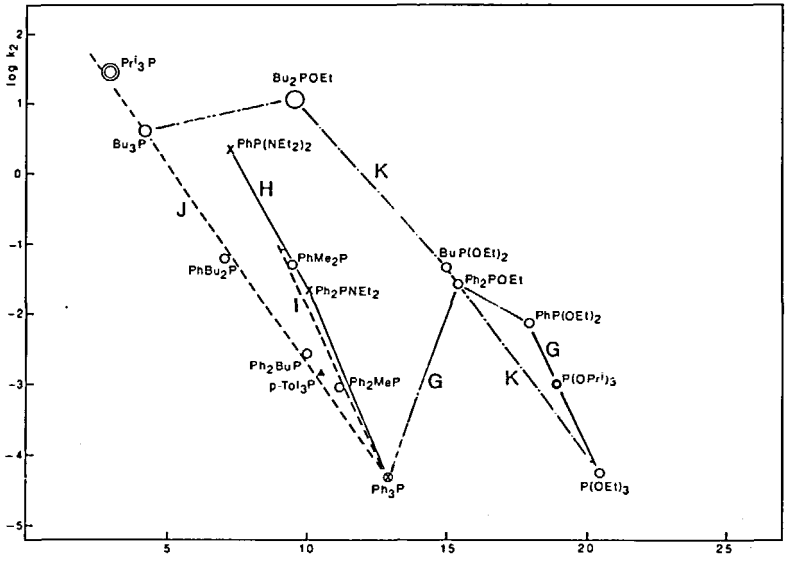


FIGURE 2 Plot of log $\mathbf{k_2}$ (this work) *versus* $\Sigma\chi_i$ for the reaction of $X^1X^2X^3P$ with S_8 in *n*-hexane at 25°C

n = 0–2) should have a marked P(V) character and be relatively stable (note [30]).

Accordingly, the formation constant k_1/k_{-1} is presumed to be much lower when all X are Alk or Ar than when at least one X is AlkO, ArO or Cl. Assuming that there is no cancelling by extensive changes in k_2, these differences ought to be reflected in the overall kinetics, i.e. by $\mathbf{k_2}$ being higher in the second case, as actually seen in Figures 1 and 2.

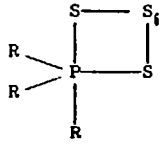
The intrinsic reluctance of $R_3P.S_8$ (R = Alk, Ar) to adopt a stable P^V structure is also predictable from the "rules of apicophilicity" for phosphoranes in their trigonal bipyramidal (TBP) most stable framework.[34,35] These rules state that, in the absence of ring strain and steric effects, substituents on P occupy the axial site according to the following approximate preference order (note [36]) :

F > OPh > OAlk > Cl » Ph (≈ S_n ?) > SR > NMe_2 > Alk, odd electron

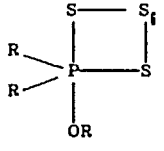
Ring strain is negligible for nine-membered PS_8 cycles. Steric interaction by Ph ligands (resulting in a further lowering of their effective api-

cophilicity) is anticipated; it is said to be sizeable for apical/equatorial Ph_2 pairs and much weaker for Ph(OR) and $(OR)_2$ pairs. [35]

It follows that hypothetical phosphoranes $R_3P.S_8$ (R = Alk, Ph), whatever their conformation (PS_8 ring either axial/equatorial as in 1, or, less probably, di-equatorial), will have two apicophobic groups forced into axial position, with, as a result, a low level of stability. The corollary is that the attack of phosphines R_3P on S_8 will be essentially nucleophilic (equation 2a), this warranting the straightness of lines D, F, I, and J in Fig. 1, 2. In contrast, the same geometry as in **1**, with the (apicophilic) OR ligand located in apex, will afford a stable phosphorane $R_2(RO)P.S_8$ (**2**). The same effect should also stabilise phosphoranes $R(RO)_2P.S_8$ and $(RO)_3P.S_8$, although, in this case, the highest stability will be reached with a di-equatorial PS_8 ring (**3** and **4**).



1



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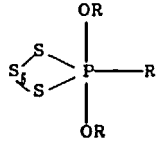

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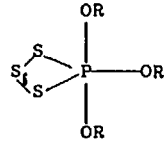

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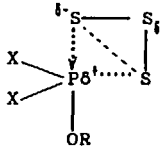


5 (X = R or OR; R = Alk, Ph)

The same criteria can be applied to the phosphorane-like (more or less distorted TBP) transition state (TS) (equation 2b), should the whole process be kinetically controlled by the formation of this intermediate ($k_2 >> k_{-1}$). In this case, all TS are expected to have the PS_8 ring spanning axial/equatorial sites; the stabilising effect in the TS (**5**) can be partly described as an incipient displacement of apical OR (a good leaving group) by the nucleophilic apical $S^{\delta-}$end.

In brief, the irregularities in the reactivity of X_3P compounds with sulfur appear to reflect the dual (amphiphilic) character of P and S, with donor and acceptor strengths of P responding in an antagonistic way to changes in $\Sigma\chi_i$ (note [37]).

The above rationale can be adapted to the reactions of P^{III} compounds with PhSSSPh or EtOOEt (Table I, entries 3,2) (note [39]). Likewise, given the preference of odd electrons for equatorial positions, the same approach

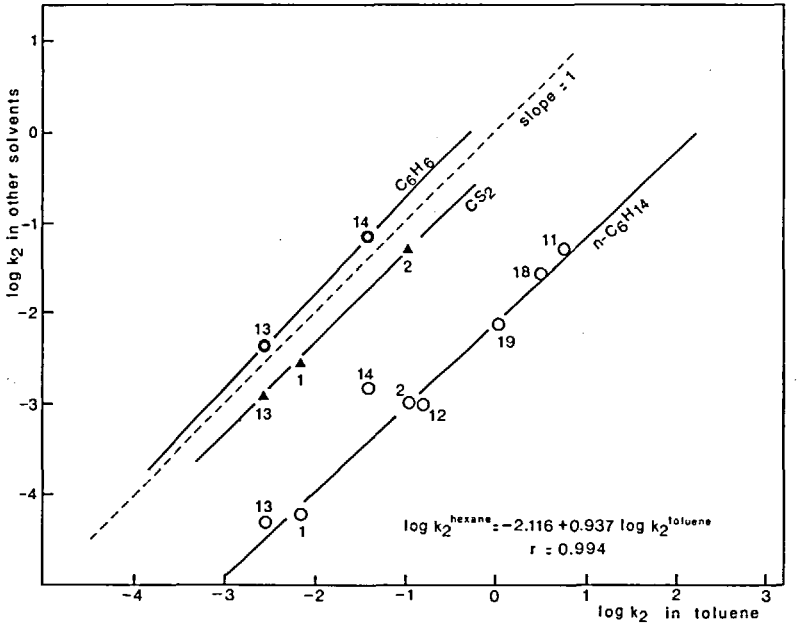


FIGURE 3 Plot of log k_2 in toluene (this work) *versus* log k_2 in hexane (this work), benzene,[14] or carbon disulfide,[9] for the reaction of $X^1X^2X^3P$ (identified by their entry number in Table II) with S_8 at 25°C. As regards the out of line position of p-Tol_3P (n° 14), see text, note [23] ; the least-squares equation log k_2 ^{hexane}/log k_2 ^{toluene} was derived from the best seven points, disregarding point 14

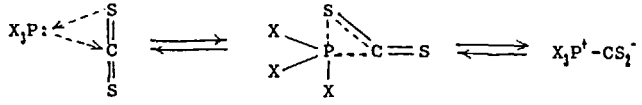
helps to understand the trends noted for the reactions with Bu^tO^- or BuS^- (Table I, entries 1,5).

In the same connexion, the very low concentration of the unstable intermediate $Ph_3P.S_8$ (equation 2a) is probably the cause of the lack of reactivity of Ph_3P in the coloured reaction with $S_8 + CS_2$ (Table I, entry 8, and Table II; equation 1b) :

$$[X_3P.S_8.CS_2] \text{ (steady state concentrations)} = (k_3/k_{-3})\,[X_3P.S_8][CS_2]$$

Finally, the order of reactivity of X_3P compounds with carbon disulfide alone (Table I, entry 7, and Table II) could mean that, in a similar way to path 2b, the attack of X_3P on CS_2 is lateral (at any rate, a nucleophilic attack at C, colinear with C=S, in this linear molecule is hardly conceivable) and synchronous with some back coordination S → P, resulting in a

transition state with a (distorted ?) TBP phosphorane structure (equation 3):



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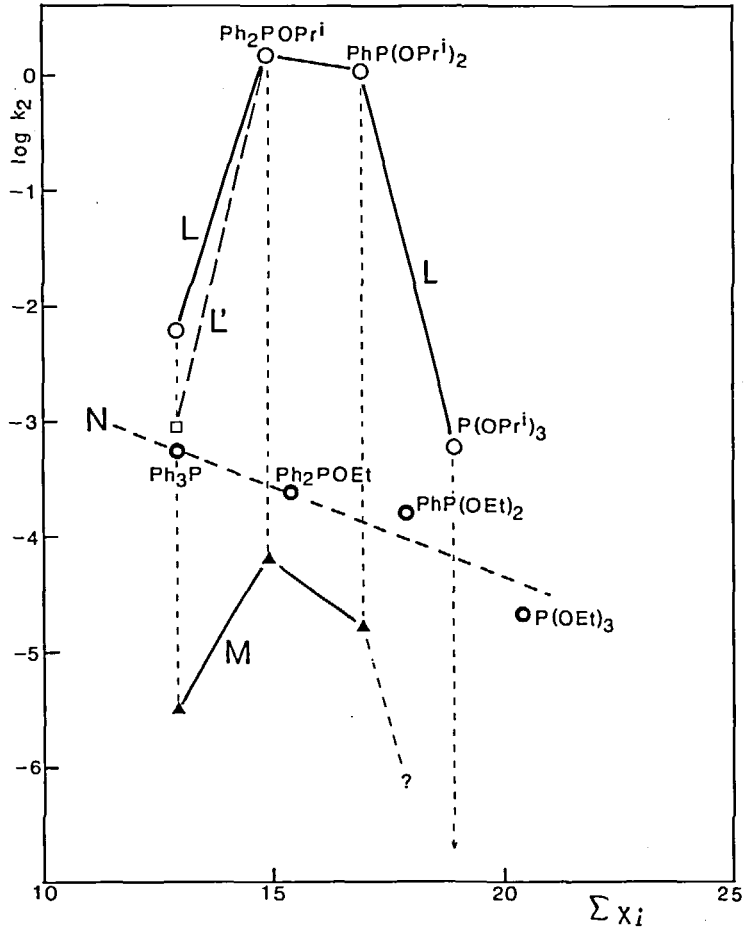

FIGURE 4 Plot of log k_2 (literature data) *versus* $\Sigma\chi_i$ for various bimolecular reactions of $Ph_nP(OR)_{3-n}$. Line L : $Ph_nP(OPr^i)_{3-n}$ + PhSSSPh in toluene at 25°C ;[6] L' refers to similar data from ref.[7]. Line M : $Ph_nP(OPr^i)_{3-n}$ + EtOOEt in benzene at 35°C.[5] Line N : $Ph_nP(OEt)_{3-n}$ + EtI in acetonitrile at 60 °C.[3]

EXPERIMENTAL

$PhPBu_2$, Bu_2POEt, and $BuP(OEt)_2$ were prepared by conventional methods by reaction of BuMgCl with $PhPCl_2$, $EtOPCl_2$, or $P(OEt)_3$ respectively; Ph_2PBu was obtained by reduction of Ph_3PBu,Br by Na metal; Ph_2PNEt_2 and $PhP(NEt_2)_2$ were prepared by treating the corresponding chlorides with $HNEt_2$; Ph_2POPh was obtained from Ph_2PCl and PhOH in the presence of Et_3N. Other X_3P compounds were commercial products (mainly from Aldrich), used as supplied, recrystallised (Ph_3P) or redistilled [$P(OEt)_3$ and $P(OPr^i)_3$]. The purity of all P^{III} compounds was checked by iodometry before any kinetic measurement and taken into account in the calculations. Toluene and hexane were analytical grades, further redistilled from triphenylphosphine (to eliminate occasional traces of sulfur impurities), then dried over molecular sieve 4 Å . All kinetic determinations were performed at least in triplicate, by using the same iodometric procedure as in [9].

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[37] In terms of frontier orbitals, these irregularities should follow the changes of the energy gap E(LUMO)-E(HOMO), when going across a substitution series such as $Ph_nP(OR)_{3-n}$ – where the HOMO consists primarily of the lone pair on phosphorus

[except for $P(NR_2)_3$ [38]] and the LUMO (for $n < 3$) is more or less based on the σ^*(P-OR) antibonding orbital. Incidentally, the departures from additivity shown in Fig. 1 and 2 correspond to similar deviations of the ^{31}P NMR chemical shift of $X^1X^2X^3P$ [J. R. Van Wazer and J. H. Letcher, in *Topics in Phosphorus Chemistry*, ed. M. Grayson and E. J. Griffith (John Wiley and Sons, 1967), Vol. 5, p. 204].

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