Intermediates in the Photochemical Reaction of Tetraphosphorus Trisulphide with Organic Disulphides; Phosphorus-31 Nuclear Magnetic Resonance Parameters for 2,6-Bis(alkylthio)- and 2,6-Di-iodo-3,5,7-trithia-1,2,4,6-tetraphosphabicyclo[2.2.1]heptanes and for 3,6-Bis(alkylthio)-2,5,7-trithia-1,3,4,6-tetraphosphabicyclo[2.2.1]heptanes

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P_4S_3 (**1**) reacts with organic disulphides RSSR under glass-filtered u.v. irradiation to give at first β-$P_4S_3(SR)_2$ (**2**) and then α-$P_4S_3(SR)_2$ (**3**) (R = Me, Et, or Ph), identified in the product mixtures by their ^{31}P n.m.r. spectra. The identities of β-$P_4S_3(SPh)_2$ and α-$P_4S_3(SR)_2$ (R = Et or Ph) have been confirmed by the preparation of products with the same spectra by substitution reactions of β-$P_4S_3I_2$ or α-$P_4S_3I_2$ respectively. The ^{31}P n.m.r. spectrum of β-$P_4S_3I_2$ is reported.

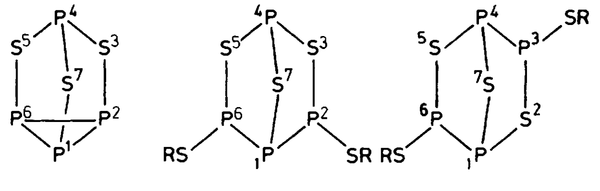
In initial work on the photochemical oxidation of P_4S_3 (**1**) by organic disulphides,[1] molar ratios RSSR:P_4S_3 of at least 6:1 were used, and it was found that the P_4S_3 cage was completely cleaved according to equation (i) (R = Me or Ph). It has now

$$P_4S_3 + 6\,RSSR \longrightarrow 3\,SP(SR)_3 + P(SR)_3 \qquad \text{(i)}$$

been found that if a 1:1 reactant ratio and mild conditions (incomplete reaction in solution in CS_2 at room temperature) are employed, then β-$P_4S_3(SR)_2$ (**2**),† the product of addition of the disulphide across a P–P bond of P_4S_3, can be identified in the solution by ^{31}P n.m.r. The reaction is similar to that of iodine with P_4S_3,[2,3] except that it occurs under photochemical rather than purely thermal conditions [equation (ii); R = Me,

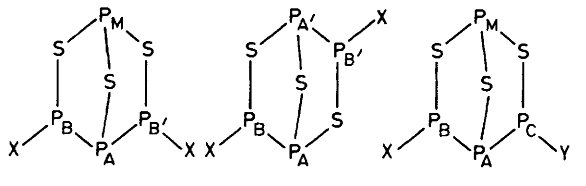
$$\underset{(\mathbf{1})}{P_4S_3} + RSSR \longrightarrow \underset{(\mathbf{2})}{\beta\text{-}P_4S_3(SR)_2} \qquad \text{(ii)}$$

Et, or Ph]. A smaller concentration of the isomeric product with a rearranged skeleton, α-$P_4S_3(SR)_2$ (**3**), is also observed (Table 1). On further irradiation, the yield of the β isomer decreases, while that of the α isomer increases. At the same time, the concentration of the cage fragmentation product $SP(SR)_3$ increases. The rate of disappearance of the β isomer is much greater under photolysis than in the dark, and photochemical isomerisation of (**2**) to (**3**) probably takes place, analogously to the previously reported thermal isomerisation of the iodide.[2,3]



(**1**) (**2**) (**3**)

Figure 1. Skeletal arrangement of P_4S_3 (**1**), β-$P_4S_3(SR)_2$ (**2**), and α-$P_4S_3(SR)_2$ (**3**)



(*a*) (*b*) (*c*)

Figure 2. ^{31}P N.m.r. spin systems for compounds with the β-P_4S_3 and α-P_4S_3 bicyclic skeletons: (*a*) β isomer, (*b*) α isomer, and (*c*) asymmetric compounds (**4**) with β-P_4S_3 skeleton

Results and Discussion

The ^{31}P n.m.r. spectra of β- and α-$P_4S_3(SR)_2$ have been accurately measured, and fitted by the NUMARIT computer program to the anticipated AB_2M and AA′BB′ systems (Figure 2) respectively. In each case, at least 23 transitions have been assigned and iterative fitting has led to a r.m.s. deviation of less than 1 Hz, in spectra with widths of up to 12 000 Hz (Tables 2 and 3). A study of the ^{31}P n.m.r. spectrum at 36.4 MHz of α-$P_4S_3I_2$ has already been reported (Table 3),[4] but previous authors have found that β-$P_4S_3I_2$ was too insoluble for n.m.r. measurement.[3] Using an operating frequency of 121.5 MHz for ^{31}P, sufficient sensitivity was present to obtain a good spectrum of β-$P_4S_3I_2$ (Table 2).

It has not been possible to obtain pure samples of any of the previously unknown compounds β-$P_4S_3(SR)_2$ or α-$P_4S_3(SR)_2$, although a 97.6 mol % pure sample of α-$P_4S_3(SPh)_2$ was made by another route (see below). The case that the AB_2M- and AA′BB′-^{31}P molecules that were observed in solution are indeed the compounds stated rests not only on grounds of synthetic likelihood, but on the following evidence: (*a*) coupling constants which are entirely consistent with the proposed structures (see discussion of n.m.r. results); (*b*) similar changes in coupling constants and chemical shifts on going from β-$P_4S_3(SR)_2$ to β-$P_4S_3I_2$, as on going from α-$P_4S_3(SR)_2$ to α-$P_4S_3I_2$; and (*c*) the preparation of solutions with the same spectra of β-$P_4S_3(SPh)_2$ from β-$P_4S_3I_2$ and of α-$P_4S_3(SR)_2$ (R = Et or Ph) from α-$P_4S_3I_2$, by substitution reactions.

Substitution for iodine in α-$P_4S_3I_2$ has previously been carried out using $(SnMe_3)_2S$,[5] AgX (X = Cl, Br, CN, or NCS),[6] piperidine,[6] morpholine,[6] or aniline.[7] Corresponding reactions of β-$P_4S_3I_2$ have been reported only with $(SnMe_3)_2S$,[5] or with aniline.[7] Preparative use of nucleophilic substitution is difficult

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† Following the trivial naming of the iodides $P_4S_3I_2$ by previous authors,[2,3] compounds with the skeleton (**2**) (Figure 1) are referred to as β isomers, while those with skeleton (**3**) are α isomers. The skeletal atom numbering for P_4S_3 (3,5,7-trithia-1,2,4,6-tetraphosphatricyclo-[2.2.1.0^{2,6}]heptane) is retained for the systematic name of (**2**) (see Figure 1).

Table 1. Relative quantities of products, measured by ^{31}P n.m.r.

		% of total phosphorus as					
	X	β-$P_4S_3X_2$	'Asymmetric $P_4S_3X_2$'	α-$P_4S_3X_2$	SPX_3	PX_3	P_4S_3
(*a*) From P_4S_3 (10.2 mmol) + MeSSMe (9.8 mmol) + CS_2 (5 cm^3)							
After 1 h irradiation	SMe	22	2	2	0.5		73
After 4 h irradiation	SMe	20	2	14	5		58
(*b*) From P_4S_3 (10.1 mmol) + EtSSEt (9.4 mmol) + CS_2 (5 cm^3)							
After 1 h irradiation	SEt	7	1	1	0		90
After 4 h irradiation	SEt	15	2	5	1		76
(*c*) From P_4S_3 (10.0 mmol) + PhSSPh (10.0 mmol) + CS_2 (5 cm^3)							
After 1 h irradiation	SPh	9		4	9	4	73
After 4 h irradiation	SPh	0		4	12	4	80
(*d*) From β-$P_4S_3I_2$ (0.63 mmol) + $SiMe_3(SPh)$ (2.47 mmol) + CS_2 (2 cm^3)							
After 15 min reaction	SPh	68	23	0	0		9

Table 2. ^{31}P N.m.r. parameters for β-$P_4S_3X_2$

X	I	SMe	SEt	SPh
Chemical shifts/p.p.m.				
δ_A	150.84	103.33	105.62	114.44
δ_B	93.30	100.05	96.23	99.20
δ_M	195.52	175.96	172.38	175.73
Coupling constants[a]/Hz				
J_{AB}	−252.01 (0.08)	−296.30 (0.14)	−291.90 (0.10)	−292.29 (0.09)
J_{AM}	82.52 (0.10)	69.01 (0.30)	69.92 (0.11)	71.86 (0.11)
J_{BM}	56.08 (0.08)	50.45 (0.20)	50.31 (0.09)	50.96 (0.09)
No. of transitions assigned	24	24	24	24
R.m.s. deviation/Hz	0.17	0.42	0.19	0.18

[a] σ in parentheses.

Table 3. ^{31}P N.m.r. parameters for α-$P_4S_3X_2$

X	I[a]	I	SMe	SEt	SPh
Chemical shifts/p.p.m.					
δ_A	125.26	125.06	105.74	103.74	109.49
δ_B	128.94	128.72	126.62	122.72	127.48
$\delta_B - \delta_A$	3.68	3.67	20.88	18.98	17.98
Coupling constants[b]/Hz					
$J_{AA'}$	74.8	74.8 (0.1)	57.8 (0.5)	58.1 (0.6)	60.3 (0.2)
J_{AB}	−243.6	−243.7 (0.1)	−290.1 (0.4)	−288.8 (0.4)	−282.4 (0.1)
$J_{AB'}$	21.7	21.6 (0.1)	22.1 (0.2)	22.3 (0.3)	21.7 (0.1)
$J_{BB'}$	9.3	9.3 (0.1)	−9.0 (0.5)	−8.4 (0.6)	−6.0 (0.2)
No. of transitions assigned		24	24	23	24
R.m.s. deviation/Hz		0.17	0.87	0.99	0.34

[a] Ref. 4. [b] σ in parentheses.

because products are frequently thermally unstable, and because the only good solvent for α- or β-$P_4S_3I_2$ is CS_2, which is itself susceptible to attack by strong nucleophiles. It has now been found that while a solution of α-$P_4S_3I_2$ in CS_2 does not react at room temperature with EtSH, addition of triethylamine causes immediate reaction according to equation (iii). Except for a small quantity of product whose spectrum was barely distinguishable from the n.m.r. baseline, but which was probably $P(SEt)_3$, ^{31}P n.m.r. showed that the α-$P_4S_3I_2$ was quantitatively converted to α-$P_4S_3(SEt)_2$. There were non-phosphorus-containing components in the product, however, which could not be removed by vacuum sublimation (which caused complete decomposition) nor by crystallisation methods.

$$\alpha\text{-}P_4S_3I_2 + 2\,EtSH + 2\,NEt_3 \longrightarrow \alpha\text{-}P_4S_3(SEt)_2 + 2\,NHEt_3I \quad \text{(iii)}$$

In preparing α-$P_4S_3(SPh)_2$ from α-$P_4S_3I_2$, contamination by organic by-products was avoided by using $Hg(SPh)_2$ as the substitution reagent.[8] The solubility of this mercurial in CS_2 was inconveniently low, but addition of 4 mmol of pyridine (py) per mmol of mercurial caused it to dissolve. This solution was shown by ^{31}P n.m.r. to react quantitatively with α-$P_4S_3I_2$ [equation (iv)], but no HgI_2 was precipitated because

$$\alpha\text{-}P_4S_3I_2 + Hg(SPh)_2 \xrightarrow{py/CS_2} \alpha\text{-}P_4S_3(SPh)_2 + HgI_2(py)_2 \quad \text{(iv)}$$

$HgI_2(py)_2$ is also soluble in CS_2. Despite an old report[9] that $HgI_2(py)_2$ completely loses pyridine on warming in a few hours, an attempt to decompose it to insoluble HgI_2, by pumping away pyridine under vacuum, failed. In 6 h at 97 °C, little pyridine was removed, but the α-$P_4S_3(SPh)_2$ was shown by ^{31}P n.m.r. to have completely decomposed, approximately according to equation (v).

$$6\,\alpha\text{-}P_4S_3(SPh)_2 \longrightarrow 5\,P_4S_3 + 3\,SP(SPh)_3 + P(SPh)_3 \quad \text{(v)}$$

Pyridine did not need to be used if the reaction between α-$P_4S_3I_2$ and $Hg(SPh)_2$ was carried out quickly in refluxing benzene, in which both reagents have some solubility. Again the reaction proceeded quantitatively, but while much yellow HgI_2 was precipitated, it was not possible to remove all of the HgI_2 contaminant from the α-$P_4S_3(SPh)_2$ by fractional crystallisation. Conversion of yellow HgI_2 to the less soluble red form went very slowly, over a period of several months at room temperature. The best elemental analyses for α-$P_4S_3(SPh)_2$ corresponded to a 2.4 mol % contamination by HgI_2, and there has not yet been any success in growing crystals for a structure determination.

The known thermal instability of β-$P_4S_3I_2$ to isomerisation[2,3] made $Hg(SPh)_2$ in refluxing benzene an unsuitable reagent for its substitution. It was found, however, that there is no reaction between $SiMe_3(SPh)$ and CS_2 at room temperature, allowing this reagent to be used. β-$P_4S_3I_2$, which is only slightly soluble in CS_2 alone, rapidly dissolved in a solution of $SiMe_3(SPh)$ in CS_2. ^{31}P N.m.r. of the solution showed a strong spectrum of β-$P_4S_3(SPh)_2$, but a compound with an ABCM spectrum, and which was probably an asymmetric isomer of $P_4S_3(SPh)_2$ (see discussion of n.m.r. results), was also present, along with P_4S_3 and traces of α-$P_4S_3(SPh)_2$ and $SP(SPh)_3$.

Discussion of N.M.R. Results.—Despite previous reports of a number of compounds with the α-P_4S_3 bicyclic skeleton,[6] only for α-$P_4S_3I_2$ has a complete assignment of the ^{31}P n.m.r. spectrum been given.[4] No n.m.r. spectra have been reported for compounds with the β-P_4S_3 bicyclic skeleton.

The parameters for the SMe and SEt compounds in Tables 2 and 3, and for α-$P_4S_3(SPh)_2$, were obtained from spectra measured in the Fourier-transform mode with inverse gated proton decoupling. This allowed pure AB_2M and AA′BB′ spectra of the respective phosphorus cages (Figure 2) to be accumulated, uncomplicated by coupling to protons on the ligands, but also without distortion of intensities by the nuclear Overhauser effect. ^{31}P–^{1}H coupling in β-$P_4S_3(SPh)_2$ was smaller than in the SMe or SEt compounds, and was not resolved, making a decoupling experiment unnecessary in this case.

Coupling constants in these phosphorus spectra are generally an order of magnitude larger than those found for the same spin systems of protons in organic compounds, yet spectral linewidths are not much wider. This means that considerably more detail can be seen for a given spin system in the phosphorus case, and use of the first-order approximation in interpreting the spectra tends frequently to lead to wrong conclusions. For example, in the spectrum of β-$P_4S_3I_2$, the P_A resonance clearly appears as a doublet of doublets of doublets. One might conclude that the nuclei marked P_B and $P_{B'}$ in Figure 2 are in fact non-equivalent in the iodide, coalescence of peaks separated by 9 Hz being required to produce the triplet expected for a symmetrical molecule. In fact, despite the large internal shift δ_{AB} (6 990.7 Hz, 57.538 p.p.m.) and small J_{AB}/δ_{AB} (0.036), the system should not be treated as first order, and simulation by NUMARIT using the symmetrical AB_2M model correctly predicts the observed spectrum.

The first-order approximation predicts a doublet of triplets for P_M of β-$P_4S_3(SMe)_2$, as was indeed found for the other three compounds in Table 2. In fact, the centre peak of the low-field triplet of the SMe compound was split by 4.5 Hz, while that of the high-field triplet was split by 2.4 Hz (Figure 3). This too could be simulated, provided that J_{AM} and J_{BM} were of opposite sign to J_{AB}. When this sign relationship was tried for the other β isomers, it was found in each case that iterative fitting converged to significantly better r.m.s. deviations than with all positive coupling constants.

While only 24 major transitions are expected in the ^{31}P-{^{1}H} spectrum of β-$P_4S_3(SMe)_2$, and these are readily assigned to the observed spectrum, the undecoupled ^{31}P spectrum, treated as an $ABB'MX_3X_3'$ system with $J_{BX'} = 0$, is expected to contain 728 major transitions, making total assignment and iterative fitting impractical. We therefore estimated J_{BX} ($^{3}J_{PH}$) as 12.0 ± 0.5 Hz by trial and error, by visually comparing the region of the spectrum mainly due to P_B and $P_{B'}$ (Figure 4) with the envelope predicted by NUMARIT simulations. The appearance of the simulated spectrum was found to be insensitive to $J_{BB'}$, and a value of 0 was assumed.

Like P_4S_3,[10] these bicyclic derivatives show ^{31}P chemical

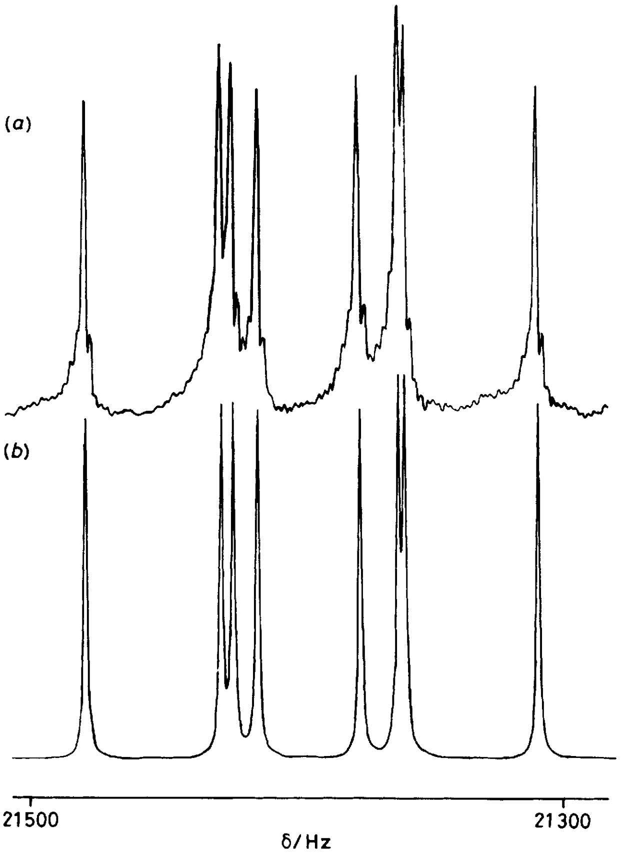

Figure 3. The P_M part of the observed (*a*) and calculated (*b*) ^{31}P-{^{1}H} n.m.r. spectrum of β-$P_4S_3(SMe)_2$

Table 4. ^{31}P Chemical shifts [in p.p.m. relative to $SP(SPh)_3$ as internal standard] for β-$P_4S_3(SPh)_2$ and P_4S_3 in solution in CS_2 (a) from the photolytic reaction of P_4S_3 with PhSSPh, and (b) from the reaction of β-$P_4S_3I_2$ with $SiMe_3(SPh)$

	Solution (a)	Solution (b)
β-$P_4S_3(SPh)_2$		
δ_A	25.36	24.76
δ_B	9.74	9.52
δ_M	87.22	86.05
$\delta_A - \delta_B$	15.62	15.24
$\delta_M - \delta_A$	61.86	61.28
$\delta_M - \delta_B$	77.48	76.53
P_4S_3 (P_A axial, P_B basal)		
δ_A	−19.47	−21.45
δ_B	−206.97	−210.06
$\delta_A - \delta_B$	187.50	188.61

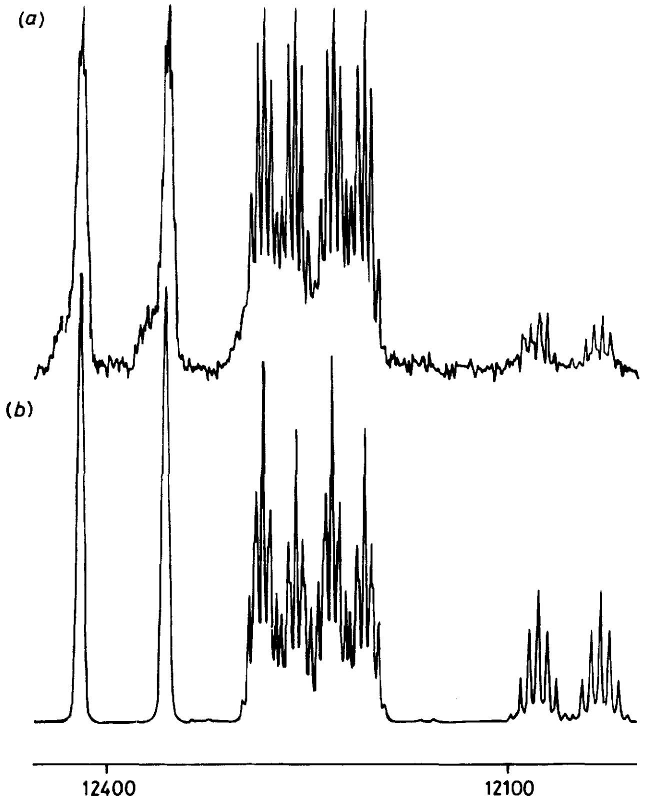

Figure 4. Part of the observed (*a*) and calculated (*b*) undecoupled ^{31}P n.m.r. spectrum of β-$P_4S_3(SMe)_2$; the two peaks on the left are mainly due to P_A, while the others are mainly due to P_B and $P_{B'}$

shifts which are unusually sensitive to concentration in CS_2 solution. For example, spectra of solutions of β-$P_4S_3(SPh)_2$ obtained from addition of PhSSPh to P_4S_3 and from reaction of β-$P_4S_3I_2$ with $SiMe_3(SPh)$ [Table 4, solutions (a) and (b) respectively] yielded the same coupling constants to within 4σ (0.4 Hz), but gave chemical shifts [measured from $SP(SPh)_3$ as internal standard] which were different by up to 143 Hz (1.17 p.p.m.). Although the bridgehead atom P_M absorbed at highest frequency, its chemical shift was the most sensitive to environment. This is in contrast to the cases of P_4, P_4S_3, and PBr_3, where the sizes of dispersion interactions and hence solvent shifts were found to decrease linearly with absorption frequency.[11] The standard deviations found by NUMARIT for chemical shifts for particular samples (typically 0.001—0.003 p.p.m.) were much smaller than solvent shifts which would limit reproducibility of data, and are therefore omitted from Tables 2 and 3.

Similarity of electronic structure between β- and α-isomers is reflected in the similarity of the corresponding coupling constants (Tables 2 and 3). Taking the SMe compounds as examples, the similarity of $^1J_{AB}$ [296.3 and 290.1 Hz respectively; *cf.* 277.7 Hz for $P_4(SiMe_2)_3Bu^t_2$ which has the α isomer structure[12]] is not surprising, but $^2J_{AM}$ (β isomer) is similar to $^2J_{AA'}$ (α isomer) [69.0 and 57.8 Hz respectively; *cf.* 73.9 for $P_4(SiMe_2)_3Bu^t_2$, 69.8 for P_4S_3, and 85 Hz for P_4Se_3[13]], and $^2J_{BM}$ (β isomer) and $^2J_{AB'}$ (α isomer) are smaller than this [50.5 and 22.1 Hz respectively; *cf.* 12.4 Hz for $P_4(SiMe_2)_3Bu^t_2$]. The change in $^1J_{AB}$ in going from $P_4S_3(SMe)_2$ to $P_4S_3I_2$ is almost the same for the two isomers (44.3 and 46.4 Hz respectively), as is the change in $^2J_{AM}$ (β isomer) and $^2J_{AA'}$ (α isomer) (13.5 and 17.0 Hz respectively). $^2J_{AB'}$ almost does not change in going from α-$P_4S_3(SMe)_2$ to α-$P_4S_3I_2$, and there is likewise little change (5.6 Hz) in $^2J_{BM}$ for the β isomers. Of the changes in chemical shift on going from $P_4S_3(SMe)_2$ to $P_4S_3I_2$, it is for both isomers the bridgehead atom P_A which changes most.

The greater sensitivity of chemical shift of the bridgehead phosphorus atoms, compared with the atoms carrying the exocyclic substituents, both to change of substituent and to intermolecular interactions in solution, appears strange. I have made a related observation in a preliminary investigation of the photochemical reaction of P_4S_3 with a cyclic disulphide, 1,2-dithiolane, which gave a polymeric product. ^{31}P N.m.r. showed this to contain the β-$P_4S_3X_2$ skeleton. While the shifts and couplings (δ_A 107.25, δ_B 97.62, δ_M 174.42 p.p.m.; J_{AB} 292, J_{AM} 66, J_{BM} 50 Hz) were similar to those for β-$P_4S_3(SEt)_2$ (Table 2), the peaks were much broader; those in the B grouping were the narrowest (23 Hz at half height), while in the A group J_{AM} was barely resolved, and the M group of peaks was not resolved at all. Here again the bridgehead atoms P_A and P_M are showing greater sensitivity to a varying environment than P_B. These effects may be attributed to a tendency of the book-shaped molecules to open or close to a small extent by changing the intercyclic angles 3–4–5 and 2–1–6 (Figure 1), in response to electronic effects. Proof of this hypothesis must await crystals for a structure determination.

In the ^{31}P spectrum of the product of reaction of β-$P_4S_3I_2$ with $SiMe_3(SPh)$, besides the spectrum of β-$P_4S_3(SPh)_2$, 24 peaks could be assigned to an ABCM spectrum. Similar spectra were found for compounds present in low yield in the products of photolysis of P_4S_3 with MeSSMe and with EtSSEt (though not with PhSSPh). The resulting parameters are shown in Table 5 (the multiplet due to P_C of the ethyl case was obscured, so a computer fit was not done, the given parameters being obtained by a first-order analysis of the other three multiplets). They may be assigned to a series of bicyclic compounds (**4**) (Figure 2), isomeric with and having the same structure as β-$P_4S_3(SR)_2$, but with P_B chemically non-equivalent to P_C. The evidence that these are indeed third isomers of $P_4S_3(SR)_2$ is as follows. Because the formation of the SPh compound was by a reaction different from the one by which the SMe and SEt compounds were formed, and no obvious ligand other than SR was present in all cases, it is probable that X and Y in (**4**) are both SR. $^1J_{AB}$ and $^1J_{AC}$ have similar values to each other and to $^1J_{AB}$ in β-$P_4S_3(SR)_2$, so it is probable that P_B and P_C carry SR groups and no additional ligands. The proposed reason for the non-equivalence of P_B and P_C is that pyramidal bonding around one phosphorus is inverted with respect to the other. If the SR ligands in the symmetrical β-$P_4S_3(SR)_2$ are on the same side of

Table 5. ^{31}P N.m.r. parameters for asymmetric $P_4S_3(SR)_2$ isomers

R	Me	Et	Ph
Chemical shifts/p.p.m.			
δ_A	90.54	89.7	95.33
δ_B	108.18	104.4	110.60
δ_C	130.66	*a*	128.10
δ_M	187.42	186.21	187.42
Coupling constants[b]/Hz			
J_{AB}	−322.9 (0.3)	−323	−317.39 (0.08)
J_{AC}	−309.4 (0.3)	−308	−303.30 (0.08)
J_{AM}	66.7 (0.3)	65.5	67.83 (0.08)
J_{BC}	2.0 (0.3)	*c*	2.63 (0.08)
J_{BM}	35.4 (0.3)	35.2	36.46 (0.08)
J_{CM}	15.6 (0.3)	15.0	17.65 (0.08)
No. of transitions assigned	32		32
R.m.s. deviation/Hz	0.54	*c*	0.13

[a] Not observed. [b] σ in parentheses. [c] Not obtained; no computer fit done.

the $P_BP_MP_{B'}$ plane (Figure 2) as the bridging sulphur atom, as was found[2] in the solid β-$P_4S_3I_2$, then by comparison of J_{BM} and J_{CM} in the asymmetric molecules (Table 5) with J_{BM} in β-$P_4S_3(SR)_2$ (Table 2), it may be concluded that X in (**4**) is probably on the same side as the bridging sulphur, and Y is on the opposite side. A second symmetrical isomer is possible, with both X and Y on the opposite side of the phosphorus plane from the bridging sulphur. No spectra corresponding to this isomer could be identified in the products of photolysis of P_4S_3 with RSSR, and its yield, if any, must be even smaller than that of the unsymmetrical isomer (**4**).

Experimental

General techniques and photolysis procedures were as described previously,[1] except that n.m.r. spectra were measured using a Bruker WM300WB spectrometer operating at 121.5 MHz for ^{31}P. A capillary containing D_3PO_4–D_2O (molar ratio equivalent to 85% H_3PO_4–H_2O) was used as lock and external standard; chemical shifts of known compounds were not significantly different from those measured from H_3PO_4–H_2O.

EtSSEt (Pfalz and Bauer) and $SiMe_3(SPh)$ (Aldrich) were used as received. α-$P_4S_3I_2$,[14] β-$P_4S_3I_2$,[2] and $Hg(SPh)_2$[8b] were prepared by literature methods.

Reaction of α-$P_4S_3I_2$ *with* EtSH–NEt_3.—α-$P_4S_3I_2$ (5.39 g, 11.4 mmol) was flushed with N_2 in a three-necked flask equipped with a micro dropping funnel and magnetic stir-bar, and dissolved in dry CS_2 (60 cm^3). EtSH (dried over $CaCl_2$) (1.70 cm^3, 23.0 mmol) was added. The i.r. spectrum showed no reaction. NEt_3 (dried over NaOH) (3.20 cm^3, 22.9 mmol) was then added dropwise to the stirred solution at 0 °C over 15 min, and stirring at 0 °C was continued for a further 30 min. Filtration using positive nitrogen pressure gave a pale yellow solution, from which CS_2 was removed at low temperature by vacuum transfer, yielding a bright yellow oil. ^{31}P N.m.r. showed α-$P_4S_3(SEt)_2$ (see Results and Discussion section) and no remaining α-$P_4S_3I_2$, nor P_4S_3. The mass spectrum (m.s.) showed *m/e* 341.8333 (M^+, $C_4H_{10}P_4S_5^+$ requires 341.8337), 313 (M − Et), 281 (M − SEt), 252 (M − SEt_2), 220 (M − S_2Et_2); m^* 286.5 ($M \longrightarrow 313$), 230.9 ($M \longrightarrow 281$). The oil was immiscible with light petroleum (b.p. 40—60 °C). Attempted crystallisation from toluene failed to yield pure α-$P_4S_3(SEt)_2$, ^{31}P n.m.r. and m.s. showing traces of its decomposition products $SP(SEt)_3$ and $P(SEt)_3$. Vacuum sublimation/molecular distillation at 85 °C for 2 h gave $SP(SEt)_3$ as distillate (i.r. and m.s.), with P_4S_3 remaining in the residue.

Reaction of α-$P_4S_3I_2$ *with* $Hg(SPh)_2$.—α-$P_4S_3I_2$ (2.76 g, 5.82 mmol) and $Hg(SPh)_2$ (2.44 g, 5.82 mmol) were separately flushed with nitrogen and dissolved in refluxing dry benzene (70 and 80 cm^3 respectively). The hot solution of $Hg(SPh)_2$ was quickly added to the stirred solution of α-$P_4S_3I_2$ and reflux resumed for 10 min. After 5 min an orange-yellow precipitate formed. The reactor was removed from the heating bath and allowed to cool with stirring for a further 1 h. The colourless solution was filtered and solvent removed (as above), to yield a bright yellow solid. ^{31}P N.m.r. showed only α-$P_4S_3(SPh)_2$ (see Results and Discussion section), but m.s. showed first HgI_2 (at probe temperature < 100 °C) then α-$P_4S_3(SPh)_2$ (at probe temperature 200 °C) giving *m/e* 438 (M^+), 329 (M − SPh), 252 (M − SPh_2), 220 (M − S_2Ph_2). Fractional recrystallisation from CS_2 or toluene separated yellow HgI_2 and yielded a near-colourless product [(Found: C, 32.1; H, 2.2. $C_{12}H_{10}P_4S_5$ requires C, 32.9; H, 2.3%). These results can be explained by assuming a 2.4 mol % HgI_2 impurity]. Complete removal of HgI_2 could not be effected.

Reaction of β-$P_4S_3I_2$ *with* $SiMe_3(SPh)$.—β-$P_4S_3I_2$ (0.30 g, 0.63 mmol) was added to a stirred solution of $SiMe_3(SPh)$ (0.45 g, 2.47 mmol) in CS_2 (2 cm^3) at 20 °C. The brown-orange β-$P_4S_3I_2$ rapidly dissolved to give a pale yellow solution. A sample was taken after 15 min for ^{31}P n.m.r., which showed mainly β-$P_4S_3(SPh)_2$, together with a compound with an ABCM spectrum (see Results and Discussion section; for relative concentrations, see also Table 1). Removal of volatiles under vacuum at 20 °C yielded a pale yellow oil which crystallised to a pasty consistency on standing. M.s. showed $S(SPh)_3$, $P(SPh)_3$, and P_4S_3, with no M^+ for $P_4S_3(SPh)_2$, indicating extensive decomposition on removal of solvent.

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