Cyclic Organophosphorus Compounds. Part 20.[1] Structural Correlations in the 2-Amino-4-methyl-1,3,2-dioxaphosphinane Series. *X*-Ray Molecular Structure of *cis*-2-t-Butylamino-4-methyl-1,3,2-dioxaphosphinane 2-Oxide

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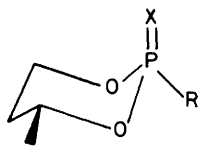
The oxidation of *cis*-2-t-butylamino-4-methyl-1,3,2-dioxaphosphinane 2-selenide with hydrogen peroxide yields *cis*-2-t-butylamino-4-methyl-1,3,2-dioxaphosphinane 2-oxide. The oxide has been shown, by *X*-ray analysis, to exist in the chair form with the methyl and t-butylamino groups orientated equatorially, and the structure has been refined to $R = 0.097$, with $a = 11.304(1)$, $b = 9.702(1)$, $c = 11.386(1)$ Å, and $\beta = 116.16(2)°$. Predictions regarding the stereoretentive course of this oxidation procedure made elsewhere on the basis of n.m.r. data are thus confirmed. Further ^{31}P chemical shift and $^{1}J(^{31}P,^{77}Se)$ data now suggest that the correlation can be extended to include the 2-anilino and 2-benzylamino compounds.

To a large extent, and particularly more recently, investigations into the stereochemical changes accompanying the cleavage of phosphorus–halogen bonds by nucleophiles have employed a variety of ester-halides based upon phosphorus-containing ring systems as substrates. The outcome of such studies obviously depends upon a knowledge of the configurations of both substrate and product(s). In only a few cases, *e.g.* for *cis*-2-chloro-5-chloromethyl-5-methyl-1,3,2-dioxaphosphinane 2-oxide, can the molecular configuration (but not necessarily conformations at carbon and phosphorus) be assigned unequivocally from the manner of preparation. *X*-Ray analysis has provided some confirmation of the course of nucleophilic displacements for this substrate (which possesses an achiral phosphorus atom) and these reactions are conveniently followed by easy application of ^{1}H n.m.r. spectroscopy.[2]

In spite of the profusion of i.r. and ^{1}H, ^{31}P, and ^{13}C n.m.r. data for phosphorus-containing ring systems, it is still not easy to assign configurations at a chiral phosphorus atom. In such cases, predictions based upon spectroscopic techniques, although convenient to use, remain largely unsubstantiated by the use of independent, *e.g.* *X*-ray diffraction, techniques.[2,3]

Compounds in the 4-methyl-1,3,2-dioxaphosphinane system have been used particularly widely in mechanistic work, and conclusions reached have relied almost entirely on n.m.r. evidence coupled, sometimes, with chemical correlation.[2] Because of the scarcity of diffraction data pertaining to this system, importance should be attached to the determination of the configurations of *cis*-† (**1**; R = NHBu^t, X = Se)[4] and *trans*-2-t-butylamino-4-methyl-1,3,2-dioxaphosphinane 2-selenide (**2**; R = NHBu^t, X = Se)[5] by *X*-ray methods. The high stereoretentivity of formation of these from selenium and the corresponding amides of tervalent phosphorus determines the configuration at phosphorus in the latter amides.



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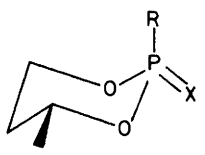

(2)

† The terms *cis* and *trans* refer to the relative spatial disposition of the substituent at C-4 and the singly bonded substituent at phosphorus.

Concentrated aqueous hydrogen peroxide has been reported to oxidize the compounds (**1**; R = OMe or NMe_2, X = S; R = OMe, X = Se) and (**2**; R = NMe_2, X = Se) to the oxides with high, but not exclusive, retentivity of configuration.[6]

This paper records the results and implications of an *X*-ray analysis of the 2-oxide derived from *cis*-2-t-butylamino-4-methyl-1,3,2-dioxaphosphinane 2-selenide using this oxidant.

Results and Discussion

Using procedures similar to those already recorded elsewhere, 2-chloro-4-methyl-1,3,2-dioxaphosphinane, stereochemically homogeneous and of assumed *trans* geometry (**2**; R = Cl, X = lone pair),[7] was allowed to react with t-butylamine[8] or with aniline in the presence of triethylamine to give mixtures of the stereoisomeric amides (**1**, **2**; R = NHBu^t or $NHPh_3$, X = lone pair).[9] The mixtures were not separated, but were converted, by direct addition of selenium, into mixtures of the 2-selenides (**1**, **2**; R = NHBu^t or NHPh, X = Se) which were then separated by chromatography. The pure selenides had spectral properties close to those already published.[8,9] As examples of compounds derived from a third type of amine, the stereoisomeric 2-benzylamino-4-methyl-1,3,2-dioxaphosphinane 2-selenides, hitherto unrecorded, were prepared. They were obtained in an equimolar ratio and had δ_P 67.8 and 67.5 p.p.m., with $^{1}J(^{31}P, ^{77}Se)$ 887 and 911 Hz respectively, and were assigned the structures (**1**; R = $NHCH_2Ph$, X = Se) and (**2**; R = $NHCH_2Ph$, X = Se).

Of the two diastereoisomeric 2-t-butylamino-4-methyl-1,3,2-dioxaphosphinane 2-selenides, with δ_P 66.0 and 59.5 p.p.m. respectively, the former has been shown to have the *cis* geometry, and the latter the *trans* geometry, following examination by *X*-ray analysis; these show that the 4-methyl substituent occupies the equatorial position in the solid state. Numerous ^{1}H n.m.r. studies lead to the conclusion that for solutions, also, the 4-methyl group in 4-methyl-1,3,2-dioxaphosphinanes generally prefers to occupy the equatorial position, although both chair conformations are to be observed for many compounds of *trans* geometry.[2] This appears to be so for the stereoisomeric 2-t-butylamino-4-methyl-1,3,2-dioxaphosphinane 2-selenides.[8]

The dangers in the assignment of configurations at phosphorus solely on the basis of phosphorus chemical shift values have been emphasized, and, whenever possible, the use of

$^1J(^{31}P, ^{77}Se)$ values, preferably in association with chemical shifts, is to be preferred.[10]

A comparison of the n.m.r. data for each of the stereoisomeric 2-anilino and 2-benzylamino compounds with each other, and with those of the 2-t-butylamino stereoisomers of known molecular geometry and known configuration at phosphorus, suggests the emergence of a self-consistent pattern in which, apparently, the *cis* stereoisomers, with axial P=Se bonds, possess more positive ^{31}P chemical shifts, but smaller $^1J(^{31}P, ^{77}Se)$ values, than do the *trans* forms. A similar situation has been found for other types of derivatives of the same system.[10,11] It would thus seem reasonable to suppose that, providing the comparison is being made for compounds possessing the same ring system with the same substituents on ring carbon atoms and similar (at least) substituents on phosphorus, assignments of geometries and configurations at phosphorus can be made on the basis of phosphorus chemical shifts and coupling constants.

Each of the six stereochemically homogeneous selenides was oxidized with 50% aqueous hydrogen peroxide to give (in principle) a mixture of the stereoisomeric 2-substituted amino-4-methyl-1,3,2-dioxaphosphinane 2-oxides in highly exothermic reactions. Typically, *trans*-2-t-butylamino-4-methyl-1,3,2-dioxaphosphinane 2-selenide afforded a mixture of oxides with δ_P 4.6 and 0.35 p.p.m. in the ratio 2:98; the *cis*-2-selenide gave the same 2-oxides in the ratio 90:10.

An *X*-ray analysis of the 2-t-butylamino-4-methyl-1,3,2-dioxaphosphinane 2-oxide having δ_P 4.6 p.p.m. shows clearly that it possesses the *cis* geometry with the ring methyl and t-butylamino groups orientated equatorially (Figure), and the hydrogen peroxide oxidation of the 2-selenides may be taken to be highly stereoretentive. The same stereochemical outcome of the oxidations of the diastereoisomeric 2-anilino and 2-benzylamino selenides was inferred from the relative phosphorus chemical shifts of the oxides.

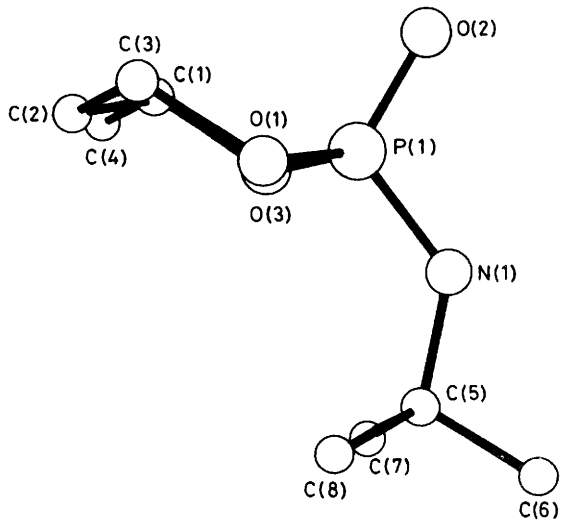

Figure. Molecular structure and crystallographic (arbitrary) numbering of *cis*-2-t-butylamino-4-methyl-1,3,2-dioxaphosphinane 2-oxide (**1**; R = NHBu^t, X = O)

Arguments advanced elsewhere for the assignment of configurations in the diastereoisomeric 2-benzylamino-4-methyl-1,3,2-dioxaphosphinane 2-oxides are tentative and unconvincing.[12] However, the stereochemistries of both the 2-oxides and the 2-selenides of 2-anilino-4-methyl-1,3,2-dioxaphosphinane are well documented; the oxides were prepared from the cyclic phosphorochloridate(s) or by reaction between phenyl azide and the stereoisomeric 2-methoxy-4-methyl-1,3,2-dioxaphosphinanes, followed by acidification of the phenylimino derivatives,[13] as well as by oxidation of the corresponding 2-selenides.[9] In the present study, the authentic 2-oxides were prepared by a variety of routes including the oxidation of the tervalent phosphorus amides with t-butyl hydroperoxide, and reactions between the stereoisomeric 2-chloro-4-methyl-1,3,2-dioxaphosphinane 2-oxides and the appropriate amines. In the case of the t-butylamino derivatives it appeared that success in the purification of the stereoisomers depended upon the composition of the initial mixtures. The oxidation of the tervalent phosphorus t-butylamides by dinitrogen tetraoxide was not totally stereoretentive; only one stereoisomeric oxide could be obtained in a pure form when t-butyl hydroperoxide was used as oxidant, and the same situation arose when the anilino compounds were oxidized. Oxidation of the tervalent benzylamides appeared to be stereospecific, but the *cis* oxide could only be obtained as an oil, although this was stereochemically pure.

The pattern, already established, for the relationship between ^{31}P chemical shifts and proven geometry for the 2-selenides can now be extended to the series of 2-oxides. For each of the three pairs of epimeric 2-oxides, each of the epimers with the more positive ^{31}P chemical shift can now be assigned the *cis* geometry with the (*R*) configuration at phosphorus. However, it is perhaps wise to emphasize that these conclusions have been reached for derivatives of the 4-methyl-1,3,2-dioxaphosph(v)inane series, and they may not apply to derivatives of 1,3,2-dioxaphosphinanes with other patterns of ring substitution.

Leaving aside considerations of phosphoryl bonding, all bond lengths in *cis*-2-t-butylamino-4-methyl-1,3,2-dioxaphosphinane 2-oxide are slightly shorter than those of either of the epimeric 2-selenides; indeed, the bond between C(1) and C(4) (crystallographic numbering) is considerably shorter (1.357 Å) compared with the same bond in each of the selenides (*ca.* 1.5 Å). The shortening of the exocyclic P–N bond (1.59 Å) relative to that in the selenides (1.62, 1.65 Å) is perhaps predictable, but, in addition, the oxide P–N bond is considerably shorter than that of 2-amino-5,5-dimethyl-1,3,2-dioxaphosphinane 2-oxides (1.65, 1.70 Å)[14] and 2-sulphides (1.62 Å);[15] values for the exocyclic bond in 2-amino-perhydro-1,3,2-oxazaphosphinines range from 1.62 to 1.64 Å.[16]

Experimental

Solutions and solvents were dried by conventional means. Light petroleum refers to the fraction boiling in the range 60—80 °C. Tervalent phosphorus compounds were distilled in an atmosphere of nitrogen. T.l.c. and column chromatography employed Merck Kieselgel. Unless otherwise stated, chloroform was used for the chromatography of the selenides, and the oxides were chromatographed with butan-2-one–propan-2-ol (3:2). A solution of iodine in ethanol was used as indicator spray; the selenides reacted much more rapidly than the oxides. I.r. spectra were determined for KBr discs (solids) or NaCl plates (liquids) using a Perkin-Elmer model 681 spectrophotometer. ^{31}P N.m.r. spectra were determined for chloroform solutions, with phosphoric acid as external standard (chemical shifts to lower field are positive), through the services of the S.E.R.C. low-field multinuclear n.m.r. spectroscopy unit at the City of London Polytechnic.

2-Chloro-4-methyl-1,3,2-dioxaphosphinane (**2**; R = Cl, X = lone pair).—This cyclic phosphorochloridite, prepared as described elsewhere,[7] had b.p. 78—84 °C at 19—22 mmHg, n_D^{25} 1.4792; δ_P 151.2 p.p.m.; $\nu_{max.}$ 1 062s, 1 032s, and 983s cm^{-1}, and was of 100% stereoisomeric purity.

2-t-Butylamino-4-methyl-1,3,2-dioxaphosphinane 2-Selenide (**1, 2**; R = NHBu^t, X = Se).—A solution of the freshly distilled

Table 1. Hydrogen peroxide oxidation of the stereoisomeric 2-amino-4-methyl-1,3,2-dioxaphosphinane 2-selenides

Selenide (1,2; X = Se) R		Oxide products yield (%)	δ_P (p.p.m.)	Ratio of products
$NHBu^t$	*cis*	99	4.6, 0.4	91:9
	trans	78	4.6, 0.35	2:98
NHPh	*cis*	83 [a]	−0.1, —	100:0
	trans	100 [b]	—, −3.7	0:100
$NHCH_2Ph$	*cis*	100	5.8, 3.3	97:3
	trans	100 [c]	—, 3.3	0:100

[a] Product had m.p. 167—168 °C (from ethyl acetate–light petroleum) (lit.,[13] 174—176 °C). [b] Product had m.p. 153—154 °C (from ethyl acetate) (lit.,[13] 154—155 °C). [c] Product was an oil which would not crystallize.

cyclic phosphorochloridite (11.0 g) in ether (25 ml) was added dropwise to a stirred solution of t-butylamine (10.5 g) in ether (250 ml) cooled in ice. The mixture was filtered, and the filtrate distilled to give a mixture of diastereoisomeric 2-t-butylamino-4-methyl-1,3,2-dioxaphosphinanes, b.p. 65—72 °C at 1 mmHg (10.0 g, 77%) which showed signals at δ_P 141.8 and 126.3 p.p.m. in the ratio 57:43 (lit.,[8] b.p. 43—44 °C at 0.6 mmHg; δ_P 143.0 and 126.5 p.p.m.).

Selenium (0.85 g) was added in portions to a solution of the mixed tervalent phosphorus t-butylamides (1.9 g) in benzene (20 ml), and after the initial exothermic reaction had subsided, the mixture was kept overnight. The filtered solution was evaporated to leave a solid (2.5 g, 91%) which showed signals at δ_P 66.0 and 59.5 p.p.m. in the ratio 57:43. Chromatography of the mixed 2-selenides yielded *cis*-2-t-butylamino-4-methyl-1,3,2-dioxaphosphinane 2-selenide (**1**; R = $NHBu^t$, X = Se), m.p. 118—119 °C; δ_P 66.0 p.p.m., $^1J(^{31}P, ^{77}Se)$ 870 Hz [lit.,[8] m.p. 120—120.5 °C; δ_P 66.5 p.p.m., $^1J(^{31}P, ^{77}Se)$ 900 Hz (C_6D_6)], followed by the *trans* isomer, m.p. 81—82 °C; δ_P 59.5 p.p.m., $^1J(^{31}P, ^{77}Se)$ 896 Hz [lit.,[8] m.p. 81—82 °C; δ_P 58.7 p.p.m., $^1J(^{31}P, ^{77}Se)$ 916 Hz (C_6D_6)].

2-*Anilino*-4-*methyl*-1,3,2-*dioxaphosphinane* 2-*Selenide* (**1**, **2**; R = NHPh, X = Se).—Using the procedure outlined above, reaction between 2-chloro-4-methyl-1,3,2-dioxaphosphinane and aniline in the presence of triethylamine gave a mixture of stereoisomers of 2-anilino-4-methyl-1,3,2-dioxaphosphinane (13 g, 62%), b.p. 115—129 °C at 0.3 mmHg (lit.,[9] 99—101 °C at 0.02 mmHg). To a solution of this mixture (4.2 g) in benzene (20 ml) was added selenium (1.6 g) in portions; after the initial reaction had subsided, the solution was heated, filtered, and the filtrate evaporated to leave the crude 2-selenides (100%) which showed signals at δ_P 59.0 and 62.3 p.p.m. in the ratio 80:20. Crystallization of this product from benzene gave the pure major component (1.5 g). The solvent was removed from the mother liquors, and the residue was chromatographed to give, first, more of the major component, followed by the minor component as an oil which crystallized. The major component was *trans*-2-anilino-4-methyl-1,3,2-dioxaphosphinane 2-selenide (**2**; R = NHPh, X = Se), m.p. 166 °C (from benzene); δ_P 59.0 p.p.m., $^1J(^{31}P, ^{77}Se)$ 994 Hz [lit.,[9] m.p. 166—167 °C; δ_P 60.0 p.p.m., $^1J(^{31}P, ^{77}Se)$ 942 Hz (dioxane)]. The *cis* isomer had m.p. 93—95 °C, δ_P 62.3 p.p.m., $^1J(^{31}P, ^{77}Se)$ 903 Hz [lit.,[9] m.p. 95—96 °C; δ_P 62.5 p.p.m., $^1J(^{31}P, ^{77}Se)$ 887 Hz (C_6H_6)].

2-*Benzylamino*-4-*methyl*-1,3,2-*dioxaphosphinane* 2-*Selenide* (**1**, **2**; R = $NHCH_2Ph$, X = Se).—Reaction between 2-chloro-4-methyl-1,3,2-dioxaphosphinane and benzylamine in the presence of triethylamine in ether gave a mixture of stereoisomeric 2-benzylamino-4-methyl-1,3,2-dioxaphosphinane (15.0 g, 67%), b.p. 116 °C at 0.3 mmHg to 124 °C at 0.4 mmHg; $\nu_{max.}$ 3 285s (NH), 1 076s, and 1 033s (POC) cm^{-1}.

The addition of selenium (1.6 g) to a solution of the mixed stereoisomeric tervalent phosphorus benzylamides (4.5 g) in benzene (5 ml) was exothermic. When the initial reaction had subsided, the solution was diluted, filtered, and the filtrate evaporated to give the mixed 2-selenides as an oil (6.1 g, 100%) which showed signals at δ_P 67.8 and 67.5 p.p.m. in the ratio 49.5:50.5. Column chromatography of the mixture yielded initially cis-2-*benzylamino*-4-*methyl*-1,3,2-*dioxaphosphinane* 2-*selenide* (**1**; R = $NHCH_2Ph$, X = Se), m.p. 93—94 °C (from ethyl acetate–light petroleum); δ_P 67.8 p.p.m., $^1J(^{31}P, ^{77}Se)$ 888 Hz; $\nu_{max.}$ 3 300s (NH), 1 088s, 1 075s, 1 060s, and 1 027s (POC) cm^{-1} (Found: C, 43.6; H, 5.3; N, 4.6. $C_{11}H_{16}NO_2PSe$ requires C, 43.4; H, 5.3; N, 4.8%), followed by the trans *isomer*, m.p. 68—68.5 °C (from benzene–light petroleum), δ_P 67.5 p.p.m., $^1J(^{31}P, ^{77}Se)$ 911 Hz; $\nu_{max.}$ 3 235s (NH), 1 082s, 1 073s, 1 058s, and 1 022s (POC) cm^{-1} (Found: C, 43.7; H, 5.3; N, 4.6%).

General Procedure for the Oxidation of the 2-*Amino*-4-*methyl*-1,3,2-*dioxaphosphinane* 2-*Selenides with Hydrogen Peroxide.*—Hydrogen peroxide (50% w/w; 0.2 ml) was added to a solution of the cyclic phosphoramido selenoate (0.001 mol) in acetone (5 ml). Heat was generated, and red selenium precipitated rapidly. After 15—30 min at ambient temperature the mixture was filtered, and the filtrate was evaporated. The residue was taken up in chloroform, and the solution was washed with water, dried, and evaporated. The residues were oils which generally solidified. Results of the oxidation experiments are collected in Table 1. In some cases the major products of the oxidations were isolated and their identity with previously recorded compounds, or compounds prepared here for the first time, was confirmed.

Preparation of the 2-*Amino*-4-*methyl*-1,3,2-*dioxaphosphinane* 2-*Oxides by Alternative Routes.*—2-*t-Butylamino*-4-*methyl*-1,3,2-*dioxaphosphinane* 2-*oxide.* (*a*) Oxidation of a solution of the mixed diastereoisomers of 2-t-butylamino-4-methyl-1,3,2-dioxaphosphinane in dichloromethane, the same sample used for the preparation of the selenides, by dinitrogen tetraoxide gave, after removal of the solvent, a solid which showed signals at δ_P 4.6 and 0.5 p.p.m. in the ratio 51.5:48.5, together with other signals of low intensity.

(*b*) The same mixture of diastereoisomeric tervalent phosphorus t-butylamides (3.8 g) was dissolved in ether (50 ml) and the solution was cooled in ice and stirred magnetically while a solution of t-butyl hydroperoxide (80%; 1.7 g) in ether was added dropwise. The mixture was stirred at ambient temperature for 2 h and then filtered to give a solid (1.5 g), m.p. 163—164 °C (from benzene); δ_P 0.4 p.p.m., pure by t.l.c.

(*c*) A solution of 2-chloro-4-methyl-1,3,2-dioxaphosphinane in dichloromethane was oxidized with dinitrogen tetraoxide; removal of the solvent left an oil which showed signals at δ_P

Table 2. Bond lengths (Å) (standard deviations in parentheses)

P(1)–O(3)	1.556(8)	C(1)–C(2)	1.462(18)
P(1)–O(1)	1.562(9)	C(1)–C(4)	1.357(26)
P(1)–O(2)	1.447(7)	C(2)–C(3)	1.455(19)
P(1)–N(1)	1.591(8)	C(5)–C(6)	1.420(20)
O(3)–C(1)	1.460(16)	C(5)–C(7)	1.357(19)
O(1)–C(3)	1.476(17)	C(5)–C(8)	1.432(23)
N(1)–C(5)	1.450(13)		

Table 3. Bond angles (°) (standard deviations in parentheses)

O(3)–P(1)–O(1)	102.4(4)	O(3)–C(1)–C(4)	107.1(16)
O(3)–P(1)–O(2)	113.8(5)	C(2)–C(1)–C(4)	112.8(18)
O(3)–P(1)–N(1)	106.9(5)	C(1)–C(2)–C(3)	119.9(12)
O(1)–P(1)–O(2)	112.9(6)	O(1)–C(3)–C(2)	108.2(13)
O(1)–P(1)–N(1)	107.6(5)	N(1)–C(5)–C(6)	108.7(11)
O(2)–P(1)–N(1)	112.5(4)	N(1)–C(5)–C(7)	114.0(11)
P(1)–O(3)–C(1)	114.7(8)	N(1)–C(5)–C(8)	113.3(13)
P(1)–O(1)–C(3)	119.9(10)	C(6)–C(5)–C(7)	112.3(21)
P(1)–N(1)–C(5)	131.4(7)	C(6)–C(5)–C(8)	103.4(18)
O(3)–C(1)–C(2)	112.9(12)	C(7)–C(5)–C(8)	104.6(18)

Table 4. Torsion Angles (°)

O(1)–P(1)–O(3)–C(1)	48.6
O(3)–P(1)–O(1)–C(3)	−50.2
O(3)–P(1)–N(1)–C(5)	−52.8
P(1)–O(3)–C(1)–C(2)	−57.5
P(1)–N(1)–C(5)–C(6)	−165.8
O(3)–C(1)–C(2)–C(3)	58.9
O(2)–P(1)–O(3)–C(1)	−73.5
O(2)–P(1)–O(1)–C(3)	72.6
O(1)–P(1)–N(1)–C(5)	56.6
P(1)–O(3)–C(1)–C(4)	177.7
P(1)–N(1)–C(5)–C(7)	68.0
C(4)–C(1)–C(2)–C(3)	−179.5
N(1)–P(1)–O(3)–C(1)	161.6
N(1)–P(1)–O(1)–C(3)	−162.6
O(2)–P(1)–N(1)–C(5)	−178.5
P(1)–O(1)–C(3)–C(2)	55.2
P(1)–N(1)–C(5)–C(8)	−51.5
C(1)–C(2)–C(3)–O(1)	−54.7

Table 5. Atomic co-ordinates for C, H, N, O, and P atoms with e.s.d.s in parentheses

Atom	*x*	*y*	*z*
P(1)	0.910 0(4)	0.078 1(4)	0.800 6(3)
O(1)	0.787 4(9)	0.034 0(9)	0.678 0(8)
O(2)	0.877 0(9)	0.113 4(9)	0.902 1(7)
O(3)	0.966 0(7)	0.200 7(8)	0.754 5(7)
N(1)	1.015 3(9)	−0.043 1(8)	0.837 4(7)
C(1)	0.869(2)	0.304(2)	0.681(2)
C(2)	0.760(1)	0.247(2)	0.569(1)
C(3)	0.691(2)	0.139(2)	0.601(2)
C(4)	0.934(3)	0.405(2)	0.653(2)
C(5)	1.078(1)	−0.109(1)	0.767(1)
C(6)	1.138(3)	−0.233(3)	0.829(2)
C(7)	1.163(3)	−0.026(2)	0.747(3)
C(8)	0.986(2)	−0.154(3)	0.645(2)
H(1)	0.9426	0.0707	0.0616*
H(2)	0.8283	0.3505	0.7308*
H(3)	0.7966	0.2070	0.5126*
H(4)	0.6967	0.3220	0.5235*
H(5)	0.6468	0.1791	0.6504*
H(6)	0.6236	0.0952	0.5227*
H(7)	1.0066	0.4406	0.7323*
H(8)	0.9715	0.3669	0.5971*
H(9)	0.8714	0.4815	0.6085*
H(10)	1.1813	−0.2786	0.7814*
H(11)	1.2056	−0.2114	0.9164*
H(12)	1.0695	−0.2953	0.8327*
H(13)	1.2023	−0.0776	0.6986*
H(14)	1.2351	0.0041	0.8297*
H(15)	1.1154	0.0570	0.6980*
H(16)	1.0349	−0.1983	0.6019*
H(17)	0.9241	−0.2227	0.6532*
H(18)	0.9349	−0.0735	0.5946*

* U(iso) = 0.800

−2.4 and −4.4 p.p.m. in the ratio 84.5:15.5, together with other trace signals. The cyclic phosphorochloridate, thus obtained as a mixture of stereoisomers, was added in one portion to a solution of t-butylamine and triethylamine (one molar proportion of each) in ether. After 2 h at ambient temperature the mixture was filtered and the filtrate was evaporated to leave a mixture of complex composition, but which showed *inter alia* signals at δ_P 4.6 and 0.6 p.p.m. in the ratio 86:14.

Success in separating the isomers from the product mixtures in experiments (*a*) and (*c*), or in obtaining the second stereoisomer from any of the three reaction products by crystallization or chromatography, appeared to depend upon the composition of the mixture.

cis-2-*t-Butylamino*-4-*methyl*-1,3,2-*dioxaphosphinane* 2-*oxide* (**1**; R = NHBu^t, X = O), m.p. 166 °C (from tetrachloromethane), was eventually obtained by crystallization of the crude product, initially from benzene and then from tetrachloromethane; the product had δ_P 4.5 p.p.m.; $\nu_{max.}$ 3 180s (NH), 1 250s br (P=O), 1 065s br, and 1 035s (POC) cm^{-1} (Found: C, 46.2; H, 8.95; N, 6.8. $C_8H_{18}NO_3P$ requires C, 46.35; H, 8.75; N, 6.75%).

trans-2-*t-Butylamino*-4-*methyl*-1,3,2-*dioxaphosphinane* 2-*oxide* (**2**; R = NHBu^t, X = O) had m.p. 163—164 °C (from benzene), δ_P 0.4 p.p.m.; $\nu_{max.}$ 3 205s (NH), 1 270s, 1 245s, 1 233s (P=O), 1 075s, and 1 035s (POC) cm^{-1} (Found: C, 46.4; H, 9.0; N, 6.6%).

2-*Anilino*-4-*methyl*-1,3,2-*dioxaphosphinane* 2-*oxide* (**1**; **2**; R = NHPh, X = O). (*a*) A solution of aniline (8.0 g) in benzene (90 ml) was added dropwise to a solution of 2-chloro-4-methyl-1,3,2-dioxaphosphinane 2-oxide (prepared as described above, but of unknown stereochemical composition; 7.2 g) in benzene (50 ml) during 0.5 h. After a further 1 h at ambient temperature, the mixture was worked up by filtration and evaporation. The residual solid was crystallized from benzene to give *cis*-2-anilino-4-methyl-1,3,2-dioxaphosphinane 2-oxide (5.0 g, 52%), m.p. 172—173 °C (lit.,[13] 174—175 °C); $\nu_{max.}$ 3 140s (NH), 1 248s, 1 218s (P=O), 1 077s, 1 034s, 1 024s, and 1 003s (POC) cm^{-1}.

(*b*) A solution of 2-anilino-4-methyl-1,3,2-dioxaphosphinane (4.2 g; composition: *cis*: *trans* 20:80) in ether (30 ml) was stirred at 0 °C. A solution of t-butyl hydroperoxide (2.2 g) in ether (20 ml) was added dropwise. Some precipitation occurred, but the complete mixture was evaporated. A homogeneous solution of the gummy residue in chloroform showed a signal at δ_P −3.8 p.p.m., along with other trace signals. Crystallization of the crude product from ethyl acetate gave *trans*-2-anilino-4-methyl-1,3,2-dioxaphosphinane 2-oxide (**2**; R = NHPh, X = O) (1.7 g), m.p. 155 °C (lit.,[13] 153—154 °C).

2-*Benzylamino*-4-*methyl*-1,3,2-*dioxaphosphinane* 2-*oxide* (**1**; **2**; R = NHCH$_2$Ph, X = O). (*a*) A solution of benzylamine (14.5 g) in benzene (100 ml) was added dropwise to a solution of the mixed stereoisomers (of unknown composition) of 2-chloro-4-methyl-1,3,2-dioxaphosphinane 2-oxide (13.2 g) in benzene (100 ml). After a further 1 h the mixture was filtered, and the filtrate was evaporated to leave a solid, pure by t.l.c., which

consisted of *cis*-2-benzylamino-4-methyl-1,3,2-dioxaphosphinane 2-oxide (**1**; R = $NHCH_2Ph$, X = O) (98%), m.p. 107.5—108 °C (from benzene) (lit.,[12] 105—108 °C); δ_P 5.8 p.p.m.; $\nu_{max.}$ 3 200s (NH), 1 235s (P=O), 1 073s, and 1 039s (POC) cm^{-1} (Found: C, 54.9; H, 6.7; N, 5.9. $C_{11}H_{16}NO_3P$ requires C, 54.75; H, 6.7; N, 5.8%).

(*b*) Oxidation of the mixed stereoisomers of 2-benzylamino-4-methyl-1,3,2-dioxaphosphinane with t-butyl hydroperoxide gave an oily product which consisted of a mixture of the stereoisomeric 2-oxides in the ratio *ca.* 1:1, but from which only small amounts of the *cis* isomer could be isolated. Chromatography also failed to produce a pure sample of the *trans* isomer, which was eventually isolated in chromatographically pure form by oxidation of the corresponding 2-selenide; even so the oily substance could not be crystallized, nor could a satisfactory analysis be obtained.

Crystal Data for (**1**; R = $NHBu^t$, X = O).—$C_8H_{18}NO_3P$, M = 207.2. Monoclinic, a = 11.304(1), b = 9.702(1), c = 11.386(1) Å, β = 116.16(2)°, v = 1 165.1 $Å^3$, space group $P2_1/n$, Z = 4, D_c = 1.18 g cm^{-3}, D_m = 1.17 g cm^{-3}. Crystal dimensions 0.2 × 0.2 × 0.08 mm.

Data were collected at room temperature for 23 setting angles measured on a Hilger-Watts Y290 diffractometer using monochromated molybdenum radiation, μ(Mo-K_α) = 2.2 cm^{-1}, λ = 0.710 69 Å, for reflections with $\theta < 25°$; 1 438 reflections were counted of which 823 had $I > 2\sigma(I)$ and were used in the refinement. MULTAN routinely found 10 non-hydrogen atoms and the rest were located in a difference map.

C, N, O, and P atoms were refined anisotropically (full matrix least-squares); hydrogens were included in calculated positions (the N–H hydrogen in a found position). An automatic Chebyshev weighting scheme gave a satisfactory agreement analysis and the final R and R_w values were 0.097 and 0.107. The standard deviations for bond lengths (Table 2) and bond angles (Table 3) (not involving hydrogen) were between 0.007 and 0.026 Å, and between 0.4 and 2.1°, respectively. Torsion angles and atomic co-ordinates are collected in Tables 4 and 5, respectively. Structure factors are given in Supplementary Publication No. SUP 23973 (9 pp.).*

The crystal diffracted weakly, giving broad diffuse spots, and the rather poor quality of the final result was therefore not unexpected.

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* For details of the Supplementary Publications Scheme see Instructions for Authors (1984), *J. Chem. Soc., Perkin Trans. 1*, 1984, Issue 1.

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