Reaction of Thiolo and Selenolo Esters of Phosphorus Acids with Halogens. Part 2.† Interaction of *S*-Methyl t-Butyl(phenyl)- and Di-t-butyl-phosphinothiolates with Elemental Bromine and Iodine

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The reaction of *S*-methyl t-butyl(phenyl)- and di-t-butyl-phosphinothiolates with bromine and iodine involves the transient formation of the same type of halosulphonium salts, $Bu^tRP(O)S^+(X)MeX^-$ and phosphonium salts, $Bu^tRP^+(SMe)OP(O)Bu^tRX^-$ (R = Ph, Bu^t; X = Br, I) as described[1] for the reaction of *S*-methyl t-butyl(phenyl)phosphinothiolate with chlorine and sulphuryl chloride. The considerable stability at room temperature of intermediates containing two phosphorus atoms, and their predominant decomposition with preservation of the P–O–P bridge in the reaction product, has been demonstrated. The stereochemistry of this transformation has been established by stereochemical correlations.

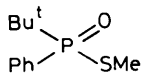
In our previous paper[1a] we described the results of stereochemical and ^{31}P NMR studies on the reaction of *S*-methyl t-butyl(phenyl)phosphinothiolate (**1a**) with chlorinating agents. This reaction has been shown to occur with scission of the P–S bond and retention of configuration at the phosphorus atom. The model compound chosen appears to be very suitable for spectroscopic observation (^{31}P NMR) of the reaction intermediates, the chloro(phosphoryl) sulphonium salts, $>P(O)S^+(Cl)MeX^-$ (X = Cl, $ClSO_2$) and the two types of phosphoryloxyphosphonium salts, $>P^+(SMe)OP(O)X^-$ and $>P^+(Cl)OP(O)X^-$ (X = Cl, Cl_3). The last two compounds were shown to have the deciding influence on the stereochemical course of the reaction under discussion.

In this paper we report the results of our studies on the interaction of the models (**1a**, **b**) with the higher halogens, bromine and iodine. The reaction of these halogens with phosphorus thioloesters, except for the early work of Stirling,[2] has not been examined in aprotic solvents. Only the use of bromine[3] and iodine[4] to modify –SR as a leaving group in the reaction of phosphorus thioloesters with different nucleophiles such as water,[4b,c] methanol,[3a] fluoride,[3b] and phosphate anions[4a] has been described in the literature. In the present paper we demonstrate that the course of the reaction of thioloesters (**1a**, **b**) with bromine and iodine differs substantially from that with chlorine; this difference is manifested in the predominant formation of the reaction products with the P–O–P bridge preserved.

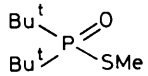
Results and Discussion

As models for stereochemical research, esters (*R*)-(+)- and (*S*)-(−)-(**1a**) were used, and these were prepared as described in our previous paper.[1a]

In the spectroscopic studies, ester (**1b**) with two bulky groups attached to phosphorus was also employed. Ester (**1b**) was prepared by standard methods.[5] The reactions of (**1a**, **b**) with bromine and iodine were carried out in dichloromethane, toluene, benzene, or acetonitrile. The identification of the intermediates was based on the observation of the variable temperature (and/or variable time) ^{31}P NMR spectra. The final products were identified by means of ^{31}P NMR spectroscopy and/or GC/MS methods; in some cases they were isolated and characterized spectroscopically and by elemental analysis.



(**1a**)



(**1b**)

^{31}P *NMR Studies.*—The ^{31}P NMR spectra of the reaction mixture were recorded in the range 183–293 K, as described in the previous paper,[1a] for the reaction with chlorinating agents. However, the reactions of esters (**1a**, **b**) with bromine and iodine in the same conditions did not reach completion; the spectra were therefore recorded at room temperature after several hours, days, or months. The ^{31}P NMR data for the reaction mixtures, depending on temperature and/or time and molar ratio of the substrates, are given in Table 1.

(a) *Reaction products.* In the preliminary communication[1c] concerning the reaction of phosphinothiolate (**1a**) with chlorinating agents we reported that the reaction of (**1a**) with bromine gave predominantly thiopyrophosphinate complexed with bromine (**7a**) (*i.e.*, when the reaction was allowed to proceed for 20–30 h). However, prolongation of the reaction time to several months (storing the reaction mixture in a sealed tube) enabled us to obtain the bromide (**5a**) in satisfactory yield. It is noteworthy that (**1b**), even after refluxing for 12 h with bromine in dichloromethane, did not give (**5b**). The latter product has been obtained in 30% yield when the reaction of (**1b**) and bromine was continued for 2 months at room temperature.

The reaction of (**1a**) with iodine produces no phosphinic iodidate, $Bu^tPhP(O)I$. The only products which were detected after the prolonged reaction time (see Table 1) were intermediates (**2a**) or (**2a**) $\rightleftharpoons$ (**3a**) and (**4a**) (X = I). After 1–2 months the salts (**4a**) gave the corresponding thiopyrophosphinate complexed with iodine, (**6a**)·I_2. For the reacting system (**1b**) + I_2, no product with a P–O–P bridge was observed. The reaction mixture after 40 days contained mainly (**2b**; X = I) and only 4% of di-t-butylphosphinic iodide, (**5b**; X = I).

(b) *Intermediates containing one phosphorus atom.* The use of phosphinothiolate (**1b**) in the reaction with bromine enabled us to obtain a solid complex (**1b**)·Br_2, which could be isolated

† For Part 1, see ref. 1(*a*).

Table 1. ^{31}P NMR analysis of the reacting systems (**1a, b**) + X_2, showing relative intensity of ^{31}P NMR signals (%).[a]

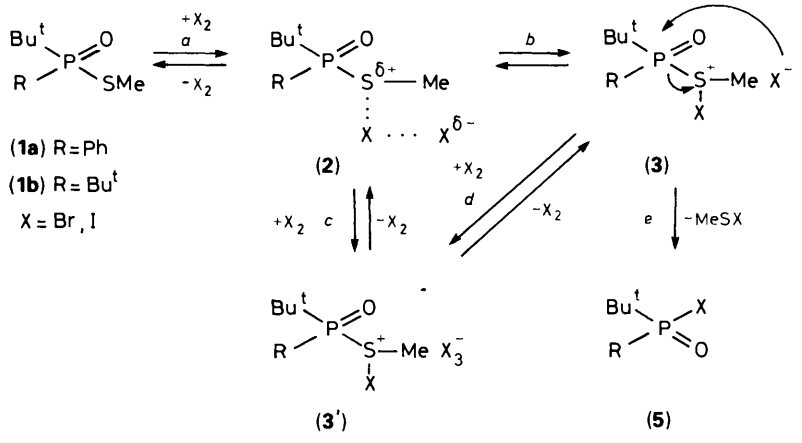
$$Bu^tRP(O)SMe + X_2 \rightleftharpoons (2) \rightleftharpoons (3) \xrightarrow[-MeSX]{+(1)} (4) + (5) + (6)\cdot X_2 \quad \text{(1a; R = Ph)} \quad \text{(1b; R = Bu}^t\text{)}$$

$$(6)\cdot X_2 \rightleftharpoons (7)$$

Reacting system

Compounds present in reaction mixture	(1a) + Br_2[b]			(1a) + $5Br_2$			(1a) + I_2				(1b) + Br_2			(1b) + $2Br_2$		(1b) + I_2	
	1 h	5 h	7 h	0.25 h	2 h	120 h	1 h	288 h	47 days	489 days	1 h	24 h	56 days	0.25 h	24 h	2 h	40 days
(1a, b)	67	43	—	63	—	—	100	64	44	—	100	—	—	—	—	90	—
(2a, b)	15	15	—	22	55	—	—	—	—	28	—	48	—	43	—	—	96
(3a, b)	—	—	—	—	—	25	—	—	—	—	—	—	45	—	45	—	—
(4a, b)	18	37	75	14	45	8	—	35	37	14	—	30	*c*	25	25	—	—
(5a, b)	—	—	25	—	—	40	—	—	—	—	—	2	15	—	—	—	4
(6a, b)$\cdot X_2 \rightleftharpoons$ **(7a, b)**	—	—	—	—	—	17	—	—	19	58	—	15	*c*	32	29	—	—

[a] Spectra recorded at r.t. in CH_2Cl_2. [b] Recorded at 198, 248, and 293 K, respectively. [c] Unresolved (**4b**) + (**7b**) comprises 40%.



Scheme 1.

and spectroscopically characterized (^{31}P, ^{13}C, ^1H NMR). The complex with chemical shift δ_P *ca.* +100 ppm gave, in the presence of an excess of bromine, another species with δ_P *ca.* +114. Similarly to the corresponding reaction of (**1a**) with chlorine,[1a] we assume that the former (δ_P *ca.* 100) is a molecular complex (donor–acceptor) of (**1b**) with bromine while the chemical shift δ_P *ca.* +114 responds to the fast equilibrium between the molecular complex (**2b**) and the bromo(phosphoryl)sulphonium salt (**3'b**) displaced considerably towards the latter (Scheme 1, equilibria *a*, *b*, *c*). The excess of bromine enhances the ionization of the molecular complex (**2b**), probably by an interaction between two molecules of bromine, leading to the formation of the bromosulphonium salt (**3'b**), which is relatively stable, due to the low nucleophilicity of Br_3^- and to steric reasons (Scheme 1). The structure of the bromosulphonium salt can also be stabilized by the addition of the corresponding Lewis acid (see Table 2). In the case of the model (**1a**) we were not able to isolate the crystalline complex, but two types of intermediate (δ_P +87 and +93, respectively), could be observed in the reaction mixture. The spectroscopic data for the molecular complexes phosphinothiolate–halogen, (**2**), and for the halosulphonium salts, (**3**) and (**3'**), are shown in Table 2.

The reaction of (**1a, b**) with iodine is very slow. From Tables 1 and 2 it can be seen that after mixing the reagents no ^{31}P NMR signal characteristic of the intermediate (**2**) or (**3**) appears but only a stepwise shifting of phosphinothiolate (**1a, b**) signals towards low field is observed. This shows that the equilibrium (**1**) + $I_2 \rightleftharpoons$ (**2**) $\rightleftharpoons$ (**3**) is strongly displaced to the left-hand side.

In order to confirm the presence of ionic species in the solutions of the molecular complex (**2b**; X = Br), molar conductivity measurements were performed. The results are displayed in Table 3. The values of the molar conductivity of complex (**2b**; X = Br) are considerable (greater in acetonitrile than in dichloromethane). This implies that even in dichloromethane the equilibrium: (**2b**) $\rightleftharpoons$ (**3b**) (X = Br) is shifted in favour of the bromosulphonium salt (**3b**). The conductivity of bromo(dimethyl)sulphonium bromide, which is the known compound of ionic structure,[6a,b,f] has been measured under the same conditions for comparison.

Attempts to substitute the anion of the salt (**3b**) with a weakly nucleophilic anion in order to obtain the relatively stable (and isolable in the pure state) bromosulphonium salt, unfortunately failed.

(c) *Intermediates containing two phosphorus atoms.* ^{31}P NMR studies of the reacting system (**1a**) + X_2 (X = Br, I) allows the observation of all reaction intermediates over a long period at room temperature. Figure 1(*a*) depicts a typical spectrum taken at room temperature for the racemic (*R*, *S*)-(**1a**) reacting with elemental bromine in dichloromethane. The multiplicity of spectral lines and coupling constants are in agreement with the presence of two different phosphorus atoms bridged by oxygen. The formation of a pair of diastereoisomers causes a duplication of the characteristic doublet of doublets. Figure 1(*b*) shows the spectrum of optically active (*R*)-(+)-(**1a**), $[\alpha]_D$ +158.41°

Table 2. The chemical shifts[a] (^{31}P, ^{1}H and ^{13}C, in ppm) of $Bu^tRP(O)\overset{+}{S}(C'H'_3)XY^-$ (**3a, b**) and complexes (**2a, b**).

No.	Compound	R	X	Y	δ_P	$\Delta\delta_P$	$\delta_{H'}$	$\Delta\delta_{H'}$	$^3J_{PH}$/Hz	$\delta_{C'}$	$\Delta\delta_{C'}$	$^2J_{PC}$/Hz	Solvent
1	(**2a**)	Ph	Br	—	86.7	20.0	2.05(d)	0.22	12	9.10	0.56	—	$CDCl_3$
2	(**3'a**)	Ph	Br	Br_3	94.1	27.4	—	—	—	—	—	—	CH_2Cl_2
3	(**3a$_1$**)	Ph	Br	$SbBr_6$	90.8	24.2	2.14(d)	0.40	12	—	—	—	$CDCl_3$
4	(**3a$_2$**)	Ph	Br	$HgBr_3$	93.6	26.9	—	—	—	—	—	—	CH_2Cl_2
5	(**2b**)	Bu^t	Br	—	100.0	17.8	—	—	—	9.49	0.65	0	$CDCl_3$
6	(**3'b**)	Bu^t	Br	Br_3	114.0	32.8	—	—	—	11.30	2.54	4	CD_2Cl_2
7	(**3b$_1$**)	Bu^t	Br	$SbBr_6$	109.1	27.9	2.43(d)	0.31	12	10.91(d)	2.07	4	$CDCl_3$
8	(**1a**) + I_2	Ph	I	—	71.7	5.0	2.10(d)	0.09	11	8.06	0.39	0	$CDCl_3$
9	(**1a**) + I_2[b]	Ph	I	—	74.3–73.4	—	2.18(d)	0.17	11	8.45	0.78	0	$CDCl_3$
10	(**2a**)[c]	Ph	I	—	85.6	18.9	—	—	—	—	—	—	CH_3CN
11	(**2b**)[d]	Bu^t	I	—	97.5	15.3	—	—	—	—	—	—	CH_2Cl_2

[a] Temperature of measurements, 293 K; δ_P (25.3 MHz), δ_H (80 MHz), δ_C (15 MHz). The dynamic situation encountered in these reactions is responsible for the minute variations in the chemical shifts from particular experiments. [b] Spectrum measured after 26 days. [c] Measured after 24 h; (**2a**) $\rightleftharpoons$ (**3a**) comprises 26% of the reaction mixture together with broad δ_P *ca.* +76.5 (61%). [d] Measured after 41 days.

Table 3. Conductances of complex (**2b**; X = Br) in methylene dichloride and acetonitrile.[a]

Compound	Solvent[b]	Molar conductance/ Ω^{-1} cm^2 mol^{-1}
(**2b**) $\rightleftharpoons$ (**3b**)	CH_2Cl_2	19.59
(**2b**) $\rightleftharpoons$ (**3b**)	CH_3CN	45.78
$Me\overset{+}{S}(Br)MeBr^-$	CH_2Cl_2	0.14
$Me\overset{+}{S}(Br)MeBr^-$	CH_3CN	47.54

[a] Concentration of (**1b**) and bromine, 0.105 mol dm^{-3}; *T*, 25 ± 0.05 °C. [b] Conductance of pure solvent/Ω^{-1} cm^{-1}; CH_2Cl_2, 5.5 × 10^{-8}; MeCN, 3.5 × 10^{-6}. Conductance of solutions of (**1b**) and bromine in the corresponding solvents/Ω^{-1} cm^{-1}: (**1b**)(CH_2Cl_2), 6.29 × 10^{-6}; (**1b**)(MeCN), 1.09 × 10^{-4}; Br_2(CH_2Cl_2), 8.88 × 10^{-8}; Br_2 (MeCN), 8.88 × 10^{-4}.

(ee 97%) reacting with bromine; in this case only one diastereoisomer, (**4a$_2$**) is visible. That means that the formation of (**4a**) is highly stereoselective. The diastereoisomeric mixture of the salts (**4a$_1$, a$_2$**) was obtained independently in the same way [1a] as for (**4a**; X = Cl) [equation (1)].

The chemical shifts of (**4a$_1$, a$_2$**) resulting from both reactions are given in Table 4.

The phosphonium salts (**4**) are formed from the reaction of the halosulphonium salt (**3**) with the starting phosphinothiolate. The phosphoryl oxygen atom acts as a nucleophile, attacking the phosphorus atom of (**3**) (Scheme 2, path *a*). It is a better nucleophile than bromide (or Br_3^-) and this reaction is therefore favoured over path *e*, Scheme 1, leading directly to the expected reaction product, (**5**).

The poor *P*-nucleophilicity of higher halogenides is also responsible for the observed stability of salts (**4**; X = Br, I). For the same reason, the manner in which salts (**4a**; X = Br, I) are stabilized differs substantially from that observed for (**4a**; X = Cl). The reaction pathways which play considerable importance in the reaction of salt (**4a**; X = Cl) (Scheme 2, path *b* and Scheme 3, path *a*) seem to be rather unimportant in the collapse of (**4a**; X = Br, I).

The reaction product, bromide (**5a**), only partly derives from pathway *b*, Scheme 2 (see *Stereochemical Studies*). Ligand exchange *a* (Scheme 3), followed by halogenation of anion RS^-, which should lead to phosphonium salt (**11**) has not been observed in any case examined for (**4**; X = Br, I). The presence of the side products bromide (**14**) and pyrophosphinate (**15**) when (**1a, b**) are treated with bromine confirms the participation (5%) of ligand exchange, pathway *c*, *d* (Scheme 3).* The most important pathway for the stabilization of (**4**; X = Br, I) appears to be one which is not applicable to (**4**; X = Cl). It consists of the attack of halogenide anion at the electrophilic carbon centre with the formation of thiopyrophosphinate (**6**), which under the reaction conditions is complexed with halogen (Scheme 2, path *c*).† Figure 2 shows the spectrum of the reacting system (**1a**) + I_2; the presence of salt (**4a**) in addition to complex (**6a**)·I_2 is clearly evident.

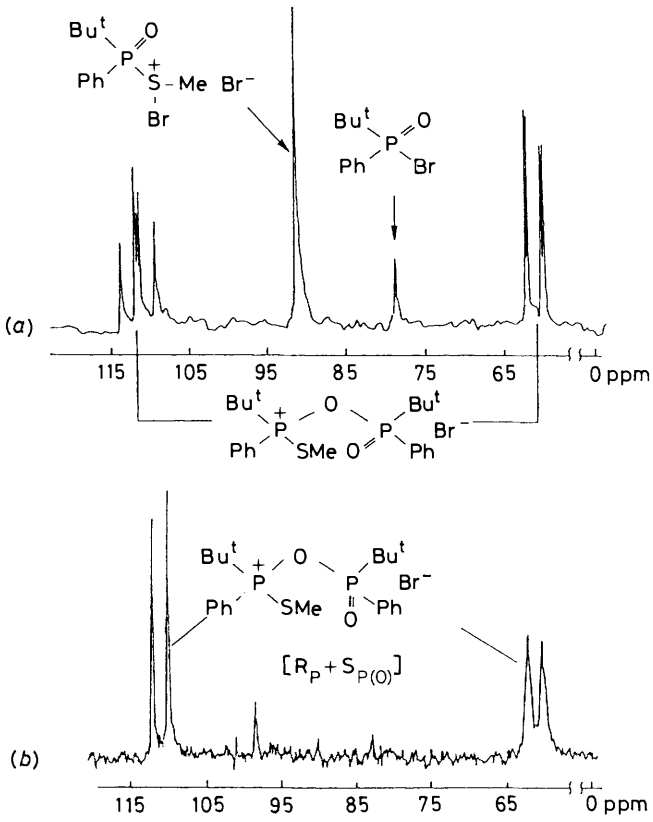


Figure 1. ^{31}P NMR spectra (24.3 MHz) of reacting systems: (*a*) (*R,S*)-(**1a**) + 5Br_2; (*b*) (*R*)-(+)-(**1a**) + Br_2. Solutions *ca.* 1 mol dm^{-3} in CH_2Cl_2; *T*, 293 K.

* Pyrophosphinate (**15**) may be additionally formed by hydrolysis of reaction product (**5**) or by other hydrolytic processes, ref. 1(*a*).

† On the basis of a comparison of the chemical shifts of these products with those of the pure thiopyrophosphinates (**6**) we suppose that for X = Br, equilibrium (**6**)·X_2 $\rightleftharpoons$ (**7**) is displaced in favour of salts (**7**), while in the case X = I it is displaced towards complex (**6**)·I_2 (see Table 4).

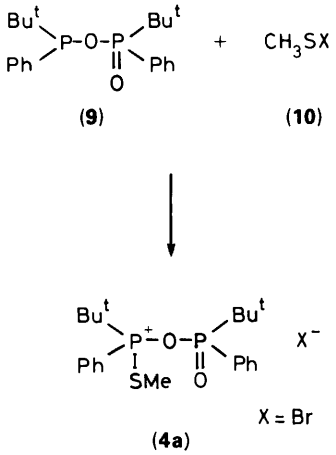
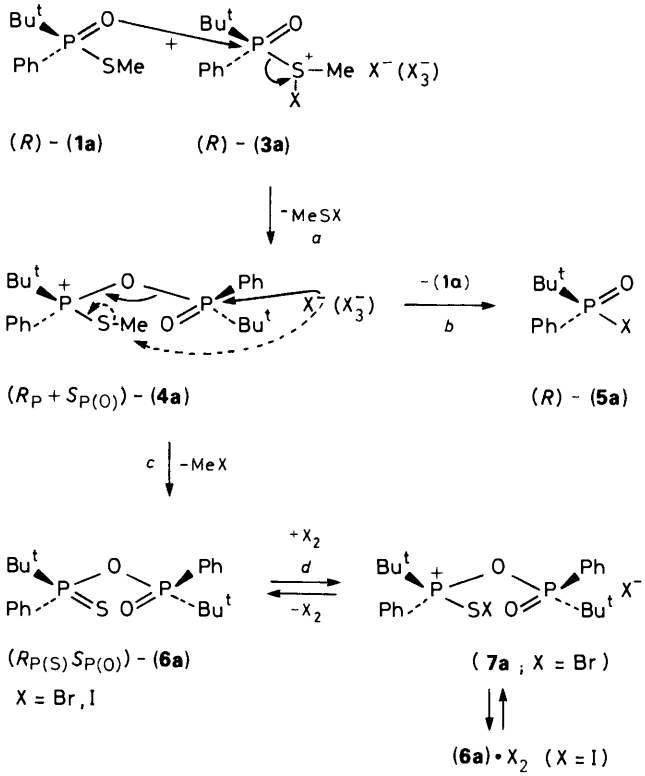


Table 4. ^{31}P NMR (24.3 MHz) chemical shifts and coupling constants of phosphonium salts (**4**) and (**7**), Bu^{t}R$\overset{+}{P}$(X)OP(O)Bu^{t}R Y^- and of complex (**6a**)•I_2.[a]

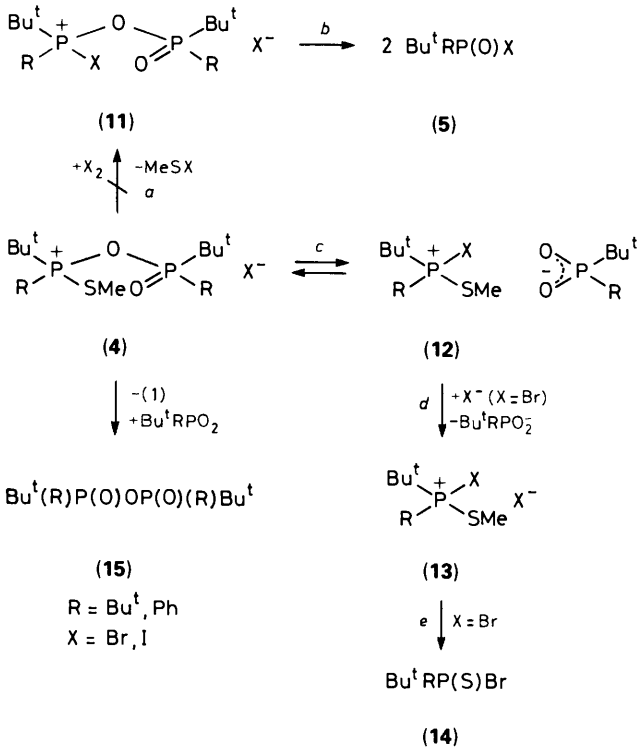
Compound	δ_{P^+} (ppm)	$\delta_{P(O)}$ (ppm)	$J_{P^+-O-P(O)}$/Hz
(**4a**$_1$)	+114.1(d)	+62.1(d)	44
(**4a**$_2$)	+111.1(d)	+60.8(d)	46
(**4a**$_1$)[b]	+114.3(d)	+62.6(d)	44
(**4a**$_2$)[b]	+111.4(d)	+61.2(d)	46
(**4a**$_1$′)	+113.7(d)	+62.0(d)	46
(**4a**$_2$′)	+111.3(d)	+61.6(d)	49
(**4b**)	+128.3(d)	+91.8(d)	78
(**4a**$_1$″)	+114.6(d)	+62.7(d)	44
(**4a**$_2$″)	+111.9(d)	+62.2(d)	47
(**7a**$_1$)	+111.8(d)	+58.4(d)	42
(**7a**$_2$)	+111.2(d)	+58.0(d)	46
(**7a**$_1$)[c]	+112.1(d)	+58.3(d)	42
(**7a**$_2$)[c]	+111.5(d)	+57.7(d)	46
(**7b**)	+126.5(d)	+84.8(d)	72
(**6a**$_1$)•I_2	+106.5(d)	+51.1(d)	42
(**6a**$_2$)•I_2	+106.1(d)	+50.8(d)	46
(**6a**$_1$)•I_2[c]	+105.7(d)	+50.0(d)	42
(**6a**$_2$)•I_2[c]	+105.2(d)	+49.5(d)	46
(**11a**$_1$)[d]	+102.4(d)	+64.8(d)	47
(**11a**$_2$)[d]	+102.0(d)	+64.5(d)	49

[a] All spectra except those of (**11a**$_1$, **a**$_2$) were measured in CH_2Cl_2 at room temperature. The dynamic situation in the reactions is responsible for the variations in the ^{31}P NMR shifts values. (**4a**) R = Ph, X = SMe, Y = $Br(Br_3)$; (**4a**′) R = Ph, X = SMe, Y = $SbBr_6$; (**4a**″) R = Ph, X = SMe, Y = I; (**4b**) R = Bu^t, X = SMe, Y = $Br(Br_3)$; (**7a**) R = Ph, X = SBr, Y = $Br(Br_3)$; (**11a**) R = Ph, X = Br, Y = $Br(Br_3)$; (**7b**) R = Bu^t, X = SBr, Y = $Br(Br_3)$. [b] From the reaction of Bu^{t}PhP–O–P(O)Bu^{t}Ph with CH_3SBr. [c] From the reaction of (**6**) with Br_2 and I_2, respectively. [d] Spectrum measured in temperature range 133–163 K.

Stereochemical Studies.—We demonstrated in our previous paper,[1a] that the participation of two phosphorus-containing intermediates determined the stereochemistry of the reaction under discussion. According to our earlier proposal[1a] the reaction leads to the product >P(O)X (X = halogen), with inversion of configuration, when the reaction course involves pathways *a*, *b*, *e* (Scheme 1), *i.e.* the reaction product is formed *via* sulphonium salt (**3a**) which undergoes decomposition by the attack of its counteranion at phosphorus. However, when the favoured reaction of sulphonium salt (**3a**) is the formation of (**4a**) (path *a*, Scheme 2) followed by decomposition to (**1a**) and (**5a**), the net stereochemical outcome of the formation of (**5a**) is retention of configuration, due to the double consecutive inversions. The first takes place during the formation of salt (**4a**)



Scheme 2.



Scheme 3.

involving attack of the phosphoryl oxygen of ester (**1a**) at the phosphorus atom of sulphonium salt (**3a**); the second is by attack of halogenide anion at the phosphoryl centre of (**4a**) (Scheme 2). These stereochemical proposals explain satisfactorily the experimental facts,[1a] however, the configurations of

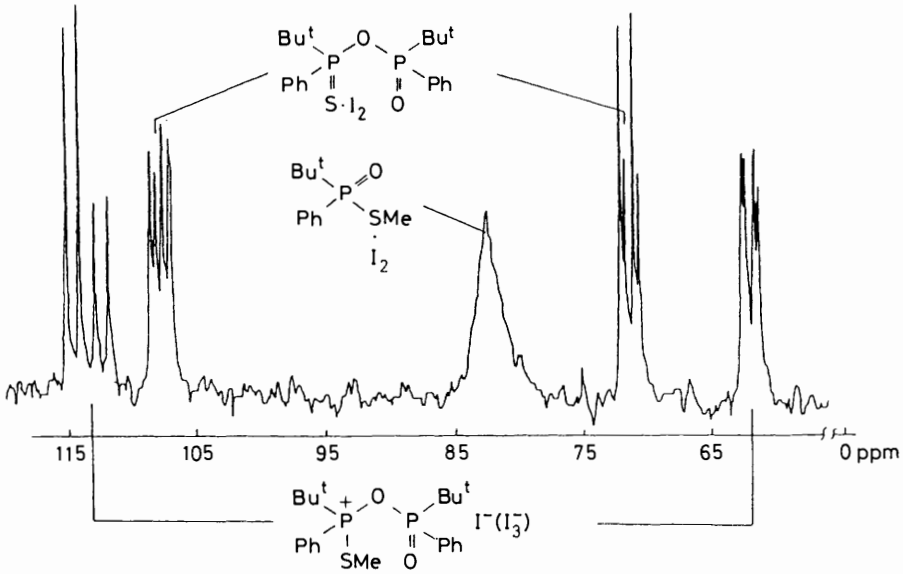
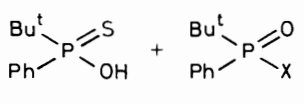


Figure 2. ^{31}P NMR spectrum (36.4 MHz) of reacting system (R, *S*)-(**1a**) + I_2 in CH_2Cl_2; *T*, 293 K. Spectrum measured after 65 days.

Table 5. Bis(t-butylphenyl)thiopyrophosphinates. Spectral and optical data.

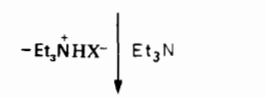
Expt. No.	Starting materials	Product	^{31}P NMR data $\delta_{P(S)}$ (ppm)	$\delta_{P(O)}$ (ppm)	J_{POP}/Hz	$[\alpha]_D$	Diastereoisomers ratio (%) by: n.m.r.	g.c.	Dominant enantiomer
1	(*R*)-(+)-(**1a**)[a]	(**6a**$_1$)	+107.97(d)	+50.17(d)	58[h]	−65.96	100	100	$R_{P(S)}S_{P(O)}$
2	(*R*)-(+)-(**1a**)[b]	(**6a**$_1$)	+108.1(d)	+49.1(d)	64[j]	−16.75	65	63	$R_{P(S)}S_{P(O)}$
		(**6a**$_2$)	+106.5(d)	+48.2(d)	54		35	37	
3	(*S*)-(−)-(**16**)[c] + (*S*)-(−)-(**5a**$_1$)[f]	(**6a**$_1$)	+108.01(d)	+50.18(d)	58[h]	+63.75	85	75	$S_{P(S)}R_{P(O)}$
		(**6a**$_2$)	+107.09(d)	+50.02(d)	48		15	25	
4	(*R*)-(+)-(**16**)[d] + (*R*)-(+)-(**5a**)[g]	(**6a**$_1$)	+107.77(d)	+50.31(d)	56[h]	−63.33	75	75	$R_{P(S)}S_{P(O)}$
		(**6a**$_2$)	+106.92(d)	+50.23(d)	48		25	25	
5	(*S*)-(−)-(**16**)[c] + (*R*)-(+)-(**5a**)[g]	(**6a**$_2$)	+105.52(d)	+47.26(d)	53[j]	−21.00	100	96	$S_{P(S)}S_{P(O)}$
6	(*R*)-(+)-(**16**)[c] + (*S*)-(−)(**5a**$_1$)[f]	(**6a**$_2$)	+107.05(d)	+49.95(d)	50[h]	+21.77	100	100	$R_{P(S)}R_{P(O)}$
7	(*R*, *S*)-(±)-(**16**) + (*S*)-(−)-(**5a**$_1$)[f]	(**6a**$_2$)	+106.90(d)	+50.10(d)	47[h]	+25.00	100	100	$R_{P(S)}R_{P(O)}$

[a] (*R*)-(+)-(**1a**): $[\alpha]_D$ +158.41° (ee 97%). [b] (*R*)-(+)-(**1a**): $[\alpha]_D$ +95.08° (ee 58%). [c] (*S*)-(−)-(**16**): $[\alpha]_D$ −27.75° (ee 99%). [d] (*R*)-(+)-(**16**): $[\alpha]_D$ +22.54° (ee 80%). [e] (*R*)-(+)-(**16**): $[\alpha]_D$ +28.13° (ee 100%). [f] (*S*)-(−)-**5a**$_1$): (X = Cl), $[\alpha]_D$ −39.68° (ee 80%). [g] (*R*)-(+)-(**5a**): (X = Br), $[\alpha]_D$ +49.91° (ee ≥74%). [h] δ_P (121.5 MHz, benzene). [j] δ_P (24.3 MHz, benzene).

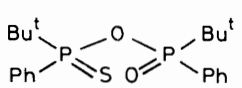


(**16**) (**5a**)

e.g. (*R*) − (+) (*R*) − (+)



(2)



(**6a**)

$[R_{P(S)}S_{P(O)}]$ − (−)

the phosphorus atoms of intermediates (**4a**) have not been directly confirmed.

The formation of bis(t-butylphenyl)thiopyrophosphinates (**6a**) in the reaction of (**1a**) with higher halogens provides the possibility of establishing the absolute configurations at each of the chiral centres. Thiopyrophosphinates (**6a**$_1$, **a**$_2$) are formed from salts (**4a**$_1$, **a**$_2$) by a demethylation process (Scheme 2, path *c*), which does not break any bond at the chiral centres. Therefore (**6a**$_1$, **a**$_2$) have the same configurations at both P(S) and P(O) phosphorus atoms as the transient salts (**4a**$_1$, **a**$_2$). Thiopyrophosphinates (**6a**$_1$, **a**$_2$) of known configuration can be readily prepared independently and compared with compounds obtained from the reaction under discussion.

Reaction of (*R*)-(+)-(**1a**), $[\alpha]_D$ +95.08° with bromine gives after 5 months nearly racemic (**5a**), $[\alpha]_D$ −0.62° and (−)bis(t-butylphenyl)thiopyrophosphinate, (**6a**$_1$, **a**$_2$), $[\alpha]_D$ −16.75° containing as the major diastereoisomer (according to GC and ^{31}P NMR) one with chemical shift at lower field and a shorter retention time (Table 5, Expt. No. 2).

In another experiment, ester (*R*)-(+)-(**1a**), $[\alpha]_D$ +158.41° (ee 97%) was treated with bromine over 24 h to give diastereoisomer (**4a**$_2$) [according to ^{31}P NMR, Figure 1(*b*)],

which was then demethylated with triethylamine to thiopyrophosphinate (**6a**$_1$), $[\alpha]_D$ −65.96° (Table 5, Expt. No. 1).

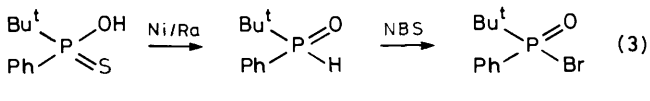
The configuration of the thiopyrophosphinates obtained (**6a**$_1$, **a**$_2$) has been established by a comparison of their physical, spectral, and optical properties with those of samples prepared independently (Table 5). The samples of thiopyrophosphinates (**6a**$_1$, **a**$_2$) of known configuration were synthesized by condensation of the corresponding optically active triethylammonium t-butylphenylphosphinothioate (**16**) with t-butyl(phenyl)phosphinic chloride or bromide (**5a**; X = Cl or Br) in benzene or dichloromethane [equation (2)].

This reaction has been shown to proceed with inversion of configuration at the phosphoryl centre.[7] There is no bond breaking at the thiophosphoryl centre and consequently retention of configuration takes place at this phosphorus atom. There is good evidence to suggest that all known reactions of the system Bu^{t}PhP(O)X with nucleophiles proceed with inversion of configuration at the phosphorus centre,[8] therefore it may be safely assumed that thiophosphorylation of (**5a**; X = Br or Cl) occurs following the stereochemical course considered above. Table 5 shows the optical properties of the starting materials and the optical and spectroscopic characteristics of thiopyrophosphinates (**6a**$_1$, **a**$_2$) obtained from the examined reaction and from equation (2).

It can be seen from Table 5 that thiopyrophosphinate (**6a**$_1$) (Table 5, Expt. No. 1) has similar properties to diastereoisomer (**6a**$_1$) ($R_{P(S)}$ $S_{P(O)}$) (Table 5, Expt. No. 4) and it is enantiomeric towards sample (**6a**$_1$) ($S_{P(S)}$ $R_{P(O)}$) (Table 5, Expt. No. 3). This confirms that (*R*)-(+)-(**1**) forms intermediate (**4a**$_2$) with the original configuration (*R*) at the phosphonium centre (precursor of thiophosphoryl centre) and inverted configuration (*S*) at the phosphoryl centre, which is in agreement with our earlier mechanistic proposal.[1b]

It is noteworthy that the reaction of (*R*, *S*)-(±)-(**16**) with (*S*)-(−)-(**5a**; X = Br) does not lead to an equimolar mixture of both (**6a**$_2$) ($R_{P(S)}$ $R_{P(O)}$) and (**6a**$_1$) ($S_{P(S)}$ $R_{P(O)}$); instead, the diastereoisomer (**6a**$_2$) ($R_{P(S)}$ $R_{P(O)}$) is formed almost exclusively. Kinetic resolution of racemic (**16**) takes place: the recovered thiophosphinic acid (**16**) has optical rotation −13.01° (ee 45%) and, therefore, the *S*-configuration. This means that there is a preference for the diastereoisomer (**6a**$_2$) with the same configuration at the P(S) and P(O) chirality centres.

The high degree of racemization of t-butyl(phenyl)phosphinic bromide (**5a**; X = Br), formed in the reaction of (**1a**) with bromine, requires some comment. Two sources of racemization may be considered: (i) the reaction occurs *via* pathway *e* (Scheme 1) and pathways *a*, *b* (Scheme 2) to give net nearly racemic product; and (ii) the bromide (**5a**) is formed stereoselectively but during the prolonged reaction time it racemizes by exchange of bromine atom at the phosphoryl centre. The following experiment excludes the second possibility. The optically active t-butyl(phenyl)phosphinic bromide [prepared independently,* see equation (3)], $[\alpha]_D$ +49.91°, was allowed to stand for two months at room temperature in dichloromethane mixed with an equimolar quantity of elemental bromine (the conditions imitating the examined reaction). Bromide (**5a**), recovered after this time, had retained 90% of its original optical purity.



(**16**) (**17**) (**5a** ; X = Br) (3)

A careful examination of the ^{31}P NMR spectroscopy results suggests that probably both intermediates, bromosulphonium salt (**3a**) and phosphonium salts (**4a**), are precursors of the bromide (**5a**). These two compounds are the main contributors to the reacting system (**1a**) + Br_2 during the lengthy reaction time. The additional source of bromide (**5a**) might be the bromination reaction of salts (**7a**) (Scheme 4) which ought to lead to the formation of the racemic (**5a**).

Although salt (**11a**) has never been observed in the reacting system (**1a**) + Br_2, the reaction sequence shown in Scheme 4 cannot be excluded. It is possible that under the reaction conditions salt (**11a**) is formed at a similar rate to that of its decomposition into monophosphorus compounds. The halogenation of phosphoranesulphenyl halogenides (**18**), with formation of phosphorus acid halogeno anhydride (Scheme 4, pathways *d*, *e*) is a known reaction.[10]

The reaction of (**1a**) with bromine in methanol follows the same stereochemical course known for other examples in the literature.[3a] It involves the displacement of the –SR group of the thioloester by –OR with inversion of configuration. No phosphoryloxyphosphonium salt of type (**4a**) was observed at low temperature.

Conclusions

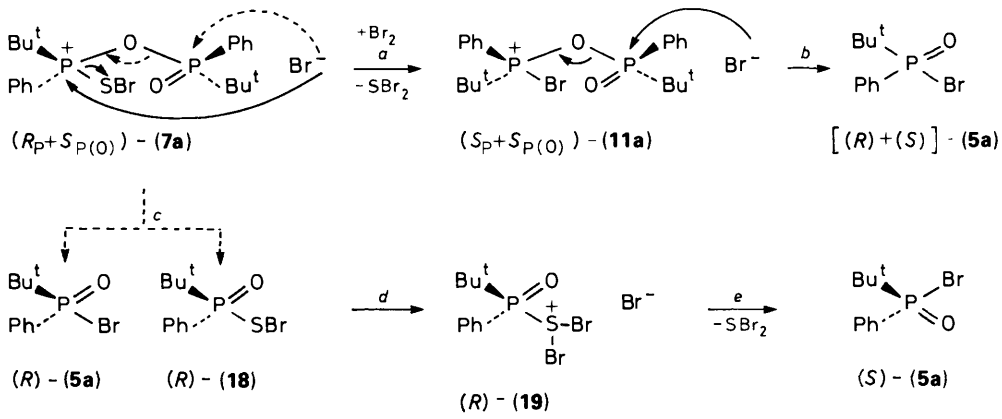
It seems reasonable to assume that the rate-determining step of the reaction under discussion is the attack of halogenide anion at the electrophilic phosphorus centre. If this is the case, the formation of the transient products (**3**) and/or (**4**) should occur instantaneously. The nature of the halogen would influence the formation of (**3**) only by its acceptor capacity, while the formation of (**4**) would be affected by changes in the leaving ability of the $\overset{+}{R}S(X)$-group. In fact, chlorine and bromine react with esters (**1a**) and (**1b**) immediately over a broad range of temperatures, and the difference in the course of the reaction confirms the dependence of the reaction rate on the nucleophilicity of halogenide anion (chlorine reacts faster than bromine).

However, the mixture of (**1a**) with iodine shows the presence of intermediate (**4a**) only after several days, and (**1a**) is completely consumed after several months. Such behaviour of iodine may be best explained by the assumption that the halosulphonium salt (**3**) is the crucial intermediate and that its formation may determine, in defined conditions, the reaction rate. It is known that the acceptor ability of iodine is even stronger than that of bromine.[11] However, the complexes of bivalent sulphur compounds with bromine have the strongest tendency to exist as bromosulphonium salts, while iodine tends to form the molecular (donor–acceptor) complexes.[6,11] In the case studied, the formation of complex is not sufficient to promote further reaction. The complexation must be followed by ionization to form an iodosulphonium salt. The examination of the reacting system (**1a**) + I_2 by spectroscopic methods (^{31}P, ^{1}H NMR) demonstrates that the equilibrium (**1**) + $I_2 \rightleftharpoons$ (**2**) $\rightleftharpoons$ (**3**) is shifted strongly towards the starting materials. In this context, it becomes clear why the addition of an excess of iodine enhances the rate of the reaction. The equilibrium (**2**) $\rightleftharpoons$ (**3**) $\rightleftharpoons$ (**3′**) (Scheme 1, X = I) is displaced in the favour of iodosulphonium salt (**3′**) due to the interaction between two iodine molecules.†

It seems to us that the formation of anions X_3^- plays an important role in the reaction under discussion, even when starting materials are used in equimolar amounts. It is known

* The synthesis of [*R*)-(+)-t-butyl(phenyl)phosphinic bromide, (**5a**; X = Br) was similar to that of one of the chlorine analogues (ref. 9).

† This clarifies the facts from the literature[4b,c] that a 10–15-fold excess of iodine was applied to activate the –SR group in the nucleophilic displacement reaction at phosphorus.



Scheme 4.

that the association constants of the anions X_3^- in aprotic solvents are very high, exceeding those of the complexes of RR'S·X_2 (X = halogen).[12] The possibility exists that the involvement of halogen in the formation of X_3^- means that a considerable amount of the starting thiolo ester remains uncomplexed and therefore capable of reacting with (**3**), with consequent formation of an intermediate containing two phosphorus atoms. It is possible that this is the true explanation for why such intermediates are observed, not only in the course of the reaction described in this paper, but also in most cases examined.[13] The presence of anions Br_3^- and I_3^- has been confirmed by measurements of the UV and visible spectra of the reaction mixtures. The absorptions λ = 273 and 293 nm were observed for Br_3^- and I_3^-, respectively.

A comparison of the results obtained for the reacting systems (**1a**) + X_2 and (**1b**) + X_2 (X = Cl, Br, I) shows that ester (**1b**) has an increased capacity to form complexes with halogens (Table 1). However, the formation of phosphonium salts (**4b**) is unfavourable, and such salts were not observed for X = Cl and I. The differences observed in the behaviour of both models may be caused by the interplay of steric and electronic factors during the individual steps of the overall reaction.

Experimental

M.p.s were measured on a Boëtius PHMK apparatus and are uncorrected. Solvents and commercial reagents were purified by conventional methods before use. NMR spectra were recorded with JEOL JNM-FX 60 FT (60 MHz, ^{1}H; 24.3 MHz, ^{31}P; 15 MHz, ^{13}C), Bruker HX-72 (90 MHz, ^{1}H; 36.4 MHz, ^{31}P; 22.5 MHz, ^{13}C), Bruker MSL 300 (300 MHz, ^{1}H; 121.5 MHz, ^{31}P), and Tesla BS 347 (80 MHz, ^{1}H) spectrometers; positive chemical shifts are downfield from external 85% H_3PO_4, and internal $SiMe_4$, respectively. Products were identified with an LKB Model 2091 gas-chromatograph-mass spectrometer and/or ^{31}P NMR spectroscopy. Optical rotations were measured at 589 nm and 20 ± 2 °C using a Perkin-Elmer 141 polarimeter in benzene solution unless specified otherwise. UV–VIS spectra were run on a Specord UV-VIS spectrometer and IR spectra were recorded with a Specord 71 IR instrument. Conductances were measured by means of a Radelkis conductimeter Model OK 102/1 equipped with a Philips PW 9512/01 electrode with cell constant 0.74. ^{31}P NMR spectra were recorded as described in the previous paper.[1b]

Starting Materials.—t-Butyl(phenyl)phosphinothioic acid was synthesized and resolved into optical antipodes by known methods.[14] Di-t-butylphosphine oxide,[16] optically active t-butyl(phenyl)phosphine oxide[15] and *S*-methyl t-butyl(phenyl)phosphinothiolate[1b] were obtained by earlier reported methods. Methanesulphenyl chloride and bromide[17] were prepared from the corresponding disulphide by halogenation with sulphuryl chloride or bromine, respectively. The crude product was used in subsequent reactions.

S-*Methyl Di-t-butylphosphinothiolate* (**1b**).—Into a stirred solution of di-t-butylphosphine oxide (4.71 g, 0.029 mol) in benzene (10 cm^3), was added dropwise at 0 °C freshly prepared methanesulphenyl chloride (2.5 g, 0.03 mol). The stirring was continued for 2 h at room temperature. Hydrogen chloride and solvent were removed *in vacuo* and the residue was distilled to give (**1b**) (4.28 g, 69%), b.p. 75–77 °C/0.15 mmHg; δ_P (24.3 MHz; CH_2Cl_2) +81.2; δ_H (60 MHz; $CDCl_3$) 1.23 (18 H, d, *J* 16 Hz) and 2.22 (3 H, d, *J* 9 Hz); δ_C (15 MHz; $CDCl_3$) 38.6 (d, *J* 54 Hz), 24.4 (s), and 9.49 (s).

Reaction of S-*Methyl t-butyl(phenyl)phosphinothiolate,* (**1a**) *with Bromine.*—(a) *In methylene dichloride. S*-Methyl t-butyl(phenyl)phosphinothiolate (0.3380 g, 1.4 mmol) and bromine (0.2366 g, 1.4 mmol), dissolved in methylene dichloride (3 cm^3), were sealed in an NMR tube. ^{31}P NMR spectra were recorded every month (see Table 1). After 6 months the reaction mixture contained as the main product t-butyl(phenyl)phosphinic bromide, (**5a**), δ_P +73.7. The tube was opened and the crude product distilled to give t-butyl(phenyl)phosphinic bromide (0.2704 g, 70%). (Found: P, 11.6; Br, 30.5. $C_{10}H_{14}$BrOP requires P, 11.9; Br, 30.6%); *m/z* (70 eV) 260 (M^+, 4%), 261(3), 262 (M^+ + 2, 4%), 263(2), 206(54), 204(58), 125(100), 57(53), and 47(19).

Starting from (*S*)-(−)*S*-methyl t-butyl(phenyl)phosphinothiolate, (1.198 g, 5.2 mmol), $[\alpha]_D$ −55.62° (ee 34%) (*c*, 1.21) and bromine (0.839 g, 5.2 mol) in methylene dichloride (2 cm^3), was obtained after 6 months: t-butyl(phenyl)phosphinic bromide (0.891 g, 65%), $[\alpha]_D$ +4.12 (*c* 2.08), b.p. 85.5 °C/0.25 mmHg; δ_P +72.4; (Found: P, 11.6; Br, 30.5. $C_{10}H_{14}$BrOP requires P, 11.9; Br, 30.6%); *m/z* (70 eV) 260 (M^+, 4%), 261(3), 262 (M^+ + 2, 4%), 263(2), 206(54), 204(58), 125(100), 57(53), and 47(19).

In another experiment, from (*R*)-(+)-(**1a**) (0.7301 g, 3.1 mmol), $[\alpha]_D$ +95.08° (*c* 2.8) (ee 59%) and bromine (0.5110 g, 3.1 mmol), two fractions were obtained after 5 months: (i), t-butyl(phenyl)phosphinic bromide, (**5a**) (0.41 g, 50%), b.p. 85–87 °C/0.2 mmHg, $[\alpha]_D$ −0.63° (*c* 0.90), δ_P (24.3 MHz; benzene) +68.7 ppm and (ii), bis(t-butylphenyl)thiopyrophosphinate (0.35 g, 59%), b.p. 130–133 °C/0.2 mmHg, $[\alpha]_D$ −16.75° (*c* 1.9), diastereomeric mixture (**6a**$_1$, **a**$_2$). NMR data and diastereoisomer ratios are given in Table 5.

Starting from (*R*)-(+)-(**1a**) (0.1200 g, 0.52 mmol), $[\alpha]_D$ +158.41° (*c* 0.915) (ee 97%) and bromine (0.0931 g, 0.58 mmol)

in methylene dichloride was obtained, after only 4 h, the phosphonium salt ($4a_2$) (for NMR data see Table 4). To the solution of ($4a_2$) was added triethylamine (excess) and the resulting white precipitate was filtered off. The filtrate, containing (by NMR spectroscopy) one diastereoisomer of thiopyrophosphinate, ($6a_1$), was washed with water, dried, evaporated and purified by column chromatography as described in the general procedure for the preparation of (**6**). Physical, optical and spectroscopic data for ($6a_1$) are given in the Table 5 (Exp. 1).

(b) *In methanol.* Into a solution of *S*-methyl t-butyl(phenyl)-phosphinothiolate, (**1a**) (0.5934 g, 2.5 mmol) in methanol (5 cm^3) was added bromine dropwise at −70 °C until the mixture appeared coloured. The stirring was continued for 2 h at room temperature, then the reaction mixture was evaporated and the residue distilled *in vacuo* to give *O*-methyl t-butyl-(phenyl)phosphinate (0.359 g, 65%), b.p. 115 °C/0.2 mmHg, δ_P (24.3 MHz; CH_2Cl_2) +55.95 ppm.

Starting from (*R*)-(+)-*S*-methyl t-butylphenylphosphino-thiolate, (**1a**), $[\alpha]_D$ +89.09 (*c* 1.98) (0.457 g, 2 mmol), was obtained (*S*)-(−)-*O*-methyl t-butyl(phenyl)phosphinate (0.213 g, 50%), $[\alpha]_D$ −17.32 (*c* 4.74); δ_P (24.3 MHz; benzene) +56.30 [lit.,[18] (*R*)-(+)-*O*-methyl t-butyl(phenyl)phosphinate, $[\alpha]_D$ +42.3 (*c* 0.6 g), δ_P(benzene) +50.1 ppm].

Reaction of S-*Methyl Di-t-butylphosphinothiolate with Bromine.*—(a) *Isolation of crystalline complex* (**2b**). To a solution of *S*-methyl di-t-butylphosphinothiolate (**1b**) (0.4941 g, 2.3 mmol) in pentane (5 cm^3), was added bromine (0.3790 g, 2.3 mmol) dropwise at room temperature. Yellow-orange crystals precipitated immediately, and these were filtered off and dried *in vacuo*, 0.42 g (48%), m.p. 92–96 °C. Complex (**2b**) is stable for several weeks in a desiccator. ^{31}P, ^1H and ^{13}C NMR data are given in Table 2. ν_{max}(KBr) 2 950 s (C–H), 1 460ms (C–H), and 1 190s cm^{-1} (P=O); λ_{max}(CH_2Cl_2) 273 (Br_3^-), 232, and 408 nm (Br_2). The analysis found for (**2b**): C, 25.65; H, 5.50; P, 7.50; Br, 47.08% suggests a mixture of (**1b**)·Br_2 and (**1b**)·$2Br_2$.

(b) *Reaction in methylene dichloride with distillation of the reaction mixture.* To a stirred solution of *S*-methyl di-t-butylphosphinothiolate (0.9688 g, 4.6 mmol) in methylene dichloride (5 cm^3) was added dropwise elemental bromine (0.7432 g, 4.6 mmol), dissolved in methylene dichloride (5 cm^3), at room temperature. The reaction mixture was refluxed for 12 h. Following removal of the solvent, the residue was distilled at 76–78 °C/0.55 mmHg to give an orange oil, which solidified after distillation (0.40 g, 23%), δ_P(24.3 MHz, CH_2Cl_2) +100.4; δ_H(80 MHz; $CDCl_3$) 1.29 (18 H, d, *J* 16.5 Hz) and 2.32 (3 H, d, *J* 10 Hz) (Found: S, 10.40%; Br, 37.54. Mixture of 85% $C_9H_{21}Br_2OPS$ and 15% $C_9H_{21}PSO$ required S, 9.71; Br, 36.92%).

Halogenation Reactions in NMR Tubes.—Equimolar (unless specified otherwise) amounts (*ca.* 0.5–1 mmol) of *S*-methyl di-t-butyl- (or t-butylphenyl-) phosphinothiolate and halogen were sealed or closed tightly with a rubber septum under dry argon in a cooled NMR tube containing a suitable solvent (toluene, methylene dichloride, benzene or acetonitrile, 3–4 cm^3). The progress of the reaction was monitored periodically by means of ^{31}P NMR spectroscopy. The compositions of the reaction mixtures (by ^{31}P NMR spectroscopy), depending on the reaction conditions, are shown in the Table 1.

Preparation of Bis(t-butylphenyl)thiopyrophosphinates (**6**). *General Procedure.*—Equimolar amounts of t-butyl(phenyl)-phosphinothioic acid, (**16**), t-butyl(phenyl)phosphinic chloride or bromide (**5a**; X = Cl or Br) and triethylamine were allowed to react for *ca.* 24 h at 40 °C in methylene dichloride or benzene (5–6 cm^3). Triethylamine hydrochloride was filtered off, and the filtrate was washed with water and dried under $MgSO_4$. After evaporation of solvent, crude bis(t-butylphenyl)-thiopyrophosphinate (**6**) was chromatographed on silica gel with chloroform–acetone as the eluant. The physical, optical, and spectroscopic data of ($6a_1$, a_2) and the optical data of the precursors are given in Table 5.

(R)-(+)-*t-Butylphenylphosphinic Bromide* (**5a**).—Into a stirred suspension of *N*-bromosuccinimide (0.2710 g, 1.52 mmol) in CCl_4 (5 cm^3), was added dropwise a solution of (*S*)-(−)-t-butyl(phenyl)phosphine oxide,[15] $[\alpha]_D$ −25.46° (*c*, 0.0108) (0.2675 g, 1.52 mmol) in CCl_4 (5 cm^3) at 0 °C. Stirring was continued for 1 h and succinimide was filtered off. The residue was recrystallized from hexane to give t-butyl(phenyl)-phosphinic bromide (0.2864 g, 74%); $[\alpha]_D$ +49.91° (*c* 0.0107); δ_P (24.3 MHz; benzene) +69.41.

Acknowledgements

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