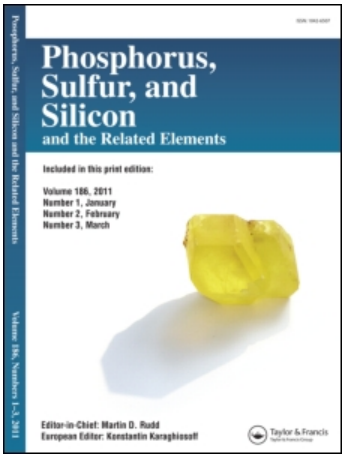

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STEREOCHEMISTRY OF CYCLIC ORGANOPHOSPHORUS COMPOUNDS-XVI.[1] SYNTHESIS AND THE CRYSTAL AND MOLECULAR STRUCTURE OF *meso*-BIS-(4,6-DIMETHYL-2-THIO-1,3,2-DIOXAPHOSPHORINANE-2-YL)-OXIDE DERIVED FROM RACEMIC PENTANE-2,4-DIOL

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STEREOCHEMISTRY OF CYCLIC ORGANOPHOSPHORUS COMPOUNDS—XVI.[1] SYNTHESIS AND THE CRYSTAL AND MOLECULAR STRUCTURE OF *meso*-BIS-(4,6-DIMETHYL-2-THIO-1,3,2-DIOXAPHOSPHORINANE-2-YL)-OXIDE DERIVED FROM RACEMIC PENTANE-2,4-DIOL

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4,6-Dimethyl-2-chloro-1,3,2-dioxaphosphorinane-2-thione **5** and the tetramethylammonium salt of 4,6-dimethyl-2-oxo-1,3,2-dioxaphosphorinane-2-thione **4** were prepared from racemic pentane-2,4-diol. Their condensation was found to give a mixture of two diastereoisomeric bis-(4,6-dimethyl-2-thio-1,3,2-dioxaphosphorinane-2-yl)-oxides **3C**: racemic and *meso*-form. The crystal structure of the latter has been determined by the direct method and refined by least-squares to $R = 0.072$, monoclinic space group $P2_1/n$, a = 13.542(3), b = 11.175(1), c = 10.731(2)Å, $\beta = 94.81(1)°$. Both dioxaphosphorinane rings adopt chair conformations flattened at phosphorus and the carbon atom C(5). The thiophosphoryl sulphur atoms are in equatorial positions whereas the bridging oxygen atom is axial. Two methyl groups on C(4) and C(6) in each dioxaphosphorinane ring occupy an axial and equatorial position, respectively.

Recently, we have been interested in the stereochemistry and conformation of the bicylic dithiopyrophosphates derived from butane-1,3-diol and pentane-2,4-diol. The dithiopyrophosphate **1** obtained from butane-1,3-diol contains four chiral centres and it was shown to exist in six diastereoisomeric forms. Their solution and solid state conformations were elucidated by NMR, IR and X-ray crystallography.[2]

Although the dithiopyrophosphate **2** prepared from *meso*-pentane-2,4-diol has six chiral centres, it represents stereochemically simpler system. Of three possible diastereoisomers of **2**, two were prepared and analyzed by X-ray method.[3] In this paper we would like to report the results of X-ray analysis of the dithiopyrophosphate **3** derived from racemic pentane-2,4-diol.

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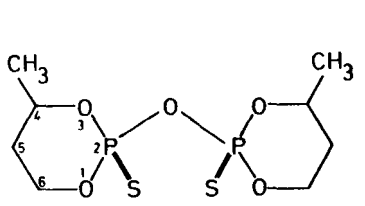
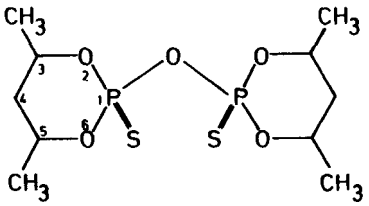


(1)



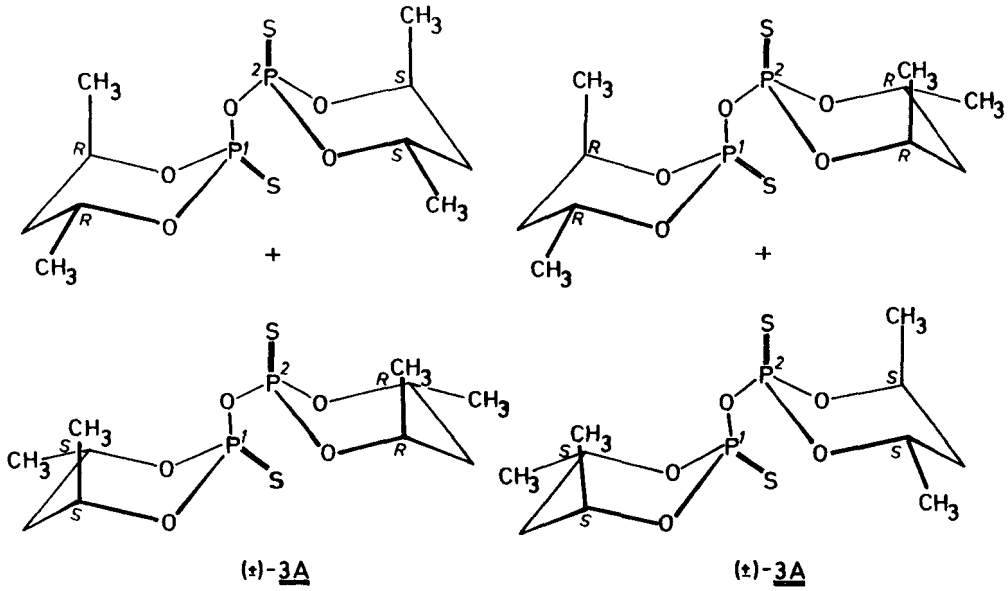
(2) (from meso-pentan-2,4-diol)

(3) (from rac.pentan-2,4-diol)

RESULTS AND DISCUSSION

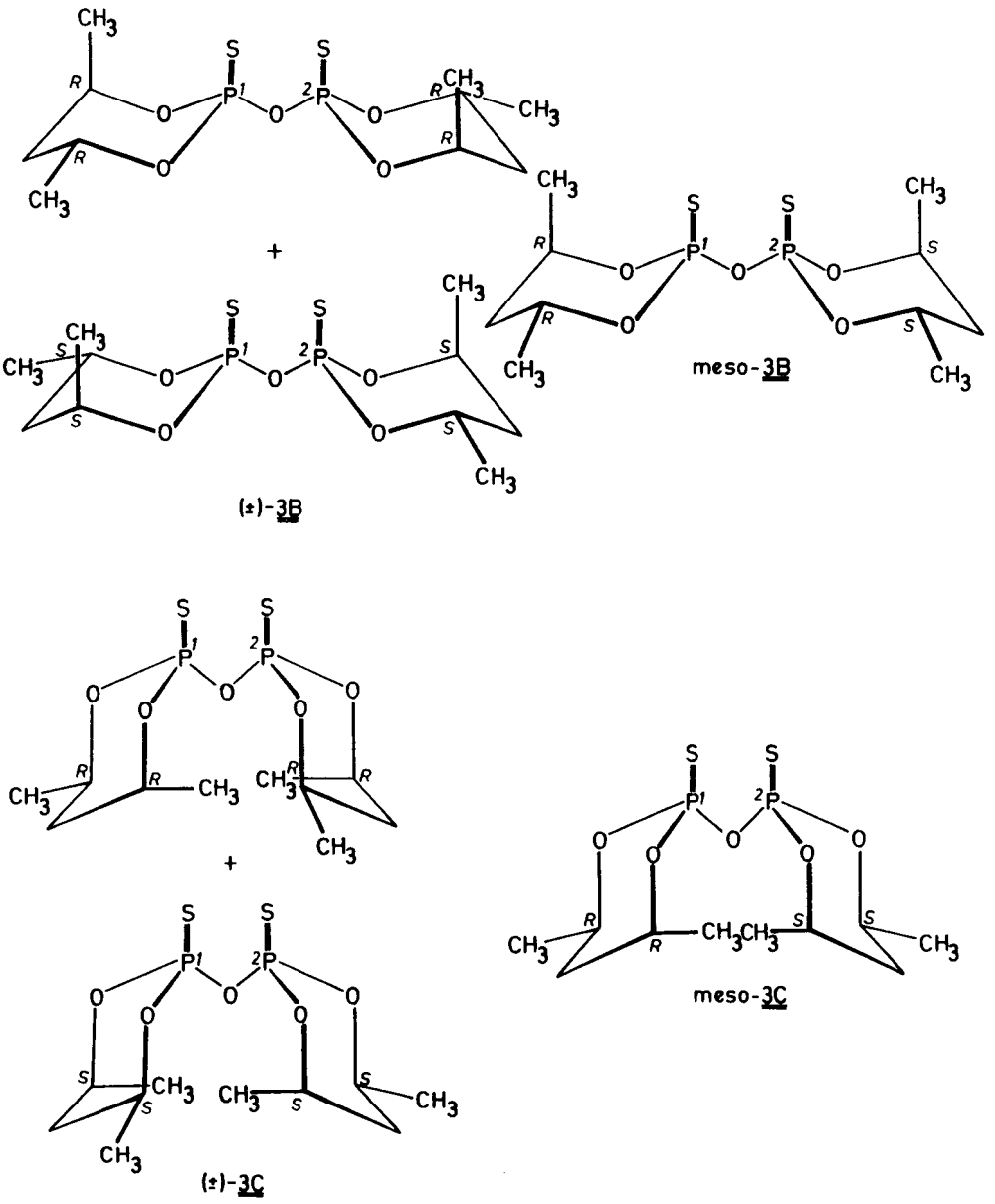
Theoretically, the dithiopyrophosphate **3** may be considered to exist in three isomeric forms **3A**, **3B** and **3C** having a different geometry of the P(S)OP(S) bridge. The unsymmetrical form, **3A**, in which the phosphorus atoms P(1) and P(2) are nonequivalent, may consist, in turn, of four enantiomers forming two racemic pairs. Two symmetrical isomers **3B** and **3C** with the equivalent phosphorus atoms, P(1) and P(2) may exist as mixtures of the racemic and *meso* forms. Scheme 1 shows all the possible enantiomeric and diastereoisomeric forms of the dithiopyrophosphate **3**.

However, in contrast to the conformationally rigid 4,6-dimethyl-1,3,2-dioxaphosphorinane ring derived from meso-pentane-2,4-diol, the analogous six-mem-



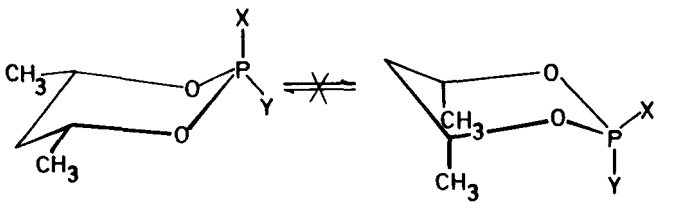
(±)-3A (±)-3A

SCHEME 1 Enantiomeric and diastereoisomeric conformers of dithiopyrophosphate (3).

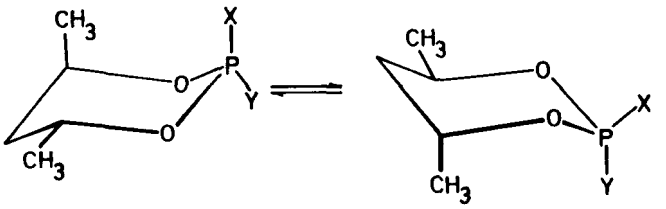


SCHEME 1 (*Continued*).

bered ring derived from racemic diol may easily undergo ring inversion which should cause a change in the configurational relationship at both phosphorus atoms. In this particular system, the fast conformational flipping of one or two 4,6-dimethyl-1,3,2-dioxaphosphorinane rings should lead to **3A** ⇌ **3B** ⇌ **3C** interconversion. If this were the case, one could expect that the thermodynamically more stable conformers of **3** will be formed.



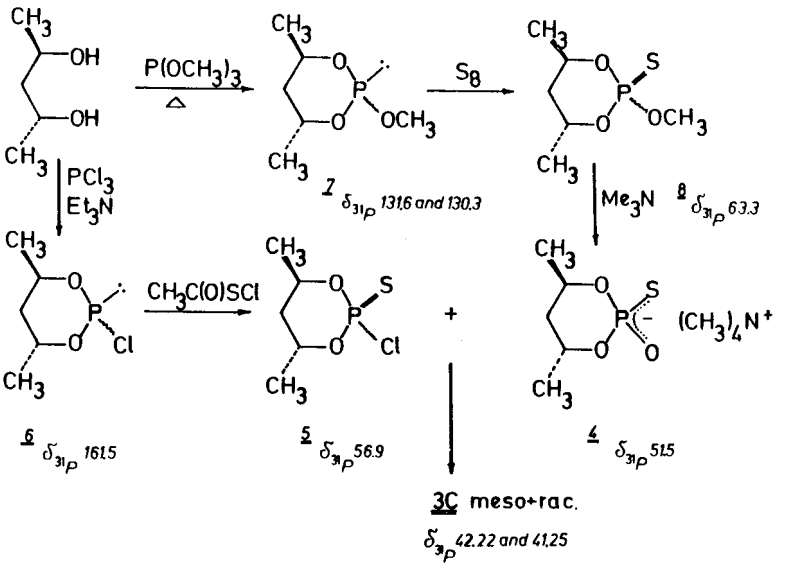
A



B

In accord with our previous studies on the synthesis of **1** and **2**, the dithiopyrophosphate **3** was prepared by condensation of the tetramethylammonium salt of the cyclic thioacid **4** and chloride **5** in acetonitrile solution. Their synthesis was accomplished as shown in Scheme 2. Thus, reaction of phosphorus trichloride with racemic pentane-2,4-diol in the presence of triethylamine afforded the cyclic chlorophosphite **6** which, on treatment with acetylsulphenyl chloride—a reagent which is known to sulphurize trivalent phosphorus compounds under very mild conditions[4]—was transformed into the corresponding phosphorochloridothionate **5**. The cyclic thioacid **4** was prepared as follows. Transesterification of trimethyl phosphite with racemic pentane-2,4-diol gave the cyclic methyl phosphite **7**. It is interesting, to point out that its $^{31}P\{^1H\}$-NMR spectrum, in contrast to other monocyclic compounds **4**, **5**, **6** and **8** prepared in this work, showed two signals of equal intensity at δ 131.6 and 130.3 ppm. This may be interpreted as an indication of the presence of two conformers of **7**, differing in the configuration at the phosphorus atom. Addition of elemental sulphur to **7** resulted in the formation of the cyclic methoxy thionophosphate **8** which was, in turn, demethylated by means of trimethyl amine to give the tetramethylammonium salt of the acid **4**. Since both condensation components, **4** and **5**, were prepared from racemic diol and used as racemic compounds, it was obvious that the racemic and *meso* forms of **3** will only be generated on condensation.

The progress of the reaction between **4** and **5** was monitored by the $^{31}P\{^1H\}$-NMR spectra which, after completion of the reaction, showed two singlets of a nearly equal intensity at δ_P 42.2 and 41.25 ppm. This observation ruled out the formation of the unsymmetrical isomers **3A** since their $^{31}P\{^1H\}$-NMR spectrum should consist of two AB quartets. However, the spectrum was consistent with the presence of the *meso* and racemic forms of **3B** or **3C**. For this reason, the crude condensation product was cystallised very slowly from benzene–cyclohexane solution and the suitable crystals having m.p. 158–159°C were taken for an X-ray crystallographic



SCHEME 2 Synthesis of Bis-(4,6-dimethyl-2-thio-1,3,2-dioxaphosphorinane-2-yl)-oxide (**3**) from Racemic Pentane-2,4-diol.

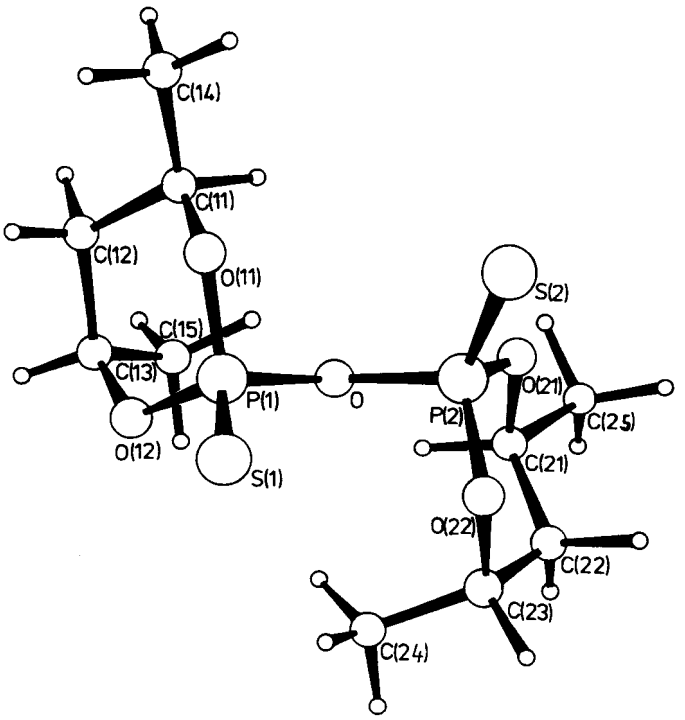


FIGURE 1 Three-dimensional view of *meso*-**3C** with atom numbering.

TABLE I

Positional parameters ($\times 10^4$) for non-hydrogen atoms

	X	Y	Z
P(1)	7917(1)	1220(1)	6366(1)
S(1)	8746(1)	126(1)	5592(1)
O	7480(3)	2296(3)	5490(3)
O(11)	8430(3)	1858(3)	7546(3)
O(12)	6937(3)	671(3)	6791(3)
C(11)	7823(4)	2543(5)	8372(5)
C(12)	7011(4)	1751(6)	8776(5)
C(13)	6348(5)	1260(5)	7703(5)
C(14)	8529(5)	2979(6)	9425(5)
C(15)	5627(5)	2151(7)	7060(6)
P(2)	7966(1)	3085(1)	4435(1)
S(2)	9255(1)	3679(2)	4903(2)
O(21)	7161(3)	4079(3)	4212(3)
O(22)	7876(3)	2276(4)	3245(3)
C(21)	6182(5)	3799(6)	3587(6)
C(22)	6305(5)	3159(6)	2389(5)
C(23)	6907(5)	2016(6)	2527(5)
C(25)	5632(5)	4991(6)	3431(7)
C(24)	6404(6)	989(7)	3118(7)

study in order to determine the geometry and conformation of the dithiopyrophosphate **3** formed.

A three dimensional view of the molecule investigated and the atom numbering are shown in Figure 1. The atomic fractional coordinates for non-hydrogen atoms are listed in Table I and for hydrogen in Table II.† Tables III and IV contain bond distances and angles.†

An inspection of Figure 1 reveals that both phosphorus atoms, P(1) and P(2) are equivalent. The thiophosphoryl sulphur atoms are in equatorial positions and the bridging oxygen atom is axial. Furthermore, analysis of the chirality at the carbon atoms C(11), C(13), C(21) and C(23) bearing methyl groups indicates that the dithiopyrophosphate **3** has the structure of *meso*-**3C**. Therefore, one can conclude that structure **3C** is the most stable conformation of the dithiopyrophosphate **3**. This is due to the fact that both P=S groups are in energetically favourable equatorial positions, and the exocyclic oxygen atom occupies the preferred axial position in 1,3,2-dioxaphosphorinane rings.[5]

As expected, the two structurally independent dioxaphosphorinane rings have distorted chair conformations. The flattening is observed at the phosphorus and C(5) ends. The asymmetry parameters[6] for the two dioxaphosphorinane rings are $\Delta C_s^{P(1)} = 7.9$, $\Delta C_2^{P(1)-O(12)} = 2.0$ and $\Delta C_s^{P(2)} = 5.9$, $\Delta C_2^{P(2)-O(22)} = 3.8°$, respectively. Detailed information on the geometry of the six-membered rings in **3** is given in *Table V*. The orientation of substituents in the six-membered rings may be described by the angle between the substituent vector and the best least-squares plane through the

†The structure factors and anisotropic thermal parameters are deposited with the British Library Lending Division as Supplementary Publication.

TABLE II

Hydrogen atom positional parameters ($\times 10^4$)

	X	Y	Z
H(111)	7452(4)	3306(5)	7928(5)
H(121)	7347(4)	1009(6)	9298(5)
H(122)	6564(4)	2264(6)	9371(5)
H(131)	5882(5)	615(5)	8121(5)
H(141)	8181(5)	3581(6)	10043(5)
H(142)	9128(5)	3437(6)	9022(5)
H(143)	8817(5)	2211(6)	9948(5)
H(151)	5079(5)	2517(7)	7630(6)
H(152)	5264(5)	1602(7)	6331(6)
H(153)	6016(5)	2873(7)	6644(6)
H(211)	5747(5)	3205(6)	4116(6)
H(221)	5579(5)	2943(6)	1950(5)
H(222)	6678(5)	3756(6)	1791(5)
H(231)	6697(5)	1721(6)	1585(5)
H(241)	4888(5)	4904(6)	2993(7)
H(242)	6061(5)	5555(6)	2862(7)
H(243)	5608(5)	5388(6)	4346(7)
H(251)	5827(6)	765(7)	2399(7)
H(252)	6078(6)	1158(7)	3986(7)
H(253)	6919(6)	252(7)	3243(7)

TABLE III

Bond lengths (Å)

P(1)—O	1.609(4)	P(2)—O	1.617(4)
S(1)—P(1)	1.898(2)	S(2)—P(2)	1.895(2)
O(11)—P(1)	1.565(4)	O(21)—P(2)	1.561(4)
O(12)—P(1)	1.565(4)	O(22)—P(2)	1.561(4)
C(11)—O(11)	1.473(7)	C(21)—O(21)	1.468(7)
C(13)—O(12)	1.468(7)	C(23)—O(22)	1.493(8)
C(12)—C(11)	1.504(8)	C(22)—C(21)	1.493(9)
C(14)—C(11)	1.499(8)	C(25)—C(21)	1.528(9)
C(13)—C(12)	1.503(8)	C(23)—C(22)	1.516(10)
C(15)—C(13)	1.520(9)	C(24)—C(23)	1.502(10)

TABLE IV

Bond angles (°)

O—P(1)—S(1)	115.3(2)	S(2)—P(2)—O	115.2(1)
O(11)—P(1)—S(1)	114.1(2)	O(21)—P(2)—O	100.1(2)
O(11)—P(1)—O	104.4(2)	O(21)—P(2)—S(2)	114.0(2)
O(12)—P(1)—S(1)	115.0(2)	O(22)—P(2)—O	104.4(2)
O(12)—P(1)—O	100.6(2)	O(22)—P(2)—S(2)	115.3(2)
O(12)—P(1)—O(11)	105.8(2)	O(22)—P(2)—O(21)	106.3(2)
P(2)—O—P(1)	131.7(2)	C(21)—O(21)—P(2)	120.7(3)
C(11)—O(11)—P(1)	119.4(3)	C(23)—O(22)—P(2)	122.7(4)
C(13)—O(12)—P(1)	122.7(3)	C(22)—C(21)—O(21)	109.5(5)
C(12)—C(11)—O(11)	109.0(5)	C(25)—C(21)—O(21)	106.1(5)
C(14)—C(11)—O(11)	105.7(5)	C(25)—C(21)—C(22)	114.3(5)
C(14)—C(11)—C(12)	114.2(5)	C(23)—C(22)—C(21)	114.7(5)
C(13)—C(12)—C(11)	113.4(5)	C(22)—C(23)—O(22)	109.2(5)
C(12)—C(13)—O(12)	110.6(5)	C(24)—C(23)—O(22)	109.9(5)
C(15)—C(13)—O(12)	110.8(4)	C(24)—C(23)—C(22)	115.2(6)
C(15)—C(13)—C(12)	115.4(5)		

TABLE V

Geometry of the 1,3,2-dioxaphosphorinane rings in *meso*-**3C**

Plane	Atoms in the plane	Deviations (Å) from plane	Inclination angles (°)
(i)	O(11)	0.035	α_1 = (i)/(ii) = 31.8
	O(12)	−0.035	
	C(11)	−0.035	β_1 = (i)/(iii) = 51.0
	C(13)	0.035	
(ii)	P(1)O(11)O(12)		
(iii)	C(11)C(12)C(13)		
(j)	O(21)	−0.024	α_2 = (j)/(jj) = 30.5
	O(22)	0.024	
	C(21)	−0.024	β_2 = (j)/(jjj) = 50.7
	C(23)	0.024	
(jj)	P(2)O(21)O(22)		(j)/(i) = 29.8
(jjj)	C(21)C(22)C(23)		

atoms O(11)O(12)C(11)C(13) and O(21)O(22)C(21)C(23). The following values were obtained:

	ring with P(1)	ring with P(2)
P=S	14.6°	15.5°
CH_3eq	25.4°	26.0°
CH_3ax	−62.3°	−64.8°

Finally, the *Figure* 2 shows the Newman projection around P(1) · · · P(2). It is interesting that the dihedral angle between the planes S(1)P(1)O and S(2)P(2)O is 76.1°. This angle is very sensitive to changes in configuration at the phosphorus atoms and the carbon atoms bearing methyl groups in diastereomeric dithiopyrophosphates. Thus, the dihedral angle between the planes S(1)P(1)O and S(2)P(2)O in trans-trans-**1** and cis-cis-**1** is 172.4° and 99.7°, respectively. In trans-cis-**2** and trans-trans-**2** these values are: 11.8° and 79.2°, respectively.

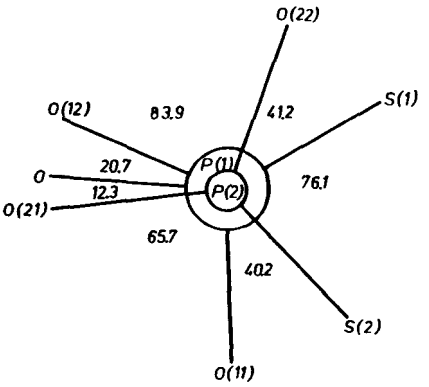


FIGURE 2 Newman projection around p(1) · · · P(2) showing the relevant torsion angles (°) in *meso*-**3C**.

EXPERIMENTAL

M.ps and b.p. are uncorrected. Solvents and reactants were of reagent grade. ^{31}P NMR spectra were obtained with a JEOL-JNM-C-60 HL spectrometer using 85% phosphoric acid as an external standard; positive $\delta^{31}P$ values refer to down-field shifts from H_3PO_4. Pentane-2,4-diol was separated into *meso* and racemic forms using the method described by Pritchard and Vollmer.[7]

4,6-Dimethyl-2-chloro-1,3,2-dioxaphosphorinane **6** *from Racemic Pentane-2,4-diol.* To a solution of phosphorus trichloride (13.8 g; 0.1 mol) in ether (100 ml), triethylamine (20.2 g; 0.2 mol) and racemic pentane-2,4-diol (10.4 g; 0.1 mol) in ether (30 ml) were added at 0 –5°C. After stirring the reaction mixture for 0.5 hr at 5°C triethylamine hydrochloride was filtered off and ether was evaporated. The residue was distilled to give the cyclic chlorophosphite **6**; 10.8 g (64%), b.p. 68–70°C/9 mmHg; n_D^{20} 1.4788; δ_{31P} 161.5 ppm.

4,6-Dimethyl-2-chloro-1,3,2-dioxaphosphorinane-2-thione **5**. This compound was prepared from the chlorophosphite **6** (5.5 g, 0.0325 mol) and acetylsulphenyl chloride (3.6 g, 0.0325 mol) according to the procedure described by us.[4] The crude product was distilled to give 5.4 g (83%) of the pure product **5**; b.p. 82–87°C/0.015 mmHg; n_D^{20} 1.5195; δ_{31P} 56.9 ppm (Found: C, 29.96; H, 5, 12; P, 16, 32. Calc. for $C_5H_{10}O_2CIPS$: C, 29.93; H, 5.02; P, 15.44%).

4,6-Dimethyl-2-methoxy-1,3,2-dioxaphosphorinane **7** *from racemic Pentane-2,4-Diol.* Transesterification of trimethyl phosphite (6.2 g, 0.05 mol) with racemic pentane-2,4-diol (5.2 g, 0.05 mol) carried out according to the procedure described by Verkade *et al.*[8] afforded 5.6 g (68%) of the cyclic phosphite **7** after distillation; b.p. 64–65°C/12 mmHg; n_D^{20} 1.4393; δ_{31P} 131.6 and 130.3 ppm.

4,6-Dimethyl-2-methoxy-1,3,2-dioxaphosphorinane-2-thione **8**. To the phosphite, **7** (4.5 g, 0.027 mol), prepared as above, sulphur (0.88 g, 0.027 mol) was added in a standard manner[4] giving the product **8** which was purified by distillation; 4.6 g (86%); b.p. 85–87°C/0.3 mmHg; n_D^{20} 1.4920; δ_{31P} 63.3 ppm.

Tetramethylammonium Salt of 4,6-Dimethyl-2-oxo-1,3,2-dioxaphosphorinane-2-thione **4**. To a benzene solution (25 ml) of the thionophosphate **8** (4.6 g, 0.032 mol) trimethylamine (1.4 g, 0.023 mol) was added and the reaction mixture was left for three days. The precipitated salt was filtered off and crystallised from chloroform; 5.1 g (87%), m.p. ca. 200°C (dec.), δ_{31P} 51.5 ppm (Found: C, 41.72; H, 8.75; P, 12.21; S, 12.06; N, 5.19. Calc. for $C_9H_{22}O_3NPS$: C, 42.33; H, 8.67; P, 12.13; S, 12.55; N, 5.48%).

Bis-(4,6-dimethyl-2-thio-1,3,2-dioxaphosphorinane-2-yl)-oxide **3**. A mixture of the above prepared salt of **4** (0.77 g, 0.003 mol) and the cyclic chloride **5** (0.6 g, 0.003 mol) in acetonitrile (20 ml) was stirred at room temperature for three days. After removal of the solvent the residue was treated with benzene (50 ml). The benzene solution was washed with water (2 × 10 ml), dried over anhydrous magnesium sulphate and evaporated. The crude condensation product showing two signals in $^{31}P\{^1H\}$NMR spectrum at δ_{31P} 42.22 and 41.25 ppm (toluene as solvent) was crystallised several times from a mixture of benzene–cyclohexane (1 : 1) to give the diastereoisomerically pure dithiopyrophosphate *meso*-**3C** (0.1 g), as revealed by X-ray analysis; m.p. 158–159°C, δ_{31P} 42.20 ppm (dichloromethane) (Found: C, 34.58; H, 5.90; P, 18.38; S, 18.65. Calc. for $C_{10}H_{20}O_5P_2S_2$: C, 34.67; H, 5.82; P, 17.89; S, 18.51%).

X-ray Structure Determination of meso-Bis(4,6-dimethyl-2-thio 1,3,2-dioxaphosphorinane-2-yl)-oxide **3C**. *Crystal data.* $C_{10}H_{20}O_5P_2S_2$. M = 346.17. Monoclinic space group $P2_1/n$, a = 13.542(3), b = 11.175(1), c = 10.731(2)Å, β = 94.81(1)°, V = 1613.1(4)Å^3, Z = 4, F(000) = 728, D_c 1.42 Mg · m^{-3}, λ(CuKα) = 1.54178Å, μ(CuKα) = 4.79 mm^{-1}.

Crystallographic Measurements and Structure Analysis. Single crystals of **3** were grown from benzene–cyclohexane solution. The cell parameters were determined from oscillation and rotation photographs, using CuKα radiation. These parameters were redetermined on the Syntex $P2_1$ diffractometer, using CuKα radiation. The space group is $P2_1/n$. Intensity data were collected in the θ–2θ mode ($3.0 \leqslant 2\theta \leqslant 115.0°$) with graphite-monochromated CuKα radiation. No absorption correction was applied [μ(CuKα) = 4.79 mm^{-1}]. After application of the acceptance criterion $F \geqslant 3\sigma(F)$, of 2089 collected reflections 1649 unique reflexions were retained for the refinement. The structures were solved by direct methods (SHELX 76)[9] and refined by blocked-fullmatrix least squares with anisotropic temperature factors for all non-hydrogen atoms. The methyl H atoms, to which a group isotropic temperature factor was assigned, were taken as a part of a rigid methyl group. The remaining H atoms were refined freely with two group isotropic temperature factors. The terminal value of R_W was 0.081 with R 0.072. Weights were given by $w = k|\delta^2(Fo) + gFo^2|^{-1}$, where k and g were refined to 2.0918 and 0.003017, respectively. Complex natural-atom scattering factors were employed.[10]

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