Stereochemistry of Organophosphorus Cyclic Compounds. Part 5.[1] Synthesis and Geometry of Some 4,5-Disubstituted 1,3,2-Dioxaphospholan-2-thiones and Stereochemistry of Nucleophilic Displacement Reactions at Phosphorus

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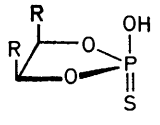
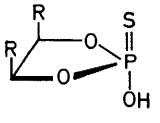
Geometrical isomers of 2-hydroxy-4,5-dimethyl-1,3,2-dioxaphospholan-2-thione, 2-halogeno-4,5-dimethyl-1,3,2-dioxaphospholan-2-thione (X = Cl, Br, or F) and 2-hydroxy-4,5-diphenyl-1,3,2-dioxaphospholan-2-thione have been prepared in a stereospecific manner. Stereochemistries of these isomers are assigned on the basis of chemical correlations and n.m.r. measurements. 2-Chloro- and 2-bromo-4,5-dimethyl-1,3,2-dioxaphospholan-2-thione have been found to undergo methanolysis, aminolysis, and mercaptolysis with retention of configuration at phosphorus. Halogen–halogen exchange at the phosphorus atom is also described. The relationship between *cis*- and *trans*-geometry of disubstituted 1,3,2-dioxaphospholan-2-thiones and their ^{31}P and ^{13}C n.m.r. spectral parameters is briefly discussed.

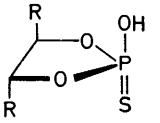
We have described previously [1] a general synthesis of cyclic, five-membered phosphorus monothioacids, and geometrical isomerism in 2-hydroxy-4-methyl-1,3,2-dioxaphospholan-2-thione which exists in two diastereoisomeric *cis*- and *trans*-forms owing to the presence of two centres of chirality (at P-2 at C-4). We have now extended this study to 4,5-disubstituted 2-hydroxy-1,3,2-dioxaphospholan-2-thiones, which should exist in three diastereoisomeric forms: in addition to the *cis*- and *trans*-pair derived from *meso*-diols a (±)-form is also possible.† The availability of these isomers may be of interest for further stereochemical and biochemical studies.



trans–(1) R = Me
trans–(2) R = Ph

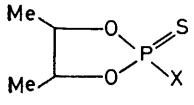


cis–(1)
cis–(2)



(±)–(1)
(±)–(2)

In this paper we report the stereospecific synthesis of the diastereoisomers of (1) and (2) as well as the results of closely related stereochemical studies on nucleophilic displacement reactions in 2-halogeno-4,5-dimethyl-1,3,2-dioxaphospholan-2-thiones (3)—(5).



(3) X = Cl
(4) X = Br
(5) X = F

RESULTS AND DISCUSSION

Synthesis and Configuration of Geometrical Isomers of 2-Hydroxy-4,5-dimethyl-1,3,2-dioxaphospholan-2-thione (1).—The route to (±)-(1) from racemic butane-2,3-diol was apparent. Thus, the imidazolium salt of (±)-(1) (m.p. 117—118°) was prepared in three steps from the (±)-diol *via* the phosphonate (±)-(6). An alternative route leading to the tetramethylammonium salt of (±)-(1) (m.p. 155—158°) involved the reaction of trimethylamine with the cyclic methyl thiophosphate (±)-(7) prepared as shown in Scheme 1.

† In contrast to our previous work,[1] the terms *cis* and *trans* for the P^V compounds refer to the relationship between the methyl (phenyl) group and the senior exocyclic group on phosphorus as determined by the Sequence Rule (*J. Org. Chem.*, 1970, **35**, 2849).

As expected, the phosphonate (6) obtained from *meso*-butane-2,3-diol was a mixture of geometrical isomers. Addition of sulphur to this phosphite in the presence of imidazole gave a mixture of two diastereoisomeric imidazolium salts of *cis*- and *trans*-(1) (m.p. 87—98°) which are hardly distinguishable by ^1H and ^{31}P n.m.r. spectra. Therefore the resulting salt was converted into *S*-methyl and *O*-trimethylsilyl derivatives, (8) and (9), spectra of which revealed the presence of both geometrical isomers. For instance, in the $^{31}P\{^1H\}$ n.m.r. spectrum two signals appeared at −44.6 and −44.8 p.p.m. for (8) and at −67.8 and −69.5 p.p.m. for (9).

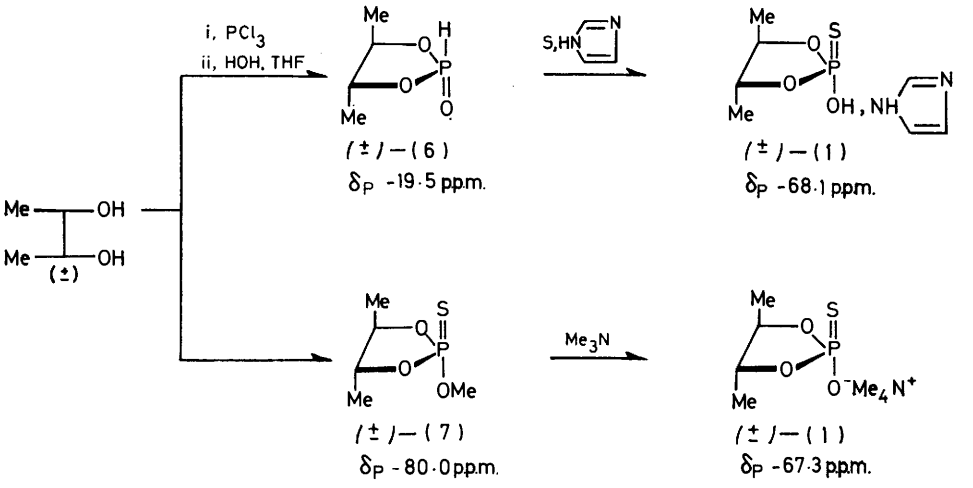
Fractional crystallisation of the imidazolium salt obtained from propan-1-ol–ether gave one isomerically pure imidazolium salt of *meso*-(1) (m.p. 114—116°). This salt gave the *S*-methyl ester (8), δ_P −44.8 p.p.m., and the *O*-trimethylsilyl derivative (9), δ_P −67.8 p.p.m.

The geometry of the salt isolated was established as follows (Scheme 2). The starting methyl phosphite (10),[2] which exists as a 9 : 1 mixture of *trans*- and *cis*-isomers, was treated with sulphur to give the corresponding mixture of diastereoisomeric *cis*- and *trans*-thiophosphates (7) in the same ratio, since the sulphur addition takes place stereospecifically with retention of configuration at phosphorus.[3] The mixture (7) was then treated with trimethylamine, and the tetramethylammonium salt formed was silylated to give (9) as a 9 : 1 mixture of isomers, δ_P −67.8 and −69.5 p.p.m., respectively. Since neither demethylation nor silylation changes the configuration at phosphorus on going from (7) to (9), the predominant diastereoisomer of (9) with δ_P −67.8 p.p.m. should have the *cis*-configuration. Consequently, the imidazolium salt of (1), m.p. 114—116°, which gave on silylation the same diastereoisomer of (9), should also have the *cis*-geometry.

The above reaction sequence represents a very convenient synthesis of the tetramethylammonium salt of *cis*-(1) (m.p. 174—176°); the small amounts of the other isomer are easily removed by crystallisation.

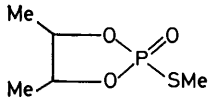
[1] Part 4, M. Mikołajczyk, M. Witczak, M. Wieczorek, N. G. Bokij, and J. T. Struchkov, *J.C.S. Perkin I*, 1976, 371.
[2] D. Z. Denney, G. Y. Chen, and D. B. Denney, *J. Amer. Chem. Soc.*, 1969, **91**, 6838.
[3] W. C. McEven, *Topics Phosphorus Chem.*, 1965, **2**, 25.

A different approach was used to obtain the *trans*-isomer of (1) (Scheme 3). In the first step *meso*-butane-2,3-diol was condensed with thiophosphoryl bromide in the presence of pyridine to afford a 3 : 1 mixture of the

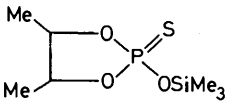


SCHEME 1

diastereoisomeric 2-bromo-4,5-dimethyl-1,3,2-dioxaphospholan-2-thiones (4), from which the major isomer, *cis*-(7) (m.p. 56—58°), was isolated by crystallisation (for the configurational assignment see below). Its



(8)



(9)

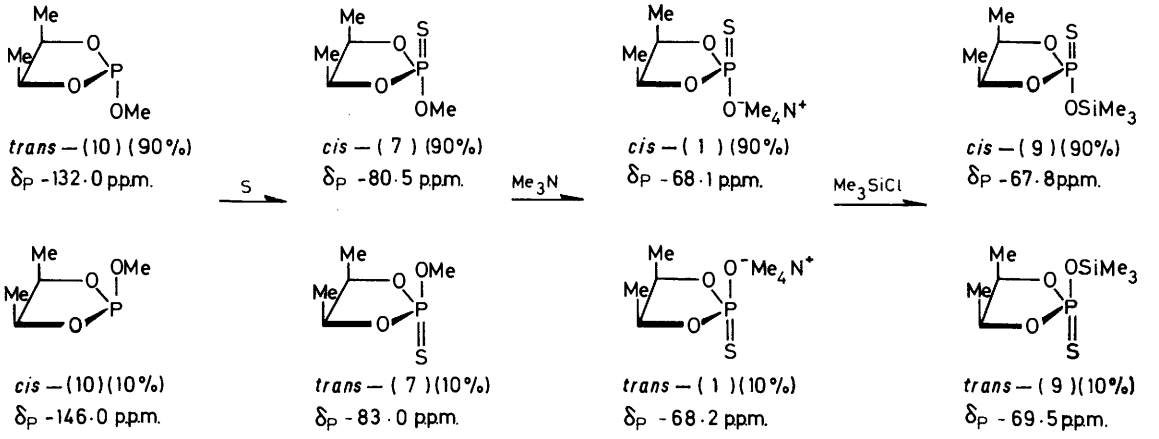
reaction with methanol in the presence of triethylamine gave *trans*-2-methoxy-4,5-dimethyl-1,3,2-dioxaphospholan-2-thione (7), which was converted into the tetramethylammonium salt of *trans*-(1) (m.p. 178—180°) with trimethylamine. As expected, this salt on silylation gave *trans*-(9), δ_P —69.5 p.p.m.

The configurational assignments to *cis*- and *trans*-(1) based on chemical correlations are in full agreement with the results of *X*-ray studies to be published elsewhere.

Synthesis and Configuration of Geometrical Isomers of 2-Hydroxy-4,5-diphenyl-1,3,2-dioxaphospholan-2-thione

(2).—We have also synthesised in a stereospecific manner both *cis*- and *trans*-isomers of the thioacid (2). The synthesis of *cis*-(2) was accomplished in two steps from *trans*-2-methoxy-4,5-diphenyl-1,3,2-dioxaphospholan (11).[4] Treatment of *trans*-(11) with acetyl thiohypochlorite gave the pure *cis*-isomer of the corresponding thiophosphate (12) (m.p. 93—97°). Demethylation of this ester by means of trimethylamine afforded the tetramethylammonium salt of *cis*-(2) (m.p. 239—241°).

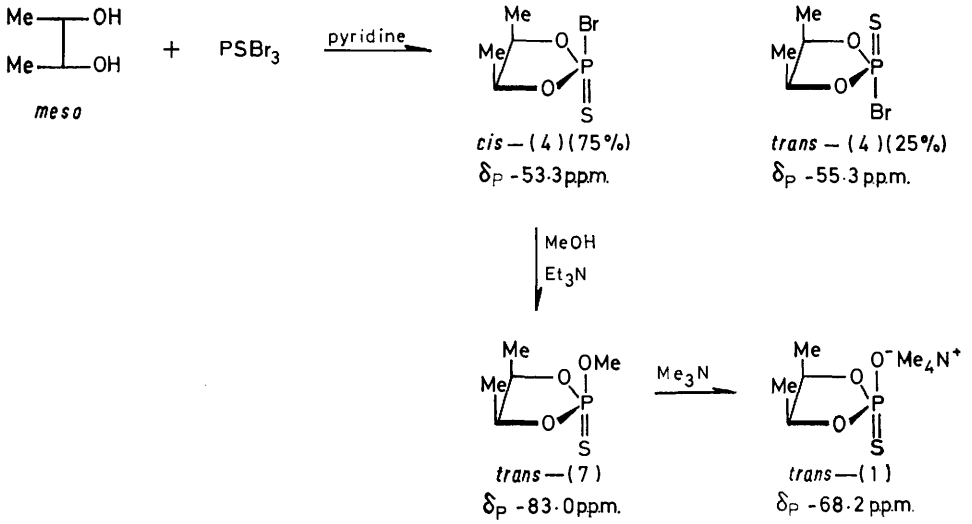
The diastereoisomerically pure tetramethylammonium salt of *trans*-(2) was prepared *via* the corresponding cyclic phosphorobromidothioates (13). Thus, the reaction of *meso*-1,2-diphenylethane-1,2-diol with thiophosphoryl bromide in the presence of pyridine afforded a mixture



SCHEME 2

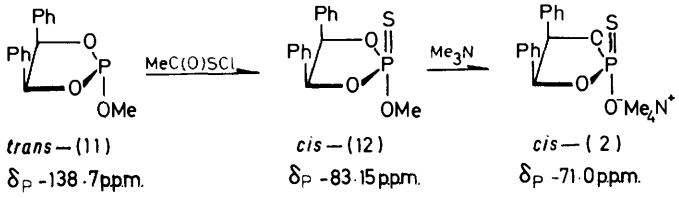
of *cis*- and *trans*-2-bromo-4,5-diphenyl-1,3,2-dioxaphospholan-2-thione (13). Treatment of this mixture with

[4] M. G. Newton and B. S. Campbell, *J. Amer. Chem. Soc.*, 1974, **96**, 7790.



SCHEME 3

methanol in the presence of triethylamine resulted in *trans*- and *cis*-(12) in the ratio 4 : 1. The ester *trans*-(12)

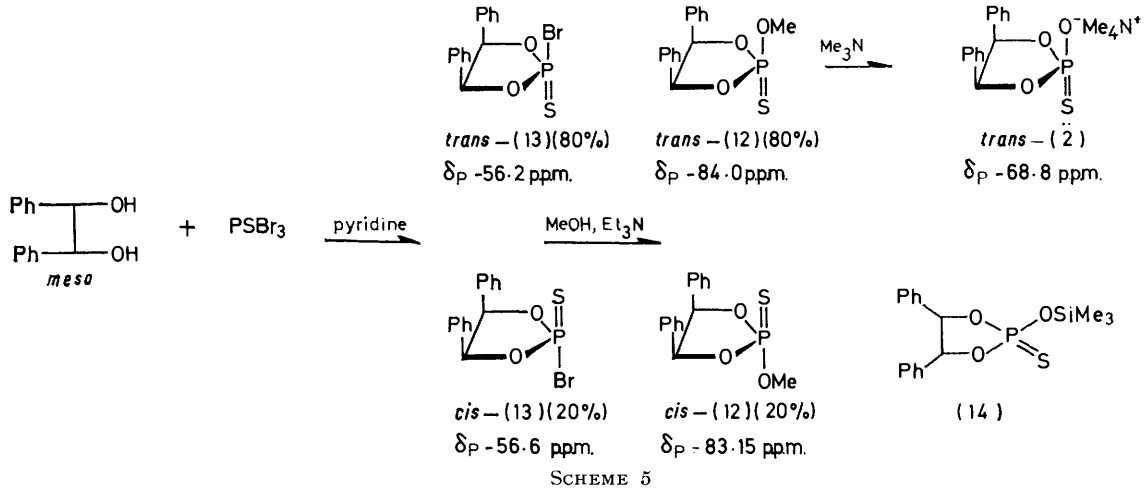


SCHEME 4

(m.p. 103—105°) was easily isolated in a diastereoisomerically pure state by crystallisation, and gave on

of (2) were further characterised as trimethylsilyl derivatives (14). Physical properties and elemental analyses of the thioacid salts obtained are summarised in Table 1.

Synthesis, Configuration of Geometrical Isomers, and Nucleophilic Substitution at Phosphorus in 2-Halogeno-4,5-dimethyl-1,3,2-dioxaphospholan-2-thiones.—Since the stereospecific synthesis of *trans*-(1) was accomplished *via* the diastereoisomeric bromides (4), it was necessary to establish the geometry of the latter On the other hand, our continuing interest in the stereochemistry of nucleophilic substitution at the thiophosphoryl centre [5] prompted us to synthesise not only the bromides (4) but



SCHEME 5

demethylation the desired tetramethylammonium salt of *trans*-(2) (m.p. 205—206°). Both geometrical isomers also the corresponding chlorides (3) and fluorides (5) as convenient models for such a study. The only previous work dealing with the steric course of substitution at phosphorus as part of a cyclic five-membered system was published by Inch *et al.*,[6] who observed retention of

[5] J. Michalski and M. Mikołajczyk, *Tetrahedron*, 1966, **22**, 3055; M. Mikołajczyk, *ibid.*, 1967, **23**, 1543; M. Mikołajczyk, J. Omelańczuk, and J. Michalski, *Bull. Acad. Polon. Sci.*, 1968, **16**, 615; B. Pliszka-Krawiecka, M. Mikołajczyk, and J. Michalski, *ibid.*, 1969, **17**, 75; J. Michalski, M. Mikołajczyk, B. Młotkowska, and J. Omelańczuk, *Tetrahedron*, 1969, **25**, 1743; M. Mikołajczyk, J. Krzywański, and B. Ziemnicka, *Phosphorus*, 1974, **5**, 67; *Tetrahedron Letters*, 1975, 1607.

[6] D. B. Cooper, J. M. Harrison, and T. D. Inch, *Tetrahedron Letters*, 1974, 2697; see also D. B. Cooper, C. R.Hall, and T. D. Inch, *J.C.S. Chem. Comm.*, 1975, 721.

configuration in alcoholysis of 2-chloro-4-methyl-5-phenyl-1,3,2-oxazaphospholan-2-one.

The 2-halogeno-4,5-dimethyl-1,3,2-dioxaphospholan-2-thiones (3)—(5) were prepared in high yield from the corresponding halogenophosphites (15)—(17) and acetyl thiohypochlorite. Since the addition of sulphur to P^{III} compounds by means of acetyl thiohypochlorite has been demonstrated to proceed with full retention of configuration at phosphorus,[7] and the starting halogenophosphites are predominantly the *trans*-mixtures,[8] it is reasonable to assign the configuration to the prevailing isomers of thiophosphoryl halides formed in this reaction as depicted in Scheme 6.

The correctness of these configurational assignments is confirmed by the fact that all the thiophosphoryl halides in which the sulphur atom is *cis* with respect to the ring methyl groups have $^3J_{POCH}$ values smaller than those for their isomers with the opposite configuration at phosphorus. On this basis we have also assigned *cis–trans*-geometry to the diastereoisomeric thiophosphoryl bromides (13) derived from *meso*-1,2-diphenylethane-1,2-diol.

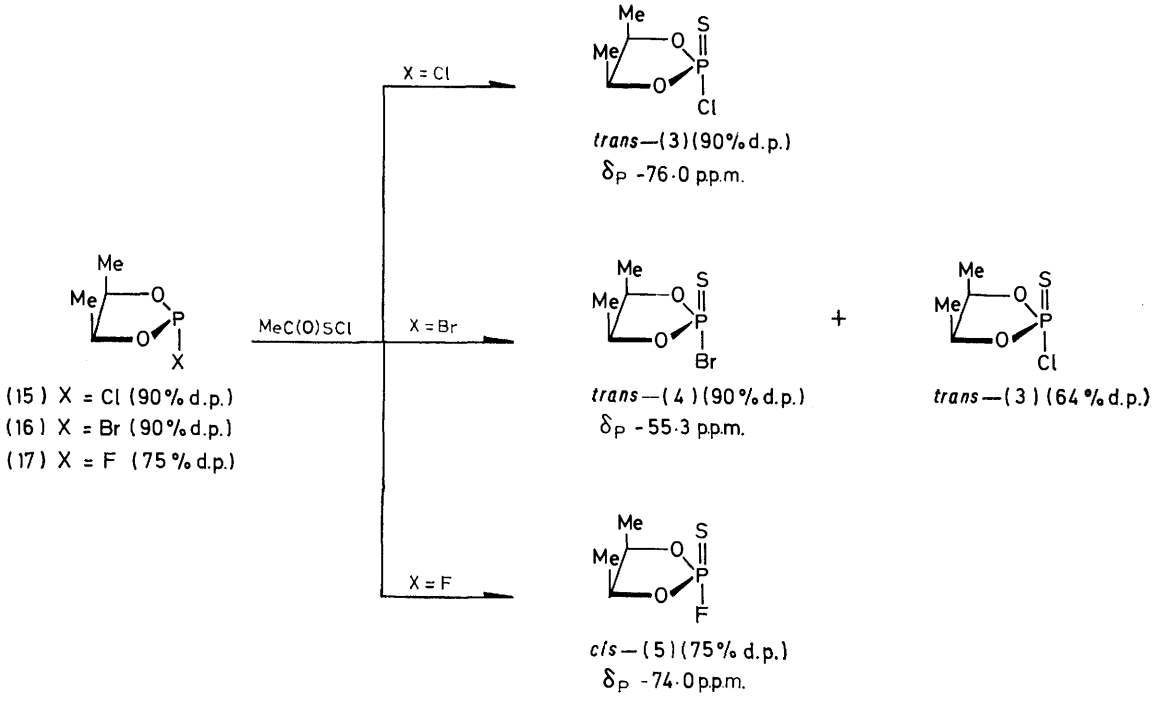
The reaction of the phosphorobromidite (16) with acetyl thiohypochlorite requires additional comment, since besides the expected bromide (4) it gave the chloride (3). This may be a consequence of bromide–chloride exchange at phosphorus at some stage in the reaction. It is probable that the bromophosphonium salt (18) first formed undergoes conversion into the chlorophosphonium salt (19) by direct nucleophilic attack of chloride anion at the phosphonium phosphorus, or, as in the case of other Arbuzov-type reactions,[9] *via* the pentaco-ordinate intermediates (20) and (21) (see Scheme 7). The latter route seems more probable, and the intervention of a pentaco-ordinate species serves to explain the loss of stereospecificity in the chloride (3) formed.

The chloride (3) may also be obtained by the treatment

TABLE 1

Salts of 4,5-disubstituted 2-hydroxy-1,3,2-dioxaphospholan-2-thiones (1) and (2)

Salt		M.p. (°C) (from PrOH–Et_2O)	Elemental analyses (%) Found:	Calc.:
(1), imidazole	*trans*	103—106	C, 35.8; H, 5.65; N, 11.55; P, 13.0	C, 35.59; H, 5.51; N, 11.86; P, 13.14 for $C_7H_{13}N_2O_3PS$
	cis	114—116	C, 35.7; H, 5.7; N, 11.5; P, 13.4	
	(±)	117—118	C, 35.8; H, 5.65; N, 11.75; P, 13.1	
(1)$^-$, NMe_4^+	*trans*	178—180	C, 40.15; H, 8.2; N, 5.8; P, 12.9	C, 39.83; H, 8.30; N, 5.81; P, 12.44 for $C_8H_{20}NO_3PS$
	cis	174—176	C, 40.2; H, 8.35; N, 5.9; P, 12.8	
	(±)	155—158	C, 40.15; H, 8.2; N, 5.85; P, 12.7	
(2)$^-$, NMe_4^+	*trans*	205—206	C, 58.95; H, 6.7; N, 3.5; P, 8.5	C, 59.18; H, 6.57; N, 3.84; P, 8.49 for $C_{18}H_{24}NO_3PS$
	cis	239—241	C, 58.7; H, 6.7; N, 4.0; P, 8.4	



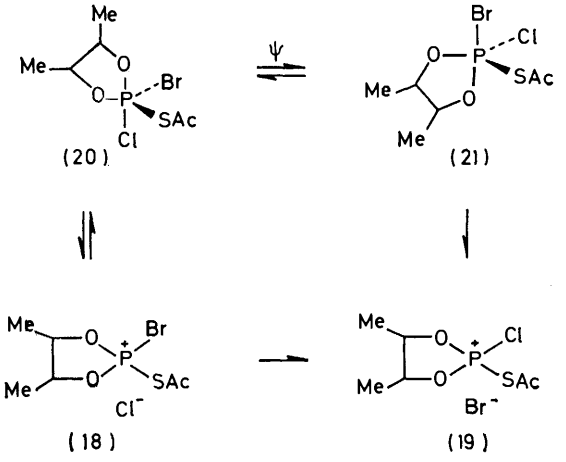
SCHEME 6

[7] M. Mikołajczyk, J. Krzywański, and B. Ziemnicka, *J. Org. Chem.*, 1977, **42**, 190.

[8] D. Gagnaire, J. B. Robert, and J. Verrier, *Bull. Soc. chim. France*, 1966, 3719.

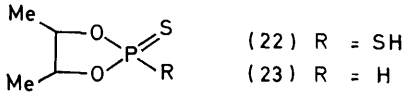
[9] A. Skowrońska, J. Mikołajczak, and J. Michalski, *J.C.S. Chem. Comm.*, 1975, 791, 986.

of 2-mercapto-4,5-dimethyl-1,3,2-dioxaphospholan-2-thione (22) with phosphorus pentachloride, by chlorination of 4,5-dimethyl-1,3,2-dioxaphospholan-2-thione (23)



SCHEME 7

with carbon tetrachloride–triethylamine, and by condensation of *meso*-butane-2,3-diol with thiophosphoryl chloride in the presence of pyridine. Samples of *trans*-(3)



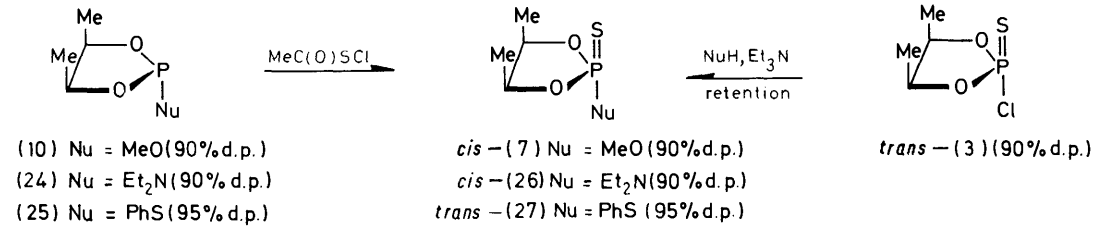
of 85, 65, and 40% diastereoisomeric purity were obtained, respectively.

Similarly, the bromide *cis*-(4), as a 90% diastereoisomerically pure sample, was prepared by bromination of 4,5-dimethyl-1,3,2-dioxaphospholan-2-thione (23).

from the experiments discussed above and shown in Scheme 2. Thus, 2-chloro-4,5-dimethyl-1,3,2-dioxaphospholan (15) gave on treatment with methanol, diethylamine, and benzenethiol in the presence of triethylamine the corresponding P^{III} compounds (10), (24), and (25) as diastereoisomeric mixtures with a great predominance of the more stable *trans*-isomers. Their reaction with acetyl thiohypochlorite afforded the thiophosphoryl derivatives *cis*-(7), *cis*-(26), and *trans*-(27), respectively. The fact that the reactions of *trans*-(3) with methanol,* diethylamine, and benzenethiol in the presence of triethylamine gave in a stereospecific manner the same products demonstrates that the replacement of chlorine by nucleophiles at phosphorus in (3) takes place with retention of configuration. Similarly, methanolysis of the bromide *cis*-(4) occurs stereospecifically with retention at phosphorus.

The best explanation of these results appears to be the intervention of a pentaco-ordinate intermediate during the nucleophilic substitution.[10] Attack of a nucleophile on the phosphorus atom in (3) from an apical position leads to the formation of the transient phosphorane (28), in which the five-membered ring spans apical and basal positions and the remaining basal positions are occupied by the sulphur and chlorine atoms. Taking into account the microscopic reversibility rule it is reasonable to assume that (28) undergoes permutational isomerisation as depicted in Scheme 9 to give a new phosphorane (29) with the chlorine atom in an apical position. Stabilisation of (29) by loss of chloride anion affords the substitution product with retained configuration at phosphorus.

In accord with this proposal is the observation that bromide–fluoride exchange at phosphorus in (4) proceeds



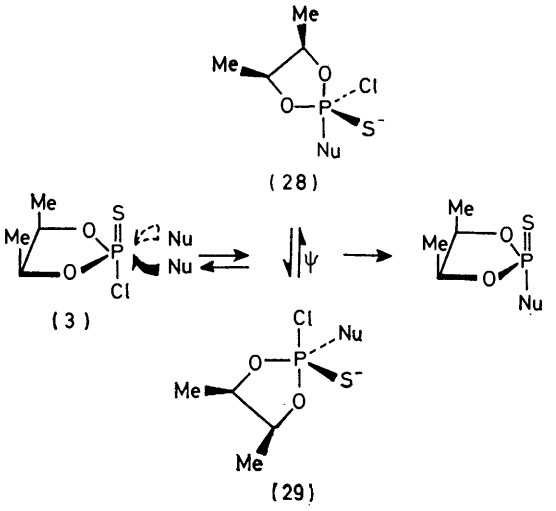
SCHEME 8

The availability of the halides (3)—(5), of known configuration and diastereoisomeric content, allowed us to study the stereochemistry of nucleophilic displacement at phosphorus. We investigated methanolysis, aminolysis, and mercaptolysis of the chloride *trans*-(3). However, in order to determine the steric course of these reactions it was first necessary to establish the configuration of the expected products, *i.e.* 2-methoxy-, 2-diethylamino-, and 2-phenylthio-4,5-dimethyl-1,3,2-dioxaphospholan-2-thione, (7), (26), and (27). The geometry of the diastereoisomeric thioesters (7) follows non-stereospecifically, and whatever the diastereoisomeric composition of (4) invariably leads to a mixture of *cis*-(5) and *trans*-(5) in the ratio 3 : 1 as a thermodynamically controlled product. It should be emphasized that the epimerisation at phosphorus during chloride–chloride exchange at phosphorus in (3) and bromide–bromide exchange at phosphorus in (4) does not take place under the comparable experimental conditions. This suggests that the stereomutation of the diastereoisomeric fluorides (5) in the presence of fluoride anion occurs *via* a phosphorane (30), formation of which is energetically favoured owing to the high nucleophilicity of the fluoride anion towards phosphorus and

* The reaction of sodium methoxide with *trans*-(3) has also been found to occur with retention at phosphorus, giving *cis*-(7). However, the simple substitution was accompanied by the formation of ring-opened products.

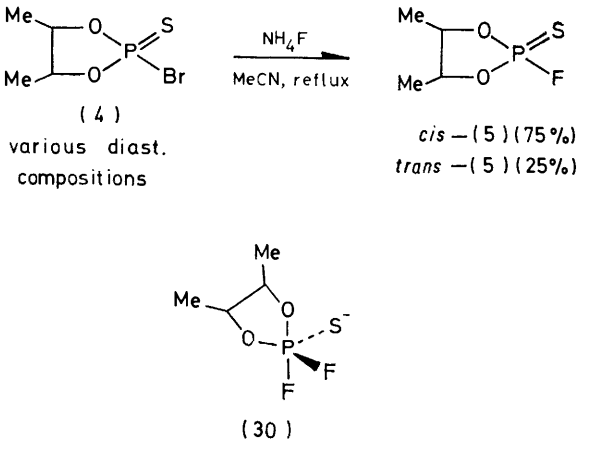
[10] S. Trippett, *Phosphorus and Sulphur*, 1976, **1**, 89.

to the well-known stabilising effect of the electronegative fluorine atoms on a pentaco-ordinate phosphorus species.[11]



SCHEME 9

The results show that there is a clear relationship between *cis–trans*-geometry of 4,5-disubstituted 1,3,2-dioxaphospholan-2-thiones and spectral parameters. In



SCHEME 10

Relationship between Geometry of 4,5-Disubstituted 1,3,2-Dioxaphospholan-2-thiones and Some Spectral Parameters.—In addition to ^{31}P n.m.r. spectroscopy, applied every case $^3J_{P,H}$ for the phospholans having the methyl groups *trans* to sulphur was greater than that for their isomers. Similarly, the ^{13}C n.m.r. coupling constant

TABLE 2

^{31}P and ^{13}C N.m.r. spectral parameters for 4,5-dimethyl(diphenyl)-1,3,2-dioxaphospholan-2-thiones

Compound		δ_P [b] ($^3J_{POCH}$) [c]	$\delta_{^{13}CH}$ [d] ($^2J_{^{13}CHP}$) [c]	$\delta_{^{13}CH_3}$ [d] ($^3J_{^{13}CHP}$) [c]	$\delta_{^{13}C}$ [d] (other) (J)
(1), imidazole	*cis* [a]	−68.52 (8.79)	82.60 (1.34)	19.70 (5.86)	138.31, 123.85 (C_{imid})
	trans	−68.60 (10.25)	81.95 (0.0)	19.89 (5.25)	
(1)$^-$, Me_4N^+	*cis*	−68.10 (8.75)	82.18 (1.27)	19.50 (5.80)	60.30 (MeN)
	trans	−68.20 (10.25)	82.63 (0.0)	19.73 (5.25)	
(2)$^-$, Me_4N^+	*cis*	−71.02 (6.25)	82.91 (0.0)		56.37 (MeN); 136.58, 129.17, 127.99, (Ph)
	trans	−68.84 (7.97)	82.91 (0.0)		
(3)	*trans*	−76.0 (8.6)	77.96 (2.38)	13.64 (7.57)	
	cis	−77.0 (14.4)	79.00 (1.46)	13.53 (4.94)	
(4)	*trans*	−55.3 (9.0)	78.01 (2.44)	13.89 (7.57)	
	cis	−53.3 (15.0)	79.27 (1.71)	13.64 (5.13)	
(5)	*cis*	−74.0 (8.4)	79.00 (1.83)	15.20 (6.84)	
	trans	−76.5 (13.0)	79.66 (1.65)	14.81 (4.40)	
(7)	*cis*	−80.5 (8.91)	78.66 (1.71)	15.53 (6.35)	55.37 (5.25), 55.90 (5.25) (MeO)
	trans	−83.0 (11.84)	78.66 (1.71)	15.46 (4.88)	
(8)	*cis*	−67.80 (9.0)	76.45 (0.0)	13.62 (7.52)	1.16 (1.64) (MeSi)
	trans	−69.5 (12.0)	76.45 (0.0)	13.52 (5.06)	
(12)	*cis*	−83.15 (7.32)	82.66 (0.0)		54.06 (2.44), 55.36 (1.89) (MeO)
	trans	−84.04 (9.23)	81.99 (0.0)		
(13)	*trans*	−56.6 (8.05)			
	cis	−56.2 (10.62)			
(14)	*cis*	−68.12 (7.20)	85.19 (2.56)		1.83 (1.87), 0.8 (MeSi); 129.46, 127.91, 135.06, 129.05 (Ph)
	trans	−68.68 (9.52)	84.63 (0.0)		
(27)	*trans*	−99.0 (9.6)	77.58 (3.05)	13.77 (5.13)	125.56—134.74 (Ph)
	cis	−101.0 (9.6)	76.80 (0.85)	12.74 (6.59)	

[a] The isomers of 1,3,2-dioxaphospholan-2-thiones having the methyl(phenyl) groups *cis* to sulphur are given in the first line. [b] ^{31}P N.m.r. spectra were obtained with a JEOL–JNM–FX60 Fourier transform spectrometer at 23.4 MHz for solutions in H_2O in the case of the salts of thioacids (1) and (2) and in deuteriated chloroform for other compounds. Chemical shifts are given in p.p.m. downfield from external 85% H_3PO_4. [c] Coupling constants in Hz. [d] ^{13}C N.m.r. spectra were obtained using a JEOL–JNM–FX60 spectrometer operating in the Fourier transform mode and chemical shifts are given in p.p.m. downfield from tetramethylsilane.

in the present work as a convenient tool for distinguishing the diastereoisomeric phospholans as well as for determining their diastereoisomeric purity, we recorded the ^{13}C n.m.r. spectra of the compounds obtained. Data are collected in Table 2.

values, $^2J_{C,P}$ and $^3J_{C,P}$, may be related to the ring geometry. In this case, however, both coupling constants are greater for the phospholans having the methyl

[11] See, for example, D. B. Denney, D. Z. Denney, and Y. F. Hsu, *Phosphorus*, 1974, **4**, 213.

groups *cis* to sulphur.* If examination of a greater number of examples shows this to be a general rule, the ^{13}C n.m.r. coupling constants as well as the $^{3}J_{P,H}$ values might allow rapid assignment of configuration to geometrical isomers of the 1,3,2-dioxaphospholans containing the pentavalent phosphorus atom. Similar observations on the relationship between the configuration of the 1,3,2-dioxaphospholans containing the trivalent phosphorus atom and ^{31}P and ^{13}C n.m.r. parameters have been reported recently.[12]

EXPERIMENTAL

^{1}H N.m.r. spectra were measured with a JEOL-JNM-60HL instrument (tetramethylsilane as internal standard). ^{31}P N.m.r. spectra were recorded with a JEOL-JNM-C-60HL spectrometer or a JEOL-JNM-FX60 Fourier transform spectrometer at 24.3 MHz, with 85% phosphoric acid as external standard. ^{13}C N.m.r. spectra were recorded with a JEOL-JNM-FX60 Fourier transform spectrometer with tetramethylsilane as internal standard. Diastereoisomeric purities were determined from integrated ^{1}H and ^{31}P n.m.r. spectra. All solvents used were purified according to standard procedures; tetrahydrofuran was distilled from lithium aluminium hydride.

(±)-4,5-*Dimethyl*-1,3,2-*dioxaphospholan*-2-*one* (6).—To a solution of (±)-2-chloro-4,5-dimethyl-1,3,2-dioxaphospholan [13] (1.55 g, 0.01 mol) in benzene, triethylamine (1.01 g, 0.01 mol), and then water (0.18 g, 0.01 mol) in tetrahydrofuran at +5° were added. The mixture was stirred at room temperature for 1 h, triethylammonium hydrochloride was filtered off, and the filtrate was evaporated. Distillation of the residue gave a pure *product* (±)-(6) (1.1 g, 80%), b.p. 60—63° at 0.05 mmHg, n_D^{20} 1.4380; δ_P −19.5 p.p.m.

Imidazolium Salt of (±)-2-*Hydroxy*-4,5-*dimethyl*-1,3,2-*dioxaphospholan*-2-*thione* (1).—To a mixture of the cyclic phosphonate (±)-(6) (2.72 g, 0.02 mol) and imidazole (1.36 g, 0.02 mol) dissolved in benzene, sulphur (0.64 g, 0.02 mol) was added. After 2 h the precipitated salt was filtered off and recrystallised from propan-1-ol–ether to afford the *salt* (2.0 g, 85%), m.p. 117—118°, $\delta_H(D_2O)$ 1.43 (6 H, d, $J_{CH_3,H}$ 6 Hz), 4.1—4.5 (2 H, m), 7.2 (2 H, s), and 8.4 (1 H, s); $\delta_P(H_3O)$ −68.12 p.p.m.

(±)-2-*Methoxy*-4,5-*dimethyl*-1,3,2-*dioxaphospholan*-2-*thione* (7).—To (±)-2-methoxy-4,5-dimethyl-1,3,2-dioxaphospholan (1.5 g, 0.01 mol) prepared from the corresponding phosphorochloridite and methanol in the presence of triethylamine, sulphur (0.32 g, 0.01 mol) was slowly added. Unchanged sulphur was then filtered off and the solution was heated at 30—40 °C under high vacuum to remove the rest of the starting phosphonate and to leave the *product* (1.6 g, 87%), n_D^{21} 1.4810, $\delta_H(D_2O)$ 1.37 (3 H, d), 1.40 (3 H, d, $J_{CH_3,H}$ 6 Hz), 3.80 (3 H, d), and 4.1—4.4 (2 H, m); δ_P(neat) −80.0 p.p.m.

Tetramethylammonium Salt of (±)-2-*Hydroxy*-4,5-*dimethyl*-1,3,2-*dioxaphospholan*-2-*thione* (1).—To a solution of the cyclic phosphorothioate (±)-(7) (1.8 g, 0.01 mol) in benzene (15 ml) an excess of trimethylamine (2 g) was added. After 48 h the precipitated *tetramethylammonium salt* was filtered off, washed with benzene, and crystallised from propan-1-ol–ether; yield 2.0 g (86%), m.p. 155—158°, $\delta_H(D_2O)$ 1.65 (6 H, d), 3.50 (12 H, s), and 4.40—4.65 (2 H, m); $\delta_P(H_2O)$ −67.31 p.p.m.

(±)-4,5-*Dimethyl*-2-*methylthio*-1,3,2-*dioxaphospholan*-2-*one* (8).—The reaction of the tetramethylammonium salt of (±)-(1) (2.41 g, 0.01 mol) with methyl iodide (2.41 g, 0.01 mol) in chloroform (20 ml) gave, after the usual work-up, the thioester (±)-(8) (0.9 g, 50%), b.p. 92—94° at 0.05 mmHg, n_D^{20} 1.4850 (Found: C, 33.2; H, 6.15; P, 17.5. $C_5H_{11}O_3PS$ requires C, 32.95; H, 6.05; P, 17.05%); $\delta_H(CDCl_3)$ 1.40 (3 H, d, $J_{CH_3,H}$ 6 Hz), 1.47 (3 H, d, $J_{CH_3,H}$ 6 Hz), 2.35 (3 H, d, $J_{CH_3S,P}$ 16 Hz), and 4.1—4.6 (2 H, m); $\delta_P(CHCl_3)$ −44.3 p.p.m

(±)-(-4,5-*Dimethyl*-2-*trimethylsilyloxy*-1,3,2-*dioxaphospholan*-2-*thione* (9).—To a solution of the tetramethylammonium salt of (±)-(1) (2.41 g, 0.01 mol) in chloroform (20 ml), trimethylsilyl chloride (1.1 g, 0.01 mol) was added at room temperature. The mixture was heated for 15 min at 50 °C and, after cooling, tetramethylammonium chloride was filtered off. After removal of solvent the residue was distilled to give a pure *product* (±)-(9) (1.7 g, 70%), b.p. 82—84° at 0.01 mmHg, n_D^{20} 1.4655 (Found: C, 35.25; H, 7.2; P, 13.2. $C_7H_{11}O_3PSSi$ requires C, 34.95; H, 7.1, P, 12.9%); $\delta_H(CCl_4)$ 0.35 (9 H, s), 1.37 (3 H, d, $J_{CH_3,H}$ 6 Hz), 1.42 (3 H, d, $J_{CH_3,H}$ 6 Hz), and 4.0—4.3 (2 H, m); δ_P(neat) −66.5 p.p.m.

meso-4,5-*Dimethyl*-1,3,2-*dioxaphospholan*-2-*one* (6).—To a solution of *meso*-2-chloro-4,5-dimethyl-1,3,2-dioxaphospholan [13] (1.55 g, 0.01 mol) in benzene, triethylamine (1.01 g, 0.01 mol) and water (0.18 g, 0.01 mol) in tetrahydrofuran at +5 °C were added. The mixture was stirred at room temperature for 1 h, triethylammonium hydrochloride was filtered off, and the filtrate was evaporated. Distillation of the residue gave a pure product, *meso*-(6) (1.1 g, 80%), b.p. 60—63° at 0.05 mmHg, n_D^{22} 1.4369; δ_P −19 (40%) and −20.5 p.p.m. (60%).

Imidazolium Salt of meso-2-*Hydroxy*-4,5-*dimethyl*-1,3,2-*dioxaphospholan*-2-*thione* (1).—To a solution of *meso*-(6) (2.72 g, 0.02 mol) prepared as above in benzene, imidazole (1.36 g, 0.02 mol), and then sulphur (0.64 g, 0.02 mol) were added. The mixture was stirred for 2 h. The precipitated imidazolium salt was filtered off (4.2 g, 93%), m.p. 87—98°. Fractional crystallisation from propan-1-ol–ether gave the diastereoisomerically pure *imidazolium salt* of *meso*, *cis*-(1), m.p. 114—116°; $\delta_H(D_2O)$ 1.35 (6 H, d, $J_{CH_3,H}$ 6 Hz), 4.4—5.1 (2 H, m), 7.6 (2 H, s), and 8.75 (1 H, s); $\delta_P(H_2O)$ −68.52 p.p.m.

cis-4,5-*Dimethyl*-2-*methylthio*-1,3,2-*dioxaphospholan*-2-*one* (8).—The reaction of the imidazolium salt of *cis*-(1) (2.36 g, 0.01 mol) with methyl iodide according to the procedure described for (±)-(4) gave the *ester cis*-(8) (0.8 g, 45%), b.p. 92—94° at 0.05 mmHg, n_D^{22} 1.4859 (Found: C, 33.1; H, 6.2; P, 17.5. $C_5H_{11}O_3PS$ requires C, 32.95; H, 6.05; P, 17.05%), $\delta_H(CDCl_3)$ 1.35 (6 H, d, $J_{CH_3,H}$ 6 Hz), 2.43 (3 H, d, $J_{CH_3S,P}$ 16 Hz), and 4.6—5.5 (2 H, m); δ_P(neat) −44.8 p.p.m.

cis-4,5-*Dimethyl*-2-*trimethylsilyloxy*-1,3,2-*dioxaphospholan*-2-*thione* (9).—Silylation of the imidazolium salt of *cis*-(1) (2.36 g, 0.01 mol) according to the procedure described for (±)-(9) yielded a pure *product* (1.7 g, 70%), b.p. 82—84° at 0.01 mmHg, n_D^{22} 1.4650 (Found: C, 35.25; H, 7.25; P, 13.5. $C_7H_{17}O_3PSSi$ requires C, 34.95; H, 7.1; P,

* The only exception was 2-diethylamino-4,5-dimethyl-1,3,2-dioxaphospholan-2-thione (26), where the opposite situation was observed. Thus, in *cis*-(26) $^{2}J_{^{13}CH,P}$ and $^{3}J_{^{13}CH_3,P}$ are 0.73 and 4.64 Hz, whereas in *trans*-(26) they are 0.98 and 7.08 Hz, respectively.

[12] W. G. Bentrude and H. W. Than, *J. Amer. Chem. Soc.*, 1976, **98**, 1850.

[13] A. Zwierzak, *Canad. J. Chem.*, 1967, 2501.

12.9%); $\delta_H(CCl_4)$ 0.27 (9 H, s), 1.31 (6 H, d, $J_{CH_3,H}$ 6 Hz), and 4.5—4.93 (2 H, m); δ_P(neat) −67.8 p.p.m.

Stereospecific Conversion of meso-2-*Methoxy*-4,5-*dimethyl*-1,3,2-*dioxaphospholan* (10) *into* meso-4,5-*Dimethyl*-2-*trimethylsilyloxy*-1,3,2-*dioxaphospholan*-2-*thione* (9).—To the phosphite (10) [2] (1.5 g, 0.01 mol) (90% *trans* and 10% *cis*), sulphur (0.32 g, 0.01 mol) was added. The mixture was heated at 60—70 °C for 1 h. After removal of small amounts of unchanged sulphur and unchanged phosphite (10) under high vacuum at 60 °C, meso-2-*methoxy*-4,5-*dimethyl*-1,3,2-*dioxaphospholan*-2-*thione* (7) (1.8 g, 95%) was obtained as a mixture of *cis*- and *trans*-isomers in the ratio 90 : 10, n_D^{25} 1.4860 (Found: C, 35.75; H, 6.0; P, 16.95. $C_5H_{11}O_3PS$ requires C, 32.95; H, 6.05; P, 17.05%); $\delta_H(CDCl_3)$ 1.35 (6 H, d, $J_{CH_3,H}$ 6 Hz), 3.75 (3 H, d, $J_{CH_3,OP}$ 15 Hz), 3.80 (3 H_{cis}, d, $J_{CH_3O,P}$ 15 Hz), and 4.25—5.0 (2 H, m); δ_P(neat) −80.5 for *cis*-(7) and −83.0 p.p.m. for *trans*-(7).

To a solution of *meso*-(7) (1.82 g, 0.01 mol), prepared as above, in benzene, trimethylamine (2 g) was added. The mixture was left for 48 h and the precipitated *tetramethylammonium salt* of *meso*-(1) was filtered off, washed with benzene, and dried; yield 2.0 g (83%), m.p. 157—167 °C.

This salt (2.41 g, 0.01 mol) was silylated with trimethylsilyl chloride (1.10 g, 0.01 mol) to give meso-4,5-*dimethyl*-2-*trimethylsilyloxy*-1,3,2-*dioxaphospholan*-2-*thione* (9) as a mixture of *cis*-(9) (90%) and *trans*-(9) (10%) (1.7 g, 71%), b.p. 80—81° at 0.01 mmHg, n_D^{22} 1.4650 (Found: C, 35.2; H, 7.25; P, 13.15. $C_7H_{17}O_3PSSi$ requires C, 34.95; H, 7.1; P, 12.9%); δ_P(neat) −67.8 for *cis*-(9) and −69.5 p.p.m. for *trans*-(9).

cis-2-*Bromo*-4,5-*dimethyl*-1,3,2-*dioxaphospholan*-2-*thione* (4).—To a solution of thiophosphoryl bromide (6.16 g, 0.02 mol) and pyridine (3.16 g, 0.04 mol) in benzene (100 ml), butane-2,3-diol (1.8 g, 0.02 mol) was added at 42 °C. The mixture was stirred at this temperature for an additional 2 h. The precipitated pyridinium bromide was filtered off and the solvent removed. The crude residue was distilled to afford the bromide (4) (3.0 g, 65%), b.p. 80—82° at 0.4 mmHg, as a mixture of *cis*-(4) (75%) and *trans*-(4) (25%) (g.l.c.). This mixture, which solidified, was crystallised from petroleum–benzene to give the pure *cis*-(4), m.p. 56—58°, $\delta_P(C_6H_6)$ −53.3 p.p.m.

trans-2-*Methoxy*-4,5-*dimethyl*-1,3,2-*dioxaphospholan*-2-*thione* (7).—To a solution of methanol (0.32 g, 0.01 mol) and triethylamine (1.01 g, 0.01 mol) in acetonitrile (10 ml), a solution of the bromide *cis*-(7), m.p. 56—58 °C (2.3 g, 0.01 mol), in acetonitrile (5 ml) was added at 25 °C. The mixture was then stirred for an additional 1 h and triethylammonium bromide was filtered off. Evaporation gave the diastereoisomerically pure *ester cis*-(7); $\delta_H(CDCl_3)$ 1.35 (6 H, d, $J_{CH_3,H}$ 6 Hz), 3.8 (3 H, d, $J_{CH_3O,P}$ 15 Hz), and 4.53—5.0 (2 H, m); $\delta_P(CDCl_3)$ −83.0 p.p.m.

Tetramethylammonium Salt of trans-2-*Hydroxy*-4,5-*dimethyl*-1,3,2-*dioxaphospholan*-2-*thione* (1).—To the ester (1.8 g, 0.01 mol) *trans*-(7) prepared as above in benzene (15 ml), trimethylamine (2 g) was added. The precipitated salt was filtered off, washed with benzene, and recrystallised from propan-1-ol–ether; yield 1.7 g (70%), m.p. 178—180°, $\delta_H(D_2O)$ 1.52 (6 H, d, $J_{CH_3,H}$ 6 Hz), 4.6—5.2 (2 H, m), and 3.5 (12 H, s); $\delta_P(H_2O)$ −68.2 p.p.m. Treatment of an aqueous solution of *trans*-(1) with Amberlite 120 IR resin and the eluate with imidazole yielded the corresponding imidazolium salt of *trans*-(1), m.p. 103—106°.

trans-4,5-*Dimethyl*-2-*trimethylsilyloxy*-1,3,2-*dioxaphospholan*-2-*thione* (9).—Silylation of the above salt gave the diastereoisomerically pure *trans*-(9), b.p. 82—84° at 0.01 mmHg, n_D^{22} 1.4652, δ_P(neat) −69.5 p.p.m.

cis-2-*Methoxy*-4,5-*diphenyl*-1,3,2-*dioxaphospholan*-2-*thione* (12).—Into a solution of *trans*-2-methoxy-4,5-diphenyl-1,3,2-dioxaphospholan (11) [4] (2.74 g, 0.01 mol) in methylene chloride (5 ml) acetyl thiohypochlorite (1.1 g, 0.01 mol) was dropped at −20 °C. The mixture was then stirred for 0.5 h, and evaporated, and the crude product was crystallised from diethyl ether–petroleum at −70 °C affording the pure *trans*-(12) (2.1 g, 70%), m.p. 93—97° (Found: C, 59.0; H, 4.9; P, 10.0. $C_{15}H_{15}O_3PS$ requires C, 58.8; H, 4.9; P, 10.15%); $\delta_H(CDCl_3)$ 3.82 (3 H, d, $J_{CH_3O,P}$ 14.65 Hz), 5.75 (2 H, d), and 6.98 (10 H, s); $\delta_P(CDCl_3)$ −83.15 p.p.m.

Tetramethylammonium Salt of cis-2-*Hydroxy*-4,5-*diphenyl*-1,3,2-*dioxaphospholan*-2-*thione* (2).—The cyclic phosphorothioate *cis*-(12) (3.1 g, 0.01 mol) gave after reaction with an excess of trimethylamine (2.4 g, 0.04 mol) the desired salt of *cis*-(2) (2.2 g, 60%), m.p. 239—241°; $\delta_H(D_2O)$ 3.45 (12 H, s), 6.38 (2 H, d), and 7.53 (10 H, s); $\delta_P(D_2O)$ −71.02 p.p.m.

meso-2-*Bromo*-4,5-*diphenyl*-1,3,2-*dioxaphospholan*-2-*thione* (13).—To a mixture of thiophosphoryl bromide (3.1 g, 0.01 mol) and pyridine (1.6 g, 0.02 mol) in benzene (30 ml), 1,2-diphenylethane-1,2-diol (2.7 g, 0.01 mol) was added in portions. The temperature was maintained between 40—45 °C. The mixture was then stirred at this temperature for an additional 2 h. The precipitated pyridinium bromide was filtered off and benzene was removed. The residue (3.4 g) consisted of *cis*- and *trans*-(13) in the ratio 80 : 20 (by ^{31}P n.m.r); $\delta_P(CDCl_3)$ −56.2 for *cis*-(13) and −56.6 p.p.m. for *trans*-(13).

trans-2-*Methoxy*-4,5-*diphenyl*-1,3,2-*dioxaphospholan*-2-*thione* (12).—The mixture of diastereoisomeric bromides (13) prepared as above was treated with methanol (0.32 g, 0.01 mol) and triethylamine (1.01 g, 0.01 mol) in acetonitrile (10 ml) at room temperature. The usual work-up gave the crude *ester* (12) as a mixture of *trans*- and *cis*-isomers in the ratio 80 : 20. Column chromatography (silica gel 100—200 mesh ASTM; benzene) afforded the pure ester (12), from which after crystallisation from carbon tetrachloride the pure *trans*-(12) (0.9 g, 30%) was obtained; m.p. 103—105° (Found: C, 59.15; H, 5.05; P, 9.8. $C_{15}H_{15}O_3PS$ requires C, 58.8; H, 4.9; P, 10.15%); $\delta_H(CDCl_3)$ 4.06 (3 H, d, $J_{CH_3O,P}$ 15.4 Hz), 5.93 (2 H, d), and 7.09 (10 H, s); $\delta_P(CDCl_3)$ −84.04 p.p.m.

Tetramethylammonium Salt of trans-2-*Hydroxy*-4,5-*diphenyl*-1,3,2-*dioxaphospholan*-2-*thione* (8).—To a solution of trans-(12) (1.53 g, 0.005 mol) in benzene (10 ml), trimethylamine (1 g) was added. After 48 h the *salt* was filtered off and crystallised from propan-1-ol–ether; yield 1.3 g (69%), m.p. 205—206°, $\delta_H(D_2O)$ 3.55 (12 H, s), 6.3 (2 H, d), and 7.57 (10 H, s); $\delta_P(D_2O)$ −68.84 p.p.m.

trans-4,5-*Diphenyl*-2-*trimethylsilyloxy*-1,3,2-*dioxaphospholan*-2-*thione* (14).—Silylation of the tetramethylammonium salt of *trans*-(2) (0.36 g, 0.001 mol) as described for (±)-(8) yielded the *product* trans-(14) (0.36 g, 100%) (Found: C, 56.05; H, 6.05; P, 8.55. $C_{17}H_{21}O_3PSSi$ requires C, 5.605; H, 5.75; P, 8.5%); $\delta_H(CDCl_3)$ 0.4 (9 H, s), 5.80 (2 H, d), and 7.05 (10 H, s); $\delta_P(CDCl_3)$ −68.86 p.p.m.

cis-4,5-*Diphenyl*-2-*trimethylsilyloxy*-1,3,2-*dioxaphospholan*-2-*thione* (14).—Silylation of the tetramethylammonium salt of *cis*-(2) (0.36 g, 0.001 mol) carried out as above yielded the *product* cis-(14) (0.36 g, 100%), m.p. 119—121 °C (Found: C, 56.1; H, 6.0; P, 8.6. $C_{17}H_{21}O_3$-

PSSi requires C, 56.05; H, 5.75; P, 8.5%); $\delta_H(CDCl_3)$ 0.4 (9 H, s), 5.87 (2 H, d), and 7.05 (10 H, s); $\delta_P(CDCl_3)$ −68.12 p.p.m.

meso-2-*Chloro*-4,5-*dimethyl*-1,3,2-*dioxaphospholan*-2-*thione* (3).—(*a*) To an ethereal solution of the phosphorochloridite (15) [13] (1.5 g, 0.01 mol) consisting of 90% *trans*- and 10% *cis*-(15), acetyl thiohypochlorite (1.1 g, 0.01 mol) was added at −20 °C. The ether was evaporated off and the residue was distilled to give the *meso*-chloride (3) (1.7 g, 90%), b.p. 78—81° at 2 mmHg, n_D^{19} 1.5046 (Found: C, 25.45; H, 4.2; P, 16.4. $C_4H_8ClO_2PS$ requires C, 25.75; H, 4.3; P, 16.6%), consisting of *trans*- and *cis*-(3) in the ratio 9 : 1; *trans*-(3): $\delta_H(CDCl_3)$ 1.42 (6 H, d, $J_{CH_3,H}$ 6 Hz), and 4.55—5.25 (2 H, m); δ_P(neat) −76 p.p.m. ($J_{P,CH}$ 8.6 Hz); *cis*-(3): δ_H 1.46 (6 H, d, $J_{CH_3,H}$ 6 Hz), 4.55—5.25 (2 H, m); δ_P(neat) −77 p.p.m. ($J_{P,CH}$ 14.4 Hz).

(*b*) A mixture of *meso*-butane-2,3-diol (4.5 g, 0.05 mol) and phosphorus pentasulphide (5.6 g, 0.025 mol) in benzene (50 ml) was refluxed until the phosphorus pentasulphide had disappeared. The resulting benzene solution of 2-mercapto-4,5-dimethyl-1,3,2-dioxaphospholan-2-thione (22) was added to a suspension of phosphorus pentachloride (10.5 g, 0.05 mol) in benzene. The mixture was stirred at 40—50 °C for 1 h. The usual work-up gave the *meso*-chloride (3) (6.5 g, 70%) as a mixture of *trans*- and *cis*-isomers in the ratio 85 : 15, respectively, b.p. 76—78° at 1.5 mmHg, n_D^{25} 1.5035.

(*c*) To a mixture of carbon tetrachloride (1.7 g) and triethylamine (0.1 g, 0.001 mol), 4,5-dimethyl-1,3,2-dioxaphospholan-2-thione (23) (1.52 g, 0.01 mol) was added below 60 °C. Work-up gave *meso*-(3) (1.7 g, 91%) as a mixture of 35% of *cis*- and 65% of *trans*-(3), b.p. 70—73° at 2 mmHg, n_D^{25} 1.5040.

(*d*) To a solution of thiophosphoryl chloride (16.9 g, 0.1 mol) and pyridine (15.8 g, 0.2 mol) in benzene (100 ml), *meso*-butane-2,3-diol (9.0 g, 0.1 mol) was added at 38—40 °C. The mixture was stirred at this temperature for 2 h and worked up as usual. The product, *meso*-(3) (9.5 g, 50%), was obtained as a 3 : 2 mixture of *cis*- and *trans*-isomers, b.p. 70—75° at 2 mmHg, n_D^{21} 1.5080.

meso-2-*Bromo*-4,5-*dimethyl*-1,3,2-*dioxaphospholan*-2-*thione* (4).—To a solution of the thiophosphonate (23) (1.52 g, 0.01 mol) and pyridine (0.8 g, 0.01 mol) in methylene chloride (20 ml), a solution of bromine (1.59 g, 0.01 mol) in methylene chloride was added at 20 °C. After stirring for 2 h pyridinium bromide was filtered off and the solution evaporated. The residue was distilled to give the *meso*-*bromide* (4) (1.6 g, 70%), which consisted of 20% *cis*- and 80% *trans*-(4) (g.l.c.); b.p. 68—72° at 0.1 mmHg, n_D^{21} 1.5403 (Found: C, 21.05; H, 3.6; P, 13.75. $C_4H_8BrO_2PS$ requires C, 20.8; H, 3.45; P, 13.4%); *cis*-(4): $\delta_H(CDCl_3)$ 1.5 (6 H, d, $J_{CH_3,H}$ 6 Hz) and 4.6—5.3 (2 H, m); δ_P(neat) −53.3 p.p.m. ($J_{P,CH}$ 15.0 Hz); *trans*-(4): $\delta_H(CDCl_3)$ 1.45 (6 H, d, $J_{CH_3,H}$ 6 Hz) and 4.6—5.3 (2 H, m); δ_P(neat) −55.3 p.p.m. ($J_{P,CH}$ 9.0 Hz).

Reaction of the meso-*Bromide* (16) *with Acetyl Thiohypochlorite.*—The phosphorobromidite (16) [14] (1.45 g, 0.0073 mol) was dissolved in methylene chloride (5 ml) and treated at −30 °C with a solution of acetyl thiohypochlorite (0.8 g, 0.0073 mol) in methylene chloride (5 ml). The mixture was stirred for 0.5 h at room temperature. Distillation gave the product (1.6 g, 96%), b.p. 60—65° at 1.5 mmHg, shown by ^{31}P n.m.r. to consist of 65% of the *trans*-bromide (4), having 90% diastereoisomeric purity, and 35% of the *trans*-chloride (3), having 64% diastereoisomeric purity.

Reaction of the meso-*Fluoride* (17) *with Acetyl Thiohypochlorite.*—To a solution of the phosphorofluoridite (17) [15] (2.76 g, 0.02 mol) in methylene chloride (10 ml), a solution of acetyl thiohypochlorite (2.2 g, 0.02 mol) in methylene chloride (5 ml) was added at −20 °C. After stirring the mixture for 0.5 h at room temperature 2-fluoro-4,5-dimethyl-1,3,2-dioxaphospholan-2-thione (5) was isolated by distillation; yield 3.2 g (94%), b.p. 56—60° at 2 mmHg (Found: C, 28.0; H, 4.6; P, 18.15. $C_4H_8FO_2PS$ requires C, 28.25; H, 4.7; P, 18.25%), consisting of 75% *cis*-(5), δ_P −74, and 25% *trans*-(5), δ_P −76.5 p.p.m. ($J_{P,F}$ 1184 Hz).

Reaction of the trans-*Phosphorochloridite* (15) *with Diethylamine.*—To a solution of *trans*-(15) (1.5 g, 0.01 mol) (90% diastereoisomerically pure) in ether, a solution of diethylamine (1.46 g, 0.02 mol) in ether was slowly added at 10 °C. After 1 h ammonium chloride was filtered off, solvent removed, and the residue distilled to afford 2-*diethylamino*-4,5-*dimethyl*-1,3,2-*dioxaphospholan* (24) having 90% diastereoisomeric purity (^{31}P n.m.r.) (1.2 g, 70%), b.p. 60—62° at 2 mmHg, n_D^{26} 1.4602 (Found: C, 50.3; H, 8.4; N, 7.35; P, 16.25. $C_8H_{18}NO_2P$ requires C, 50.25; H, 8.4; N, 7.5; P, 16.35%); $\delta_H(CDCl_3)$ 1.05 (6 H, t, NCH_2CH_3), 1.10 (6 H, d, CCH_3), 2.7—3.3 (4 H, m, NCH_2), and 4.1—4.6 (2 H, m, CCH); δ_P(neat) −143.0 for *trans*-(24) and −152 p.p.m. for *cis*-(24).

Reaction of the trans-*Phosphorochloridite* (15) *with Benzenethiol.*—To a solution of benzenethiol (1.1 g, 0.01 mol) and triethylamine (1.01 g, 0.01 mol) in benzene, the phosphochloridite (15) (1.55 g, 0.01 mol) was added at 5 °C. The mixture was stirred for 2 h. The usual work-up gave the crude 2-*phenylthio*-4,5-*dimethyl*-1,3,2-*dioxaphospholan* (25), which was isolated by distillation (1.5 g, 65%), b.p. 80—84° at 0.05 mmHg, n_D^{19} 1.5726. The pure product has been found by ^{31}P n.m.r. to be a mixture of *trans*-(25) (90%) and *cis*-(25) (10%) (Found: C, 52.35; H, 5.85; P, 14.1. $C_{10}H_{13}O_2PS$ requires C, 52.65; H, 5.7; P, 13.6%); δ_P(neat) −195.5 for *trans*-(25) and −206.8 p.p.m. for *cis*-(25).

Reaction of the trans-*Phosphoramidite* (24) *with Acetyl Thiohypochlorite.*—The *trans*-phosphoramidite (24) (1.62 g, 0.01 mol) having 90% diastereoisomeric purity was treated in ether with an equimolar amount of acetyl thiohypochlorite (1.10 g, 0.01 mol) at −20 °C. Removal of ether and distillation gave 2-*diethylamino*-4,5-*dimethyl*-1,3,2-*dioxaphospholan*-2-*thione* (26) consisting of 90% of *cis*-(26) and 10% of *trans*-(26) (g.l.c.) (1.90 g, 98%), b.p. 71—76° at 0.01 mmHg, n_D^{26} 1.4941 (Found: C, 43.0; H, 8.05; P, 14.05; N, 6.55. $C_8H_{18}NO_2PS$ requires C, 43.05; H, 8.05; P, 13.9; N, 6.3%), $\delta_H(CDCl_3)$ 1.1 (6 H, t, NCH_2CH_3), 1.38 (6 H, d, CCH_3), 3.17 (4 H, m, NCH_2), and 4.28—4.95 (2 H, m, CCH); δ_P(neat) −84 p.p.m.

Reaction of the trans-*Phenyl Thiophosphite* (25) *with Acetyl Thiohypochlorite.*—Into a solution of the *trans*-ester (25) (2.3 g, 0.01 mol) having 90% diastereoisomeric purity in methylene chloride, a solution of acetyl thiohypochlorite (1.10 g, 0.01 mol) in methylene chloride was dropped at −20 °C. The mixture was stirred for 2 h and evaporated. Distillation gave 4,5-*dimethyl*-2-*phenylthio*-1,3,2-*dioxaphospholan*-2-*thione* (27) containing 80% of the *trans*-isomer; yield 2.4 g (91%), b.p. 115—120° at 0.2 mmHg, n_D^{19} 1.5813 (Found: C, 46.45; H, 5.15; P, 11.85. $C_{10}H_{13}O_2PS_2$ requires C, 46.15; H, 5.0; P, 11.9%); $\delta_H(CDCl_3)$ 1.18 and

[14] A. Kh. Voznesenskaya and N. A. Razumova, *Zhur. obshchei Khim.*, 1969, 39(2), 387.

[15] N. A. Razumova, Zh. L. Evitkov, and A. A. Petrov, *Zhur. obshchei Khim.*, 1968, 38(5), 1117.

0.85 (6 H, d, $J_{CH_3,H}$ 6 Hz), 4.50—4.75 (2 H, m), and 7.25—7.5 (5 H, m); δ_P(neat) −99 for *trans*-(27) and −101 p.p.m. for *cis*-(27).

Methanolysis of the trans-*Chloride* (3).—To an ethereal solution of methanol (0.33 g, 0.01 mol) and triethylamine (1.01 g, 0.01 mol), the *trans*-chloride (3) (1.87 g, 0.01 mol) (90% diastereoisomerically pure) was added dropwise at −5 to 0 °C. The mixture was stirred for 1 h and then the precipitated triethylammonium chloride was filtered off. After removal of ether the residue was heated at 30—40 °C under high vacuum to remove the rest of the substrates. The methoxy-ester (7) obtained in this manner was found to be a mixture of *cis*-(7) (90%) and *trans*-(7) (10%) (by ^{31}P n.m.r.).

Starting from the chloride (3) consisting of 35% *cis*-(3) and 65% *trans*-(3) a mixture of *trans*- and *cis*-(7) was obtained in the same ratio (35 : 65).

Aminolysis of the trans-*Chloride* (3).—To a solution of a 90% diastereoisomerically pure sample of *trans*-(3) (2.8 g, 0.015 mol) in ether a solution of diethylamine (2.19 g, 0.03 mol) in ether was added at +5 to 10 °C. Stirring was continued for 1 h and diethylammonium chloride was filtered off. Removal of ether and distillation gave *2-diethylamino-4,5-dimethyl-1,3,2-dioxaphospholan-3-thione* (26) (2.7 g, 80%), b.p. 71—76° at 0.01 mmHg, n_D^{26} 1.4906. G.l.c. revealed that the amide (26) obtained is a mixture of *cis*- and *trans*-(26) in the ratio 9 : 1.

Mercaptolysis of the trans-*Chloride* (3).—A mixture of benzenethiol (1.10 g, 0.01 mol) and triethylamine (1.01 g, 0.01 mol) in acetonitrile was treated at room temperature with the *trans*-chloride (3) (1.87 g, 0.01 mol) which was 90% diastereoisomerically pure. The mixture was stirred for 15 min and the precipitated triethylammonium chloride was filtered off. Evaporation afforded 4,5-dimethyl-2-phenylthio-1,3,2-dioxaphospholan-2-thione (27) consisting of 90% of *trans*- and 10% of *cis*-(27) and some of the starting chloride (3).

The reaction of the chloride (3) containing 60% of *cis*- and 40% of *trans*-(3) with benzenethiol gave the corresponding mixture of *cis*- and *trans*-(27) in the same ratio (60 : 40).

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