Reactions of Tetraphosphorus Trisulphide with Organic Disulphides under Ultraviolet Irradiation, and with Sulphuryl Chloride †

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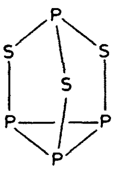
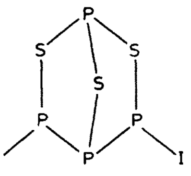
P_4S_3 under glass-filtered u.v. irradiation is rapidly cleaved by alkyl and aryl disulphides to give tetrathiophosphate esters, $SP(SR)_3$, and trithiophosphite esters, $P(SR)_3$ (R = Me or Ph), in quantitative yield, as measured in the product mixture by ^{31}P and ^1H n.m.r. spectroscopy. No sulphurisation of P_4S_3 was found. In a competition reaction, MeSSMe and PhSSPh reacted to a similar extent with P_4S_3 to give all eight possible products $S_xP(SPh)_n(SMe)_{3-n}$ (x = 0 or 1, n = 0—3) in relative quantities within each oxidation state approximating to a statistical distribution of ligands, but there was more MeS substitution of the phosphorus(v) products and more PhS substitution of the phosphorus(III) products. Reaction of MeSSPh with P_4S_3 gave similar results. Redistribution of ligands took place when a mixture of $P(SMe)_3$ and $P(SPh)_3$ was photolysed, and photolysis of a mixture of $P(SMe)_3$ and MeSSPh caused the PhS group to be distributed between the trithiophosphite and disulphide sites. $P(SMe)_3$ and $P(SPh)_3$ were not sulphurised by MeSSMe and PhSSPh respectively, but $P(SMe)_3$ was sulphurised to $SP(SMe)_3$ to a small extent by MeSSPh. P_4S_3 is similarly cleaved by sulphuryl chloride, but under thermal conditions, to give $SPCl_3$ and PCl_3, with no evidence for intermediates.



(1)



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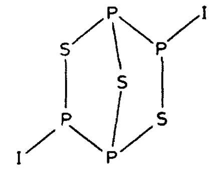

(3)

Tetraphosphorus trisulphide, P_4S_3 (1),‡ is a cage molecule containing three P–P bonds. One of these may be oxidatively opened with iodine [1] to give β-$P_4S_3I_2$ (2) which spontaneously rearranges to α-$P_4S_3I_2$ (3). This more stable iodide (3) can be made more conveniently by reaction of solutions of the elements.[2] The corresponding halides α-$P_4S_3Cl_2$ and α-$P_4S_3Br_2$ can be prepared from α-$P_4S_3I_2$ by reaction with silver halide,[3] but because CS_2 is the only solvent in which P_4S_3 and its derivatives have good solubility, the reactions are run at low temperatures and hence require an inconveniently long time. It would be desirable to prepare the derivatives $P_4S_3X_2$ directly by oxidation of P_4S_3. Direct bromination [4] of P_4S_3 gives P_4S_7, although little is known about this reaction, and direct chlorination of P_4S_3 under modern conditions appears not to have been reported.

We attempted chlorination of P_4S_3, and found that this resulted in complete destruction of the cage. We therefore sought oxidising agents which on thermodynamic grounds would be less likely to cleave the P–S bonds of P_4S_3, because the new bonds to phosphorus would be of similar energy to those broken. We chose alkyl and aryl disulphides R^1SSR^2 (which could produce RS˙ type radicals as intermediates on u.v. irradiation), and hoped to make compounds of the type $P_4S_3(SR^1)(SR^2)$. The compounds α-$P_4S_3(SEt)_2$ and α-$P_4S_3(SPh)_2$ have previously been prepared from α-$P_4S_3I_2$.[5] The desulphurisation of organic disulphides to organic monosulphides by phosphorus(III) compounds, such as triethyl phosphite, is well known. This reaction goes thermally at low temperatures by an 'ionic' Arbuzov-type mechanism [6] with some disulphides, particularly unsymmetrical ones, *e.g.* equation (i), but where this reaction is slow, an alternative free-radical reaction may be promoted by Pyrex-filtered u.v. irradiation,[7] *e.g.* equation (ii). No reactions with disulphides have been reported for P_4S_3, and no photochemical reactions of P_4S_3 appear to have been attempted previously, possibly because all practical solvents for P_4S_3 absorb u.v. light strongly.

$$P(OEt)_3 + PhSSMe \longrightarrow MeSP(O)(OEt)_2 + PhSEt \quad (i)$$

$$P(OEt)_3 + Bu^tSSBu^t \longrightarrow SP(OEt)_3 + Bu^tSBu^t \quad (ii)$$

Results and Discussion

Chlorination of P_4S_3.—An attempt was made to study the reaction of crystalline P_4S_3 with an equimolar quantity of chlorine in the absence of solvent, by condensing chlorine onto P_4S_3 at −196 °C under vacuum system conditions, and allowing the mixture to warm slowly. Reaction took place on the surface of the solid at a temperature below 0 °C; all of the chlorine was consumed. The volatile products were shown (i.r.) to be $SPCl_3$ and PCl_3. The solid residue was extracted with CS_2, and shown to contain much unreacted P_4S_3, along with some practically insoluble material shown (i.r. and mass spectra) to be P_4S_7.

Clearly a homogeneous system was required in order to study the chlorination, but no solvent could be found that was unreactive with chlorine, yet allowed sufficient concentration of P_4S_3 for the reaction to be conveniently followed. The possibility of using sulphuryl chloride, SO_2Cl_2, instead of chlorine in solution in CS_2 was therefore investigated. It was found that if free chlorine was removed from sulphuryl chloride by bubbling nitrogen through it, then the sulphuryl chloride did not react with CS_2 at room temperature in 3 d, as shown by the absence of i.r. peaks due to chlorination products.

Sulphuryl chloride reacted at room temperature with a solution of P_4S_3 in CS_2. In contrast to the reaction with chlorine, only a slight turbidity was produced, so almost no P_4S_7 had been formed. The products were SO_2, $SPCl_3$, PCl_3, and much of the equimolar quantity of P_4S_3 remained un-

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‡ 3,5,7-Trithia-1,2,4,6-tetraphosphatricyclo[2.2.1.$0^{2,6}$]heptane.

reacted when the SO_2Cl_2 was used up. The P_4S_3 cage was completely cleaved in the reaction [equation (iii)]. Use of a lower

$$P_4S_3 + 6\ SO_2Cl_2 \longrightarrow 6\ SO_2 + 3\ SPCl_3 + PCl_3 \quad \text{(iii)}$$

temperature (−10 °C) considerably slowed the reaction, but failed to reveal any more complex fragmentation products.

Reaction of P_4S_3 *with Organic Disulphides.*—Excess dimethyl disulphide was found to be a satisfactory solvent for P_4S_3 at 60 °C, showing no appreciable thermal reaction in 7 h. The solution was held at 60 °C while it was irradiated for 1 h with light from a medium-pressure mercury arc, filtered by borosilicate glass. The P_4S_3 reacted completely according to equation (iv). The product yields were quantitative (^{31}P and ^1H

$$P_4S_3 + 6\ MeSSMe \longrightarrow 3\ SP(SMe)_3 + P(SMe)_3 \quad \text{(iv)}$$

n.m.r.) in that no other phosphorus- or hydrogen-containing components could be detected, and the observed molar ratio $SP(SMe)_3 : P(SMe)_3$ was 3.06 : 1. The reaction appeared to be exactly analogous to the reaction of P_4S_3 with sulphuryl chloride.

The most satisfactory previous preparation of trimethyl tetrathiophosphate [8] or trimethyl trithiophosphite [9] was achieved by the reaction of $Pb(SMe)_2$ with thiophosphoryl chloride or phosphorus trichloride respectively. The trithiophosphite is also formed by oxidation of white phosphorus by dimethyl disulphide at high temperature.[10] The present reaction is remarkable because (*a*) reaction is rapid and quantitative; (*b*) hardly any desulphurisation of dimethyl disulphide took place, despite the known stability and insolubility of P_4S_7, which would be the expected product; and (*c*) the rate of reaction was much more rapid than photolytic desulphurisation of disulphides by phosphorus(III) compounds which commonly requires at least 27 h irradiation under similar conditions.[7]

The high rate of reaction suggested that the photochemical step was the excitation of P_4S_3 rather than of the disulphide. This was supported by the finding that addition of CS_2 to the mixture before photolysis, in equimolar quantity to the MeSSMe taken, did not appreciably slow the reaction. The products were the same, except that the observed product ratio $SP(SMe)_3 : P(SMe)_3$ was 2.5 : 1. In a 1-cm cell, MeSSMe and CS_2 each absorb all light with $\lambda < 375$ nm, whereas a solution of P_4S_3 in CS_2, in the concentration used, also absorbs all light up to 415 nm. Because light of the wavelengths of interest was totally absorbed within the thickness of solution irradiated, the photochemical step of the reaction can be assumed to have taken place in a narrow zone of the solution near to the illuminated reactor wall. Portions of the u.v. spectra of the components could be measured in cyclohexane (for CS_2 or MeSSMe) or benzene (for P_4S_3) solutions. If the absorption coefficients thus obtained approximate to those in the photolysis mixture, then absorbances corresponding to the concentrations used, and to a 5-μm-thick reaction zone, can be calculated (see Figure; the cut-off for Schott–Ruhr Duran glass, as used for the reactor, is also shown). It is seen that the tail of the absorption of MeSSMe which projects above the glass cut-off, is effectively covered by an absorption maximum of CS_2, whereas an absorption maximum of P_4S_3 stands clear. Light absorption by P_4S_3 leads to an excited state which probably stays intact until it reacts with the disulphide, since irradiation of a solution of P_4S_3 alone in CS_2 led to no reaction.

Liquid diphenyl disulphide reacted similarly to MeSSMe (Table 1). In the absence of irradiation there was no evidence for reaction in 1 h at 60 °C. Upon photolysis, except for an unidentified singlet at δ 102.9 in the ^{31}P n.m.r. spectrum (standard 80% H_3PO_4–H_2O, downfield shift positive), which accounted for 4.3% of total P, the only phosphorus-containing products were $SP(SPh)_3$ and $P(SPh)_3$ in the ratio 3.2 : 1, analogous to the methyl case. Use of a Cl_3CS-containing disulphide, Cl_3CSSEt, greatly slowed the reaction: much P_4S_3 remained after 13 h irradiation, but it had completely reacted after 36 h. The ^{31}P n.m.r. of the product mixture was poor, with the phosphorus present being distributed between many products in low concentrations. Only $SP(SEt)_3$ and possibly $P(SEt)_3$ could be identified by their published spectra.[11]

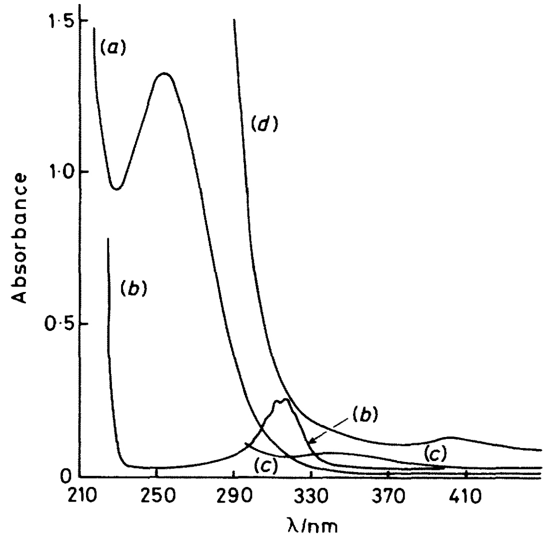

Figure. Calculated u.v. spectra for (*a*) MeSSMe, (*b*) CS_2, and (*c*) P_4S_3 in their initial concentrations in the reaction mixture, in a 5-μm-thick reaction zone; (*d*) is the actual spectrum of a single thickness of Duran glass

Since MeSSMe and PhSSPh showed similar rates of reaction with P_4S_3, a competition reaction was undertaken in which a mixture of six relative molar quantities of each disulphide was allowed to react with one relative molar quantity of P_4S_3. By ^1H n.m.r., the PhSSPh : MeSSMe ratio taken was 1.04 : 1. After 1 h irradiation at 60 °C, all of the P_4S_3 had reacted. All eight possible products $SP(SPh)_n(SMe)_{3-n}$ (n = 0—3) and $P(SPh)_n(SMe)_{3-n}$ (n = 0—3) were observed by ^{31}P n.m.r., and their quantities measured by integration (Table 2). The previously unreported mixed esters were clearly identifiable in the mixture because (*a*) the chemical shifts showed steady progressions with substitution, with δ increasing with SPh substitution for the phosphorus(III) compounds, but decreasing for the phosphorus(V) compounds; (*b*) the multiplicities of the ^{31}P absorptions showed the number of methyl groups attached, since coupling to H in phenyl was not observed; and (*c*) coupling constants *J*(PH) were constant within experimental precision within the set of tetrathiophosphates and within the set of trithiophosphites respectively. The (PhS on P) : (MeS on P) ratio (calculated from the ^{31}P integrals according to the assigned values of n for each multiplet) was 0.90 : 1 overall, showing that reaction with MeSSMe was only slightly preferred. However, there was a marked preference for PhS to become attached to phosphorus(III); the (PhS on P) : (MeS on P) ratio was 1.30 : 1 for phosphorus(III) and 0.84 : 1 for phosphorus(V). Within each oxidation state, the product distribution approximated to the statistical distribution which would be obtained in a redistribution reaction where all products had equal bond ener-

Table 1. Reaction of P_4S_3 with disulphides under u.v. irradiation

P_4S_3 (mmol)	Disulphide	Disulphide (mmol)	CS_2 (mmol)	Temp./°C	Time/h	P^V Products/P^{III} products
9.1	MeSSMe	111	0	60	1	3.06
10	MeSSMe	166	166	22	1	2.5
10	PhSSPh	60	0	60	1	3.2
10	MeSSMe PhSSPh	60 60	0	60	1	4.7
10	MeSSPh	70	0	50	1	3.7
10	Cl_3CSSEt	68	166	20	36	Not measurable

Table 2. ^{31}P N.m.r. parameters and product distributions

	$P(SPh)_n(SMe)_{3-n}$				$SP(SPh)_n(SMe)_{3-n}$			
n	0	1	2	3	0	1	2	3
δ/p.p.m.	124.4	127.4	130.0	131.9	98.8	97.4	94.8	91.3
$^3J(PH)$/Hz	10	9	9	0	18	18	18	0
Multiplicity	10	7	4	1	10	7	4	1
(*a*) P_4S_3 + MeSSMe + PhSSPh + $h\nu$								
% of total P [a]	1	6	8	3	15	30	29	8
% within each oxidation state [b]	5	35	45	15	18	37	35	10
Statistically expected %								
for 56.4% PhS, 43.6% MeS	8	32	42	18				
for 45.6% PhS, 54.4% MeS					16	40	34	10
(*b*) P_4S_3 + MeSSPh + $h\nu$								
% of total P [a]	0	3	10	8	11	39	25	4
% within each oxidation state [c]	0	15	48	37	14	50	32	4
Statistically expected %								
for 74.3% PhS, 25.7% MeS	2	15	42	41				
for 42.4% PhS, 57.6% MeS					19	42	31	8
(*c*) $P(SMe)_3$ + MeSSPh + $h\nu$								
% of total P [a]	27	35	20	6	12	0	0	0
% within +3 oxidation state [d]	31	40	23	6				
Statistically expected %								
for 35.0% PhS, 65.0% MeS	28	44	24	4				
(*d*) $P(SMe)_3$ + $P(SPh)_3$ + $h\nu$								
% of total P [e]	13	35	36	16				
Statistically expected %								
for 51.8% PhS, 48.2% MeS	11	36	39	14				

[a] ±1%. [b] ±8% for P^{III}; ±3% for P^V. [c] ±5% for P^{III}; ±3% for P^V. [d] ±2%. [e] ±3%.

gies,[12] as shown in Table 2. If the reaction were initiated by photolytic cleavage of disulphide molecules, then recombination of the resultant radicals would result in the equilibrium (v) being set up. Similar products should there-

$$\mathrm{MeSSMe + PhSSPh \rightleftharpoons 2\,MeSSPh} \qquad \text{(v)}$$

fore be formed if P_4S_3 were irradiated with MeSSPh instead of with the mixture of symmetrical disulphides. This experiment was carried out, to give the results shown in Table 2. Again, the product distributions were near to statistical within each oxidation state, but now the preference of phosphorus(III) for PhS was more marked: the (PhS on P) : (MeS on P) ratio was 0.96 : 1 overall, but 2.89 : 1 for phosphorus(III) and 0.73 : 1 for phosphorus(V). Practically no $P(SMe)_3$ was formed. This difference from the reaction with the disulphide mixture supports the hypothesis that initiation was not by disulphide fission.

The near-statistical distribution of mixed-ligand products of the disulphide competition reaction could either have been a consequence of the mechanism of breakdown of the P_4S_3 cage, or of redistribution reactions between the initial products. Trithiophosphites are reported[13] not to exchange in the absence of added catalysts at 60 °C, but there have been no reports of photochemical redistribution experiments. An approximately equimolar mixture of $P(SMe)_3$ and $P(SPh)_3$ was irradiated under similar conditions to those used for the P_4S_3 reactions. Redistribution took place as shown in Table 2. Thus the similar distribution of phosphorus(III) products in the reaction of P_4S_3 with MeSSPh to that in the reaction with the mixture of symmetrical disulphides gives no evidence about the mechanism of the reaction.

Although the phosphorus(V) : phosphorus(III) products ratio was near to 3 : 1, as expected, for the separate reactions of MeSSMe or of PhSSPh with P_4S_3, this ratio was considerably higher for the MeSSPh reaction and for the disulphide competition reaction (Table 1). Clearly, MeSSMe is not desulphurised by $P(SMe)_3$ under our reaction conditions. The non-reaction of an equimolar mixture of PhSSPh and $P(SPh)_3$ was demonstrated separately: after irradiation of the mixture for 1 h at 65 °C, ^{31}P n.m.r. showed $P(SPh)_3$ to be the only phosphorus-containing component. Irradiation of a mixture of MeSSPh and $P(SMe)_3$, however, did lead to slight sulphurisation, as well as to redistribution of PhS and MeS between the disulphide and the trithiophosphite (Table 2). A molar ratio (MeSSPh taken) : [$P(SMe)_3$ taken] of 5.7 : 1, which corresponds to a (total PhS) : (total MeS) ratio of 0.66 : 1, led to a (PhS on P^{III}) : (MeS on P^{III}) ratio of 0.54 : 1, and to formation of $SP(SMe)_3$ such that the $SP(SMe)_3$: [phosphorus(III) products] ratio was 0.13 : 1. No PhS-substituted phosphorus(V) products were observed. This sulphurisation by an unsymmetrical disulphide of a phosphorus(III) site which is not sulphurised by symmetrical disulphides is in accord with the literature[6] for reactions in which an intact disulphide molecule is attacked. However, the extent of sulphurisation does not explain the high phosphorus(V) : phosphorus(III) product ratios formed in some reactions of P_4S_3, and it may be inferred that sulphurisation of intermediates in the reaction mainly took place, rather than of the final phosphorus(III) products. Sulphurisation of $P(SMe)_3$ rather than of PhS-substituted trithiophosphites helps to explain the greater MeS substitution of phosphorus(V) products and the greater PhS substitution of phosphorus(III) products in the reactions of P_4S_3.

Experimental

Techniques.—All operations were carried out under nitrogen by Schlenk methods. Careful exclusion of air from P_4S_3 solutions and from the trithiophosphite products was necessary. The concentric irradiation apparatus was constructed from Schott-Ruhr Duran glass to fit around a 100-W Applied Photophysics medium-pressure mercury arc lamp: a tap-water annulus to dissipate heat from the lamp was surrounded by a vacuum jacket, to the outside of which was ring-sealed the reaction annulus. The apparatus was immersed in a thermostatting bath, and the vacuum jacket enabled the sample temperature to be controlled without interference by the cooling water annulus. The reaction annulus was provided with a Schlenk connection and an angled standard taper joint to allow access by a dropper; the outer wall of the annulus tapered towards the bottom ringseal so that while the maximum charge was 40 cm^3, small samples still covered the illuminated wall as much as possible.

N.m.r. spectra were measured using a Bruker HFX-90 spectrometer operating at 36.43 MHz for ^{31}P and 90.0 MHz for ^1H, and modified to operate in Fourier-transform mode for the ^{31}P measurements. Precision capillaries were used throughout to contain lock nuclei and external standards (80% H_3PO_4–H_2O for ^{31}P and $SiMe_4$ for ^1H). Liquid products were used without dilution and solid products were dissolved in CS_2.

Materials.—P_4S_3 was purchased as ' phosphorus sesquisulphide ' from ICN Pharmaceuticals and recrystallised from CS_2. MeSSMe (Aldrich) and PhSSPh (Hopkin and Williams) were used as received. MeSSPh,[6] Cl_3CSSEt,[14] and $P(SMe)_3$[9] were prepared by literature methods. AnalaR CS_2 was dried over P_4O_{10} and filtered before use.

Michaelis and Linke's method[15] for the preparation of $P(SPh)_3$ from PhSH and PCl_3 was found to be very slow, so the reaction mixture was diluted with light petroleum (b.p. 60—80 °C) and NEt_3 added to abstract HCl; after refluxing, the light petroleum was distilled off, $P(SPh)_3$ was extracted with Et_2O, and the crude product recrystallised from EtOH.

A Typical Photolysis Experiment; Reaction of P_4S_3 *with Diphenyl Disulphide.*—PhSSPh (13.1 g, 60 mmol) was weighed into a Schlenk tube equipped with a magnetic stir-bar and the tube evacuated and refilled with dry N_2 several times to dry the disulphide. P_4S_3 (2.20 g, 10 mmol) was added and the flushing was repeated. The mixture was melted to a clear yellow solution and held at 60 °C for 1 h, with stirring. I.r. spectra of a small sample taken up in CS_2 showed only peaks attributable to the starting materials. The molten mixture was transferred by pipette to the N_2-flushed irradiation vessel, which was then heated to 60 °C and irradiated for 1 h. The product was allowed to cool, taken up in the minimum quantity of CS_2, and samples were taken for i.r. and into a N_2-flushed tube for n.m.r. Both spectrometric methods showed that peaks expected for P_4S_3 had disappeared. The n.m.r. results are presented in the Results and Discussion section.

Reaction of P_4S_3 *with Sulphuryl Chloride.*—SO_2Cl_2 was distilled under N_2, and free chlorine removed from the distillate by bubbling a slow stream of N_2 through it for 3 h. P_4S_3 (2.20 g, 10 mmol) was flushed with N_2 (as above) and dissolved in CS_2 (10 cm^3). A solution of the purified SO_2Cl_2 (1.24 g, 9.2 mmol) in CS_2 (10 cm^3) was added at room temperature over 2 h with stirring. There was no turbidity nor precipitation. I.r. spectra showed that much P_4S_3 but only a little SO_2Cl_2 remained unreacted. There were strong peaks due to SO_2, $SPCl_3$, and PCl_3, but no $OPCl_3$ nor any peaks in the C–Cl stretching region due to chlorination products of CS_2, such as CCl_4 or Cl_3CSCl. After standing for 44 h the SO_2Cl_2 had completely reacted and further $SPCl_3$ and PCl_3 had been formed.

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