Scrambling of P–SP and P–SC Bonds between Tetraphosphorus Decasulphide and Phosphorotetrathioic Esters

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The thermal redistribution of P_4S_{10} with $(RS)_3PS$ (R = alkyl or aryl) generates metaphosphorotrithioic esters $(RSPS_2)_2$ and relatively smaller amounts of symmetrical $[(RS)_2P(S)]_2S$ as 'middle' and 'end' species respectively. Reacting P_4S_{10} with thiols affords similar mixtures. With dithiols $HS(CH_2)_nSH$ (n = 2 or 3), no 'middle' compound was obtained but only 'end' and 'ortho' derivatives, chiefly $[AS_2P(S)]_2Y$ (A = alkylene, Y = –S– or –SAS– respectively).

The composition of redistributed mixtures of phosphorotetrathioic esters $(RS)_3PS$ (R = Bu or Ph) with P_4S_{10} (overall R/P = r *ca.* 1.6—3), obtained by heating at ⩾155 °C, has previously been described in terms of building units $(RS)_xPS(SP)_{3-x}$, labelled as 'branch' (x = 0), 'middle' (x = 1), 'end' (x = 2), and 'ortho' (x = 3).[1] Phosphorus(III) derivatives, afforded by autoredox processes, were also found in smaller amounts.[1]

This paper describes further experiments concerning the redistribution of P_4S_{10} with $(RS)_3PS$ as monitored by ^{31}P n.m.r. spectroscopy.

Results and Discussion

It follows from new experiments (R = Me, n-$C_{12}H_{25}$, or Ph; r = 1—3; heating, 10 min to 4 h at 180—185 °C), monitored by ^{31}P n.m.r., that the molecular compositions of redistributed mixtures of P_4S_{10} and $(RS)_3PS$ are less complex than could have been imagined and do not appreciably differ from the compositions of reaction mixtures of P_4S_{10} with thiols RSH[2–5] (R = n-$C_{12}H_{25}$, Ph, or $PhCH_2$; ⩾10 min in boiling o-$C_6H_4Cl_2$). Specifically, branch units belong to P_4S_{10} and P_4S_9 almost exclusively; only in one case (R = Ph) was P_4S_7 identified in trace amounts; middle groups pertain to dimeric metaphosphorotrithioic esters $(RSPS_2)_2$ (**1**) (Table 1), probably *trans*, as borne out by comparison with authentic specimens of (**1**) [smaller satellites at δ 21.1 (t, $^3J_{PH}$ *ca.* 19.5 Hz) (R = $C_{12}H_{25}$) and 19.5 p.p.m. (R = Ph) are tentatively assigned to *cis*-(**1**)*]; end building blocks appear to belong to symmetrical molecules (**2**); and ortho species correspond to phosphorotetrathioic esters (**3**).

The distribution between the four kinds of PS_4 centres conforms to the law of mass action but is far from random; the concentration of (**2**) is peculiarly low.

The main P^{III} derivative was P_4S_9 which always accompanied P_4S_{10}. Only minute amounts of $(RS)_3P$ (δ 119.0, septet, $^3J_{PH}$ *ca.* 9 Hz; δ 132.6, singlet; δ 117.6 p.p.m., poorly resolved multiplet, for R = $C_{12}H_{25}$, Ph, or $PhCH_2$ respectively) were found; blank tests revealed in fact that, upon heating at *ca.* 180 °C for 1—4 h, thiophosphates $(RS)_3PS$ tend to expel the disulphide RSSR (with the concomitant production of insoluble materials) rather than the thioxo sulphur.

The reaction of P_4S_{10} with dithiols $HS(CH_2)_nSH$ under the same conditions (r = initial SH/P = 1.05—3) exhibits several unique features. While butane-1,4-dithiol stops reacting at an early stage, due to the coating of the solid particles of P_4S_{10} with insoluble polymers, ethane-1,2- and propane-1,3-dithiols react cleanly, giving solutions which were analysed by ^{31}P n.m.r. (Table 1). In both cases, four components were identified: P_4S_{10}, P_4S_9, (**4**) (ortho), and (**6**) (end); compounds (**4**) and (**6**) were isolated as pure crystalline solids and assigned the structures shown in Table 1 on the basis of spectroscopic evidence, advantage being taken of the comparison with model molecules (**5a**) and (**5b**). As expected from symmetrical molecules, the ^{31}P n.m.r. signals of (**4**) and (**6**) reduce to one singlet upon proton decoupling. The H-coupling pattern of the ^{31}P n.m.r. spectra is in accord with the number of P–S–C–H groups surrounding each P atom in (**4**), (**5**), and (**6**). In (**4a**), and in (**5a**), all $^3J_{PH}$ appear to be approximately equal, as is also the case with the 2-thioxo-1,3,2-dithiaphospholanes $SCH_2CH_2SP(S)X$ (X = Me or Ph).[7] The higher complexity of the spectrum of (**6a**) may indicate that in this thiodiphosphate effective P–S–P–S–C–H couplings do take place giving rise to an $AA'X_4X'_4$ spin system (A ≡ P, X ≡ H); examples of such long range couplings through S are known.[8] The J_{PH} couplings in (**4b**), (**5b**), and (**6b**) are consistent with published data on similar dithiaphosphorinanes,[9] with $^3J_{PH}(eq) > {}^3J_{PH}(acyclic) > {}^3J_{PH}(ax) \gg {}^4J_{PH}$, although, here too, the possibility of $^5J_{PH}$ coupling through the P–S–P bridge of (**6b**) could be considered.

The ^{31}P chemical shifts of (**4a**) and (**4b**) are, as expected, very close to those of (**5a**) and (**5b**) respectively. On the other hand, for each end or ortho series, the dependence of δ on the ring size, *i.e.* δ (five-membered) > δ (six-membered) < δ (open ring), fulfils a rule obeyed by a large number of P/S derivatives.[9,10] The complexity of the ^1H n.m.r. spectra of (**4a**), (**5a**), and (**6a**) is in line with the susceptibility of ring protons to develop second-order spin systems in 2-thioxo-1,3,2-dithiaphospholanes;[7] the spectrum of (**5a**) closely resembles that of $SCH_2CH_2SP(S)Ph$.[7] The heterocyclic part of the ^1H n.m.r. spectra of (**4b**), (**5b**), and (**6b**) is typical of 2-thioxo-1,3,2-dithiaphosphorinanes, with $\delta(H^5{}_{ax}) < \delta(H^5{}_{eq}) < \delta(H^4{}_{eq}) < \delta(H^4{}_{ax})$.[9]

Only a small molecular peak could be obtained for (**4a**) by mass spectroscopy (m.s.), using the field desorption technique. No such peak was observed by Baudler *et al.*[11] for a seemingly identical product.†

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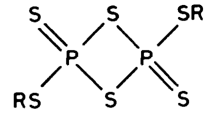
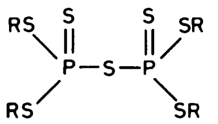
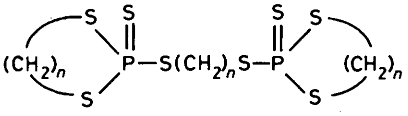
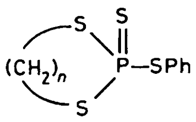
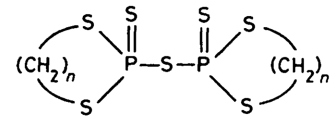
* Although dithioxodithiadiphosphetanes, RP(=S)SP(R)(=S)S (R = Me, Bu^t, Ph, $C_6H_2Me_3$-2,4,6, NMe_2, or SPh), reported to date were all *trans*, this could mean just a preference for this particular configuration, since a monocrystal has to be selected for structure determinations. The *cis* form of $Bu^tNP(=NSiMe_3)SP(NBu^t)(=NSiMe_3)S$ has been described.[6]

† This compound, obtained by reacting SCH_2CH_2S–P–P–SCH_2CH_2S with sulphur, had the same elemental analysis and i.r. spectrum as (**4a**), but, oddly enough, the reported melting point (248—252 °C) considerably departs from our result (124 °C).[11]

Table 1. ^{31}P N.m.r. data of species

Compound		Spectrum	δ/p.p.m.	$^3J_{PH}$/Hz
 (**1**) (middle)	R = Me	Quartet	22.6	23.0
	$C_{12}H_{25}$	Triplet	22.3	19.7
	Ph	Singlet	23.3	
	$PhCH_2$	Triplet	20.9	*ca.* 15
 (**2**) (end)	R = Me	Septet	80.2	18.5
	$C_{12}H_{25}$	Quintet	77.5	17.7
	Ph	Singlet	75.8	
	$PhCH_2$	Quintet	75.7	*ca.* 13
$(RS)_3PS$ (**3**) (ortho)	R = Me	Decet	96.8	17.0
	$C_{12}H_{25}$	Septet	92.4	16.4
	Ph	Singlet	89.2	
	$PhCH_2$	Septet	90.2	*ca.* 13
 (**4**) (ortho)	(**4a**) (*n* = 2)	Slightly complex Septet	102.5	*ca.* 17.6
	(**4b**) (*n* = 3)	Triplet of triplets of triplets	72.5	*ca.* 26.4, 8.8, 17.0
 (**5**)	(**5a**) (*n* = 2)	Quintet	103.8	16.6
	(**5b**) (*n* = 3)	Triplet of triplets	71.3	26.4 8—11
 (**6**) (end)	(**6a**) (*n* = 2)	Complex multiplet (11 lines)	92.3	
	(**6b**) (*n* = 3)	Triplet of triplet of triplets	61.7	24.3, 6.4 ($^{4\text{ or }5}J_{PH}$ *ca.* 2)
(**7**) (end?)	(**7a**) (*n* = 2)	Quintet	88.3	18.0
	(**7b**) (*n* = 3)	Quintet	58.8	19.0

Medium to strong i.r. absorption frequencies at *ca.* 428, 842, and 935 cm^{-1} in (**4a**), (**5a**), and (**6a**) (Table 2), absent in the spectra of (**4b**), (**5b**), (**6b**), and $(EtS)_3PS$,[12] appear to characterize the presence of the 2-thioxo-1,3,2-dithiaphospholane ring; likewise, i.r. bands at 609, 891, 1 177, and 1 264 cm^{-1} in (**4b**), (**5b**), and (**6b**) are linked to the presence of the 2-thioxo-1,3,2-dithiaphosphorinane group. On the other hand, the strong absorptions at 466 cm^{-1} in (**6a**) and 469 cm^{-1} in (**6b**) are attributed to the asymmetric ν(P–S–P) vibration, as suggested by comparison with $[Me_2P(S)]_2S$[13] and $[(RO)_2P(S)]_2S$[14] [ν_{asym}(P–S–P) at 457 and 488—495 cm^{-1} respectively]. The absence of any i.r. band near 2 560 cm^{-1} [ν(S–H)] should be noted.

Compound (**4a**) was also obtained by an independent synthesis, using the (slow) reaction of the bicyclic compound (**8a**)[15,16,*] with sulphur (in boiling toluene) or, more readily, with P_4S_{10} (in cold CS_2) as S donor.

Other (presumed) ortho derivatives (cyclic or not?) are produced in small amounts by the reaction of P_4S_{10} with dithiols; these appear as multiplets at δ 104.6, 106.2, and 109.6 p.p.m. (*n* = 2) or at δ 77.1 and 91.5 p.p.m. (*n* = 3).

Contrasting with the behaviour of monothiols, substantial concentrations of end compounds (**6**) [especially (**6a**)] were reached in the present case, at least at *r* not too far removed from 2.

A further kind of end species, (**7**), was observed as well shaped n.m.r. quintets, slightly upfield to (**6**), and with (**7b**) relatively stronger than (**7a**). These are believed to be either isomers (**9**) or, merely, rigid conformers of (**6**); examination of molecular models indeed points to the probable existence of a high

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* By contrast with (**8a**), its six-membered homologue (**8b**) could not be isolated by crystallization from the reaction mixture of $HS(CH_2)_3SH$ (3 mol equiv.) with PCl_3 (2 mol. equiv.) in 1,2-dichloroethane, despite the presence in the ^{31}P n.m.r. spectrum of one major signal (*ca.* 70%) at δ 79.95 p.p.m.; similar observations were recently reported [δ of (**8b**) 79.3 p.p.m.].[17]

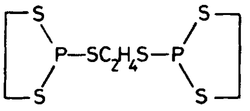
Table 2. I.r. absorption frequencies in the range *ca.* 400—950 cm^{-1}

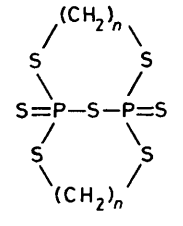
(8a)	**(4a)**	**(5a)**	**(6a)**	**(4b)**	**(5b)**	**(6b)**	$(EtS)_3PS$	$(PhS)_3PS$	Assignment
938s	931m	937m	935s						
				891ms	890m	893m	900w		ν(C–C)
	842ms	839m	844s	852s		857s	871w		
818s					802mw				
		750vs			748vs			746vs	δ(CH) (aromatic)
724m				742mw			754m	707mw	
698m	700w	690m	696 (sh)		699 (sh)			697mw	
	682vs	670vs	681vs	670vs	681vs	680vs	687vs	685vs	ν(P=S)
681m	668m								
639m	646ms	646s	644s				642m		ν(C–SP)
				610m	608m	608m			
466vs	538vs	538s	547s	550vs	550s	570s	550vs		ν(P–SC) (aliphatic)
441m	501vs	518m	523s	520vs	512vs	550m	526vs	510vs	
								488mw	ν(P–SC) (aromatic)
		476s			480s			476vs	
			466vs			469vs			ν_{asym}(P–S–P)
421 (sh)	428m	428m	428s		428w	452s	417w	408m	
			400m			396m			ν_{sym}(P–S–P)

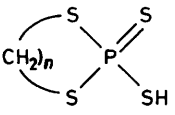
Table 3. Extent of hydrolysis (%)

	P_4S_{10}	P_4S_9	(1)^a	(2)^a	(3)^a	**(4a)**	**(4b)**	**(6a)**	**(6b)**	**(7a)**	**(7b)**
15 min	0	100	100	80	0						
45 min						0	0	*b*	6	63	97

^{a} R = n-$C_{12}H_{25}$. ^{b} Anomalous (negative) result due to the crystallization of a little (**6a**) on storage of the blank solution.


(8a)


(9)


(10)

barrier to rotation about the P–SP bonds in (**6**). That no thioacid (**10**) is involved follows from the fact that (**7**) is generated, along with disproportionation products (see below), when (**6**), either neat or dissolved in *o*-$C_6H_4Cl_2$, is heated for 1 h at 180 °C. Thioacids $(RS)_2P(S)SH$ are known to be elusive compounds.[5,18]

Finally, the most salient feature of the reaction of P_4S_{10} with dithiols is the absence of any soluble middle species (no H-coupled ^{31}P n.m.r. triplets) and, more specifically, of any compound similar to (**1**) (no chemical shift in the neighbourhood of 20 p.p.m.). This observation is consonant with the general preference of dithioxodithiadiphosphetanes for the *trans* configuration, which in the present case would most probably command a polymeric structure. Significantly, the disproportionation products of (**6**) (see above) consist chiefly of (**4**), none (*n* = 2) or only minor amounts (*n* = 3) of P_4S_{10}, and insoluble materials; stoicheiometric considerations point to the latter as being approximately middle polymers.

Hydrolysis tests (monitored by ^{31}P n.m.r. or acidimetry) substantiate the existence of water-sensitive P–S–P bridges in (**1**), (**2**), (**6**), and (**7**), with the following order of reactivity: P_4S_9, (**1**) $\gg$ (**2**), (**7b**) > (**7a**) $\gg$ (**6a**) $\geqslant$ (**6b**) $\geqslant$ P_4S_{10} $\gg$ (**3**), (**4a**), (**4b**).

Experimental

^{31}P and ^{1}H n.m.r. data (200 MHz) were obtained from CS_2 solutions and i.r. spectra from KBr pellets; t.l.c. was performed on silica gel with benzene as eluant.

$(MeSPS_2)_2$ was prepared according to Davy[5] and $(PhSPS_2)_2$ according to Rosnati.[2] $(n\text{-}C_{12}H_{25}SPS_2)_2$ was obtained by the method of Scott *et al.*[4] and recrystallized from pentane, m.p. 47 °C (Found: P, 10.40. $C_{24}H_{50}P_2S_6$ requires P, 10.45%). All $(RSPS_2)_2$ compounds were pale yellow crystals.

$(n\text{-}C_{12}H_{25}S)_3P$ was a commercial product, further recrystallized from pentane. Its reaction with S in hexane, in the presence of a little NEt_3, afforded $(n\text{-}C_{12}H_{25}S)_3PS$ as a low melting solid, which was twice recrystallized from hexane. $(PhS)_3PS$ was prepared as in ref. 2.

Preparation of Compounds (**4**) *and* (**6**).—Compounds (**4**) and (**6**) were obtained by reacting P_4S_{10} (10 mmol) with $HS(CH_2)_nSH$ [60 or 40 mmol for (**4**) and (**6**) respectively] in boiling *o*-$C_6H_4Cl_2$ (20—45 cm^3) for 10—40 min. Crystals separated from the cooled solution (several days necessary when *n* = 3) which were recrystallized from $CHCl_3$ or 1,2-$C_2H_4Cl_2$, to yield pure white solids (40—60%).

(**4a**) (*n* = 2), m.p. 124 °C (Found: P, 15.35; S, 63.9. $C_6H_{12}P_2S_8$ requires P, 15.40; S, 63.7%), R_F 0.23; ^{1}H n.m.r.: complex spectrum with main lines at δ 3.29, 3.39, 3.45, 3.53, and 3.54 p.p.m.; m.s. (field desorption); *m/z* 402 (M^+, very small peak).

(**4b**) (*n* = 3), m.p. 102 °C (Found: P, 13.40; S, 57.3. $C_9H_{18}P_2S_8$ requires P, 13.95; S, 57.70%), R_F 0.19; ^{1}H n.m.r.: δ *ca.* 1.72 and *ca.* 1.79 (4 H together, overlapping massifs, H^5_{ax} and H^5_{eq} respectively), 2.17 (2 H, quintet, $^3J_{HCCH}$ 7.1 Hz, central bridge CH_2), 2.69 [4 H, complex multiplet, $H^4_{eq}(H^4 \equiv H^6)$], 3.02 (t of t, $^3J_{PSCH}$ 17.6, $^3J_{HCCH}$ 7.1 Hz, terminal bridge CH_2), 3.07 (complex massif, H^4_{ax}), the last two (overlapping) signals contributing 8 H together.

(6a) (n = 2), m.p. 116—117 °C (Found: P, 18.00; S, 64.9. $C_4H_8P_2S_7$ requires P, 18.10; S, 65.60%), R_F 0.25; ^1H n.m.r.: complex spectrum with main lines at δ 3.34, 3.345, and 3.43 p.p.m.

(6b) (n = 3), m.p. 139—140 °C (Found: P, 17.15; S, 61.5. $C_6H_{12}P_2S_7$ requires P, 16.70; S, 60.60%), R_F 0.32; ^1H n.m.r.: 4 complex multiplets centred at δ 2.02 (1 H, H^5_{ax}), 2.22 (1 H, H^5_{eq}), 2.92 (2 H, H^4_{eq}), and 3.67 p.p.m. (2 H, H^4_{ax}).

Preparation of Compounds (**5**).—These were prepared by reacting equivalent amounts of PhS–PCl_2, $HS(CH_2)_nSH$, and NEt_3 in Et_2O. The reaction mixture was filtered, stirred with finely powdered sulphur (*ca.* 10 h), filtered again and evaporated to dryness. Two recrystallizations from ethanol afforded pure white crystals (10—15%). **(5a)** was also obtained (*ca.* 35%) by heating equivalent amounts of $(PhSPS_2)_2$ and ethane-1,2-dithiol (10 min in boiling *o*-$Cl_2C_6H_4$), stripping the solvent under reduced pressure and recrystallizing from ethanol.

(5a) (n = 2), m.p. 100—101 °C (Found: P, 11.85; S, 47.9. $C_8H_9PS_4$ requires P, 11.70; S, 48.50%), R_F 0.35; ^1H n.m.r.: δ *ca.* 7.19 and *ca.* 7.49 (5 H together, two multiplets, aromatic H), *ca.* 2.97 and 3.19 (4 H together, two complex massifs, approximately symmetrical about an axis at 3.08 p.p.m., aliphatic H).

(5b) (n = 3), m.p. 117.5 °C (Found: P, 11.00; S, 45.2. $C_9H_{11}PS_4$ requires P, 11.10; S, 46.05%), R_F 0.37; ^1H n.m.r.: δ *ca.* 7.78 and *ca.* 7.93 (5 H together, two multiplets, aromatic H), and four massifs centred at δ *ca.* 1.91 (1 H, H^5_{ax}), 2.10 (1 H, H^5_{eq}), 2.85 (2 H, H^4_{eq}), and 3.30 p.p.m. (2 H, H^4_{ax}).

Hydrolysis Experiments.—(*i*) Weighed samples of (**4**) or (**6**) (30—40 mg) were boiled with water (5 cm^3), in the presence or not of toluene (10 cm^3), for a given length of time. The extent of hydrolysis (%) was determined by acidimetry in methanol (first inflexion). Found: no toluene (4 h): (**4a**) = 2%, (**4b**) < 0.5%; no toluene (0.5 h): (**6a**) = 24.6%, (**6b**) = 5.1%; with added toluene (1 h): (**6a**) = 74%, (**6b**) = 53%. Failure to reach 100% hydrolysis upon prolonged boiling suggests that the hydrolysis process is accompanied by some redistribution of end species.

(*ii*) Reaction products of P_4S_{10} with mono- or di-thiols were dissolved in carbon disulphide and stirred with water at *ca.* 20 °C for 15 or 45 min; the organic layer was decanted off, dried over $CaCl_2$, and analysed by ^{31}P n.m.r. By comparison with the n.m.r. spectra of non-hydrolysed solutions, the approximate per cent of hydrolysis was obtained (Table 3) for two different periods of stirring with water.

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