

Axial Preference of a 2-Anilino-substituent in 4-Methyl-1,3,2-dioxaphosphorinan †

By Wojciech J. Stec* and Andrzej Okruszek, Polish Academy of Sciences, Centre of Molecular and Macromolecular Studies, Department of Hetero-organic Compounds, 90-362 Łódź, Boczna 5, Poland

In contrast with a dimethylamino-substituent a 2-anilino-group prefers the axial orientation in 4-methyl-1,3,2-dioxaphosphorinan.

THE factors governing the orientations of 2-substituents (R) in 1,3,2-dioxaphosphorinans have received much attention recently. For phosphorus(III) compounds in this series, results¹⁻⁴ point to a thermodynamic preference for an axial orientation when R = halogen, alkoxy, alkyl, phenyl, or hydrogen. This conclusion has been inferred from dipole moment measurements,¹ analysis of n.m.r. spectra,² X-ray diffraction data,³ and reasoning based on the stereochemistry of chemical transformations.⁴ However, it has been reported recently by four independent groups that the 2-dimethylamino-group prefers an equatorial orientation. This conclusion was based on chemical correlations,⁵ dipole moment data,⁶ and n.m.r. investigations,⁷ and was explained in terms of the 'modified gauche effect.'^{5a,7a,8} X-Ray analyses of several 2-substituted 1,3,2-dioxaphosphorinan 2-

oxides have shown that substituents such as phenoxy, hydroxy, bromo, phenyl, and methyl prefer to occupy an axial position,^{3,9} with the phosphoryl oxygen atom equatorial, whereas dialkylamino-groups tend to occupy equatorial positions in the solid state.¹⁰

RESULTS AND DISCUSSION

We have been interested principally in 2-substituted 4-methyl-1,3,2-dioxaphosphorinans. We have previously¹¹ outlined a procedure for determining the stereochemical course (inversion and/or retention) of reactions in which nucleophiles attack the 2-phosphorus atom. We decided to follow, by means of chemical correlations and n.m.r. spectroscopy, the stereochemical course of the reaction of aniline with 2-chloro-4-methyl-1,3,2-

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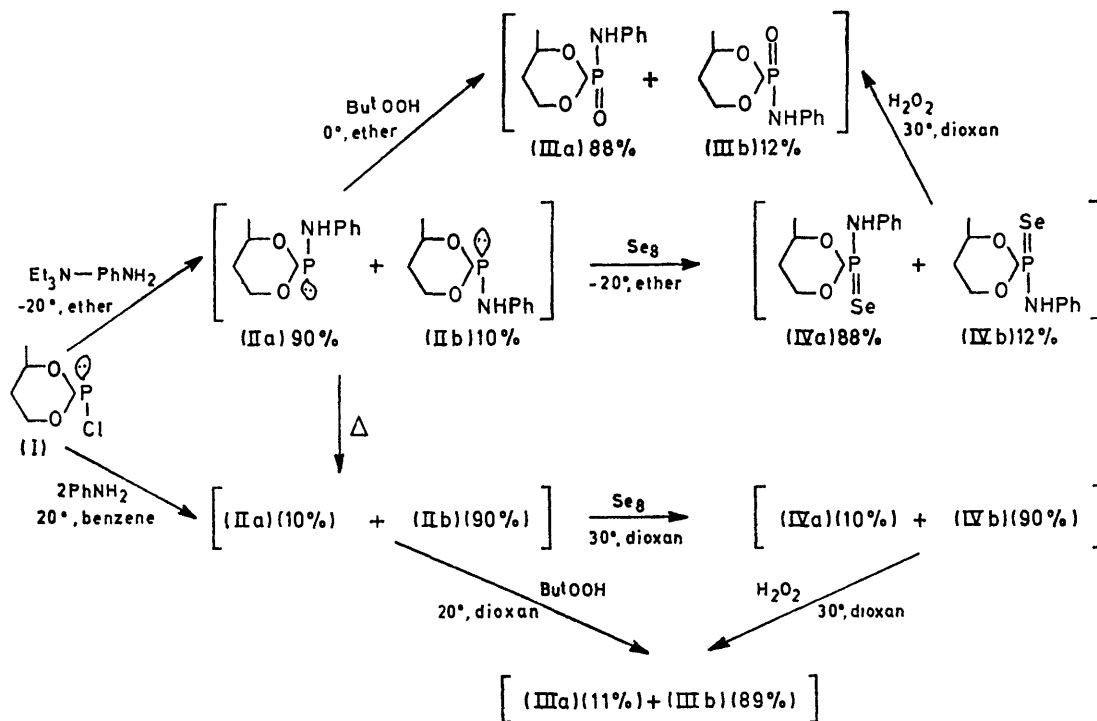
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dioxaphosphorinan (I). The product of this reaction (II) was described by Nifanteev¹² as being diastereoisomerically pure, but the stereochemistry was not determined. Since the stereochemistry of *cis*- and *trans*-2-anilino-4-methyl-1,3,2-dioxaphosphorinan 2-oxide (III) has been tentatively defined in our previous work,^{11a} stereospecific oxidation offered a way of determining the geometry of the dioxaphosphorinan (II). The distilled product of the condensation of (I) with aniline in benzene solution was a mixture of two isomers (IIa and b) in the ratio 10 : 90 (³¹P n.m.r. in benzene). Oxidation with *t*-butyl hydroperoxide in dioxan at 20 °C gave the 2-oxide (III) which, by ³¹P n.m.r. analysis,

presence of both (IIIa) (11%) and (IIIb) (89%). Because both the addition of selenium to P^{III} compounds¹⁴ and the oxidation of 4-methyl-1,3,2-dioxaphosphorinan 2-selenides with hydrogen peroxide¹⁵ are known to proceed with retention of configuration, the *trans*-geometry of (IIb) is confirmed. These conclusions are supported by ¹H and ¹³C n.m.r. data (see Tables 1 and 2). The ¹H n.m.r. spectrum of distilled (II) clearly showed that ³J(P,H-6eq) has a much smaller absolute value (11.7 Hz) than that in *cis*-2-dimethylamino-4-methyl-1,3,2-dioxaphosphorinan (21.0 Hz) which is characteristic of an axial orientation of the electron pair on phosphorus.^{7b} Also, the value of ³J(P,C-5) (4.4 Hz) indicates



SCHEME

was found to be a mixture containing 11% of the *cis*- (IIIa) and 89% of the *trans*- (IIIb) isomer. Because oxidation of P^{III} compounds with *t*-butyl hydroperoxide is known to proceed with retention of configuration at phosphorus,¹³ this result shows that the predominant isomer in the product (II) is the *trans* (see Scheme). Addition of elemental selenium to distilled (II) in dioxan solution gave the 2-selenide (IV) as a mixture of two isomers (IVa and b) in the ratio 10 : 90, respectively (³¹P n.m.r. analysis). Oxidation of this solution with 30% hydrogen peroxide enabled us to isolate pure (IIIb) in 86% yield. The ³¹P n.m.r. spectrum of the crude reaction mixture after oxidation showed the

a *trans*-configuration for (IIb).^{7b,16} The isomeric ratio of distilled (II) did not change in benzene or chloroform solution at room temperature.

The *trans* preference of (II) was unexpected in the light of the recently reported equatorial preference of dialkylamino-⁵⁻⁷ and methylamino-^{7a} substituents in 1,3,2-dioxaphosphorinans. We therefore made more detailed studies of the reaction of (I) with aniline. When this was carried out in ether in the presence of triethylamine at -20 °C, the ³¹P n.m.r. spectrum revealed the presence of (IIa) and (IIb) in the ratio 90 : 10, respectively. There was no case in which a content of (IIa) in the kinetically controlled product higher than 90% was observed, although several experiments were

¹² E. E. Nifanteev, *Zhur. obshchei Khim.*, 1971, **41**, 2011.

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¹⁵ W. J. Stec, A. Okruszek, and J. Michalski, *J. Org. Chem.*, in the press.

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carried out. The products were identified, as before by direct oxidation of the reaction mixture with *t*-butyl hydroperoxide, and by addition of selenium followed by oxidation of the resulting 2-selenides (IV) (see Scheme). Compound (II) obtained under kinetic control isomerizes slowly when stored at room temperature. Traces of acid seem to catalyse this reaction.

The predominant *cis*-disposition of the anilino-group in this kinetically controlled product was further supported by comparative analysis of the ^{13}C n.m.r. spectra of (IIa) and (IIb) (Table 2). The value of $^3J(\text{P},\text{C}-5)$ in the preponderant isomer (10.3 Hz) indicates an axial orientation of the lone electron pair on phosphorus.^{7b,16} Also, the up-field shift of the signals due to C-4 and C-6 in (IIb) with respect to those in (IIa) can be explained in terms of the so-called γ -effect, noted

2-anilino-substituent. Replacement of the chlorine atom in (I) (which is known to exist as the pure *trans*-isomer)^{2a} by aniline proceeds with inversion of configuration at phosphorus. However, the *cis*-anilino-derivative (IIa), being the 'kinetic product,' readily isomerizes to give an equilibrium mixture containing 90% of the more stable isomer (IIb). The difference in conformational preference of the dimethylamino- and the anilino-groups may be explained in terms of steric interactions between the 4- and 6-axial hydrogen atoms and the nitrogen substituents.^{5a,7a} Even if the electron pair on nitrogen has pure *p*-character (because of possible $2p-3d$ or $2p-2p$ overlap) and the requirement of perpendicularity between the lone pairs on nitrogen and phosphorus is valid,^{5a,7a,18} the interaction between the 4- and 6-axial hydrogen atoms and the hydrogen

TABLE 1
 ^1H N.m.r. spectral parameters for compound (IIb) in C_6D_6 (see Figure)

δ J/Hz	H_a 4.20		H_b 4.15		H_c 3.55		H_d 1.78		H_e 1.06		H_f 1.01			
	a,d	a,e	a,f	a,P	b,c	b,d	b,e	b,P	c,d	c,e	c,P	d,e	d,P	e,P
	11.5	2.8	6.6	3.5	11.7	12.5	2.8	3.5	4.7	2.3	11.7	14.7	1.0	1.0

TABLE 2
 ^{13}C and ^{31}P N.m.r. spectral parameters for compounds (II)—(V)

Compd.	Solvent	$\delta(\text{C}-4)$ (p.p.m.)	$^2J(\text{C}-4,\text{P})^b$ (Hz)	$\delta(\text{C}-6)^a$ (p.p.m.)	$^2J(\text{C}-6,\text{P})^b$ (Hz)	$\delta(\text{C}-5)^a$ (p.p.m.)	$^3J(\text{C}-5,\text{P})^b$ (Hz)	$\delta(\text{CH}_3)$ (p.p.m.)	$^3J(\text{CH}_3,\text{P})^b$ (Hz)	$\delta(^{31}\text{P})^c$ (p.p.m.)
(IIa)	C_6D_6	70.8	5.9	62.3	4.4	35.0	10.3	23.1	5.9	-136.0
(IIb)	C_6D_6	65.7	2.9	59.6	4.4	35.9	4.4	23.7	2.9	-121.0
(IIIa)	$(\text{CD}_3)_2\text{SO}$	75.3	5.9	66.6	2.9	33.0	5.9	22.4	8.8	+1.0
(IIIb)	$(\text{CD}_3)_2\text{SO}$	76.8	7.3	67.7	5.9	33.2	5.9	22.4	8.8	+4.5
(IVa)	C_6D_6	75.1	5.9	66.3	4.4	33.8	4.4	21.8	10.3	-62.5
(IVb)	$(\text{CD}_3)_2\text{SO}$	75.8	8.8	66.9	10.3	32.8	7.3	22.1	7.3	-60.0
(Va)	C_6D_6	74.6	4.4	66.1	5.9	33.8	4.4	22.0	10.3	-63.0
(Vb)	$(\text{CD}_3)_2\text{SO}$	76.0	8.8	67.1	8.8	32.7	7.3	21.9	8.8	-59.5

^a ± 0.1 p.p.m. ^b ± 1.5 Hz. ^c ± 0.5 p.p.m.

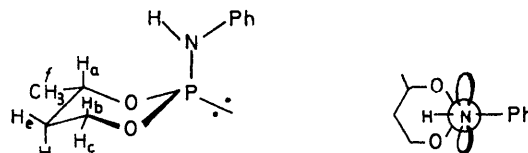
recently in substituted 1,3,2-dioxaphosphorinans,^{7a} and strongly implies the axial orientation of the *P*-substituent in (IIb).

When the reaction of (I) with aniline was carried out in ether at -20°C , in the presence of equimolar amounts of triethylamine and elemental selenium, we obtained the selenide (IVa) in 78% yield by column chromatography. The same procedure was used for the preparation of *cis*-2-anilino-4-methyl-1,3,2-dioxaphosphorinan 2-sulphide (Va). The *trans*-isomer (Vb) was obtained as the main product of the addition of elemental sulphur to an equilibrated mixture of anilino-derivatives (II).

Additional proof of the configuration of the isomeric selenides (IVa and b) was obtained from measurements of $^1J(^{31}\text{P},^{77}\text{Se})$. In the light of the recently reported relationship¹⁷ between the absolute value of $^1J(\text{P},\text{X})$ in 2-X-2-Y-4-methyl-1,3,2-dioxaphosphorinans and the orientation of X, a higher absolute value of $^1J(^{31}\text{P},^{77}\text{Se})$ indicates an equatorial disposition of the selenium atom [*trans* (IV)] and *vice versa*.

The above results show the stereochemical course of nucleophilic substitution at the P^{III} atom in our system and demonstrate the thermodynamic preference of the

attached to the anilino-nitrogen atom is less than that involving the *N*-methyl group in the corresponding dimethylamide (see Figure). For the same reason a



FIGURE

2-*t*-butylamino-group ($\text{R} = \text{NH}^t\text{Bu}$) prefers the axial orientation (30% *cis* and 70% *trans* at 25°C in benzene) whereas 2-*N*-methylanilino-substituent ($\text{R} = \text{NPhMe}$) in the preponderant isomer of 2-R-4-methyl-1,3,2-dioxaphosphorinan (80% *cis* and 20% *trans* at 25°C in benzene) is equatorially oriented.¹⁹ Further investigations are in progress.

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¹⁹ W. J. Stec and R. Kinas, unpublished results.

EXPERIMENTAL

Solvents and commercial reagents were distilled and dried by conventional methods before use. ^1H N.m.r. spectra were recorded at 60 MHz with a JEOL C-60 H spectrometer, equipped with hetero-spin-decoupler JNH-SD-HC (Me_4Si as internal standard). ^{31}P N.m.r. spectra were obtained on the same instrument operating at 24.3 MHz with external H_3PO_4 or $(\text{PhO})_3\text{P}$ as reference; chemical shifts are reported in p.p.m. to high field of H_3PO_4 . ^{13}C N.m.r. data were recorded on a Bruker-HX72 spectrometer with Me_4Si as internal standard. Mass spectra were obtained on an LKB-9000S spectrometer at 70 eV ionizing energy. The chloro-phosphite (I) was synthesized from butane-1,3-diol and phosphorus trichloride in dichloromethane.²⁰

(1) *Reaction of the Chloro-phosphite (I) with Aniline.*—(a) *trans-2-Anilino-4-methyl-1,3,2-dioxaphosphorinan (IIb)*. To a solution of compound (I) (30.8 g, 0.2 mol) in benzene (200 ml) was added dropwise at 20–30 °C, with vigorous stirring and occasional cooling, a solution of aniline (37.2 g, 0.4 mol) in benzene (100 ml). Stirring at this temperature was continued for 1 h. Aniline hydrochloride was filtered off and washed with benzene. The combined benzene solutions were evaporated and the residue was distilled under reduced pressure to give the anilino-derivative (II) (26 g, 62%) as a liquid, b.p. 99–101° at 0.02 mmHg, n_D^{20} 1.5575; m/e 119 (100%), 211 (80), 139 (16.4), 93 (26), and 55 (88) (Found: C, 55.7; H, 6.8; P, 14.9; N, 6.45. Calc. for $\text{C}_{10}\text{H}_{14}\text{NO}_2\text{P}$: C, 56.1; H, 6.7; P, 14.65; N, 6.65%), ^{31}P δ (neat) –136.0 [10%, (IIa)] and –121.0 p.p.m. [90%, (IIb)] (lit.,¹² δ –120.6 p.p.m.). A solution of distilled (II) in chloroform at room temperature did not show any change in the isomer ratio during 2 weeks.

(b) *cis-2-Anilino-4-methyl-1,3,2-dioxaphosphorinan (IIa)*. A solution of aniline (4.65 g, 0.05 mol) and triethylamine (5.1 g, 0.05 mol) in ether (20 ml) was added dropwise with vigorous stirring and cooling at –20 °C ($\text{Me}_2\text{CO}-\text{CO}_2$ bath) to a solution of compound (I) (7.7 g, 0.05 mol) in ether (30 ml). Stirring at this temperature was continued for 30 min and triethylamine hydrochloride was filtered off and washed with cold ether. The filtrate was carefully evaporated under reduced pressure to 30 ml. It was stored at –70 °C for further examination. The ^{31}P n.m.r. spectrum (ether; –20 °C) showed δ –136.0 [90%, (IIa)] and –121.0 p.p.m. [10%, (IIb)]. The ^1H n.m.r. spectrum (benzene) was too complex for first-order analysis. However, we were able to extract the spectral parameters for the 4-methyl group of (IIa): δ 0.92; $^3J(\text{CH}, \text{CH}_3)$ 6.0 Hz. The close overlap of the signals of C-4 and C-6 protons (m , δ ca. 3.95) suggests the conformational mobility of (IIa) at ambient temperature.

When the ethereal solution referred to above was warmed to room temperature a slow isomerization took place, and after 2 weeks ^{31}P n.m.r. analysis showed the presence of an equilibrium mixture containing 90% of (IIb) and 10% of (IIa). Dissolution in chloroform (after removal of the ether) considerably accelerates the equilibration.

(2) *Oxidation of the Anilino-derivative (II) with t-Butyl Hydroperoxide.*—(a) Into a solution of distilled (II) (4.22 g, 0.02 mol) in dioxan (30 ml) was added at 20 °C, dropwise, with stirring and cooling, a solution of t-butyl hydroperoxide (0.02 mol) in dioxan (10 ml). Stirring at room temperature was continued for 1 h. The ^{31}P n.m.r. spectrum of the resulting solution revealed the presence of

the 2-oxides (IIIa) (11%; δ +1.0 p.p.m.) and (IIIb) (89%; δ +4.5 p.p.m.). The solution was evaporated and the residue crystallized from ethyl acetate yielding the isomer (IIIb) (3.8 g, 84%), m.p. 153–155° [lit.,^{11a} m.p. 154–156°, ^{31}P δ +3.5 p.p.m. (methanol)].

(b) A solution of t-butyl hydroperoxide (0.02 mol) in dioxan (10 ml) was added dropwise, with stirring and cooling, at 0 °C, to an ethereal solution of (II) (0.02 mol) prepared as described in section (1b). Stirring at this temperature was continued for 1 h while precipitation of white crystals was observed. The resulting mixture was evaporated and crystallized from methanol yielding the 2-oxide (IIIa) (3.6 g, 80%), m.p. 173–175°. The ^{31}P n.m.r. spectrum of the crude product (dioxan; 50 °C) showed the presence of (IIIa) (88%, δ +1.0 p.p.m.) and (IIIb) (12%, δ +4.5 p.p.m.) [lit.^{11a} for (IIIa), m.p. 174–176°, ^{31}P δ +1.1 p.p.m. (Me_2SO)].

(3) *Addition of Selenium to the Anilino-derivative (II) followed by Oxidation with Hydrogen Peroxide.*—(a) Into a solution of distilled (II) (4.22 g, 0.02 mol) in dioxan (30 ml) was added, at 20 °C, with stirring and cooling, elemental selenium (1.58 g, 0.02 mol) in small portions. Stirring at room temperature was continued until the selenium had disappeared (10 min). The ^{31}P n.m.r. spectrum of the resulting solution revealed the presence of the 2-selenides (IVa) (10%, δ –62.5 p.p.m.) and (IVb) (90%, δ –60.0 p.p.m.).* 30% Hydrogen peroxide was then added dropwise with stirring and cooling at 30 °C. The reaction was exothermic and was accompanied by precipitation of red selenium. Stirring was continued for 15 min and the selenium (1.5 g) was filtered off and washed with dioxan. The ^{31}P n.m.r. spectrum of the resulting solution showed the presence of the 2-oxides (IIIa) (11%, δ +1.0 p.p.m.) and (IIIb) (89%, δ +4.5 p.p.m.). The solution was evaporated and the residue crystallized from ethyl acetate yielding pure (IIIb) (3.9 g, 86%), m.p. 153–155°.

(b) To an ethereal solution of (II) (0.02 mol) prepared as described in section (1b), a stoichiometric amount of elemental selenium was added, in small portions, at –20 °C, during 60 min. The resulting mixture was evaporated and the residue dissolved in dioxan (30 ml). The ^{31}P n.m.r. spectrum showed the presence of (IVa) (88%, δ –62.5 p.p.m.) and (IVb) (12%, δ –60.0 p.p.m.). The dioxan solution was oxidized as described in section (3a) to give (IIIa) (3.6 g, 80%), m.p. 173–175° (from methanol). The crude oxidation product contained 88% of (IIIa), ^{31}P δ +1.0 p.p.m., and 12% of (IIIb), ^{31}P δ +4.5 p.p.m. (dioxan; 50 °C).

(4) *Addition of Elemental Selenium to the Anilino-derivative (II).*—(a) *trans-2-Anilino-4-methyl-1,3,2-dioxaphosphorinan 2-selenide (IVb)*. A solution of aniline (9.3 g, 0.1 mol) and triethylamine (10.2 g, 0.1 mol) in benzene (50 ml) was added, with stirring at 30 °C to a solution of the chloro-phosphite (I) (15.4 g, 0.1 mol) in benzene (100 ml). The mixture was kept overnight at room temperature. Amine hydrochloride was filtered off and washed with benzene. To the resulting solution, elemental selenium (7.9 g, 0.1 mol) was added in small portions with stirring at 50 °C. The unchanged selenium was filtered off and the filtrate was evaporated. Crystallization of the residue from methanol gave the pure selenide (IVb) (23.0 g, 79%)

* For full identification of (IVa and b) see section (4).

²⁰ W. J. Lucas, F. W. Mitchell, and C. N. Scully, *J. Amer. Chem. Soc.*, 1950, **72**, 5491.

as white crystals, m.p. 166–167°, ^{31}P δ –60.0 p.p.m. (dioxan), $^1\text{J}(^{31}\text{P},^{77}\text{Se})$ 942 Hz; δ_{H} (CDCl_3) 1.45 (Me), $^4\text{J}(\text{P},\text{CH}_3)$ 1.6 Hz, $^3\text{J}(\text{CH},\text{CH}_3)$ 6.6 Hz; m/e 291 (100%), 289 (53), 237 (75), 235 (35), 156 (58), 93 (83), and 55 (95%) (Found: C, 41.1; H, 4.85; P, 10.85; N, 5.2. $\text{C}_{10}\text{H}_{14}\text{NO}_2^-$ PSe requires C, 41.4; H, 4.85; P, 10.7; N, 4.85%). Oxidation with 30% hydrogen peroxide in dioxan solution, according to the procedure described in section (3a), gave pure (IIIb), m.p. 154–156°, in 93% yield.

(b) *cis-2-Anilino-4-methyl-1,3,2-dioxaphosphorinan 2-selenide* (IVa). To a solution of aniline (9.3 g, 0.1 mol) and triethylamine (10.2 g, 0.1 mol) in ether (150 ml) containing a suspension of an equimolar amount of fine powdered selenium was added dropwise at –20 °C a solution of the chloro-phosphite (I) (15.4 g, 0.1 mol) in ether (50 ml), with vigorous stirring and cooling. Stirring at this temperature was continued for 1 h. The resulting amine hydrochloride was filtered off and washed with ether. The solution was evaporated and the residue chromatographed (300 g of silica gel, 100–200 mesh) in benzene. The separation was followed by t.l.c. [Silufol UV254 plates; benzene as developing system; R_{F} 0.02 (IVb) and 0.18 (IVa)]. Evaporation gave pure *selenide* (IVa) as white crystals (22.5 g, 78%), m.p. 95–96° (from benzene–hexane), ^{31}P δ –62.5 p.p.m. (benzene), $^1\text{J}(^{31}\text{P},^{77}\text{Se})$ 887 Hz; δ_{H} (CDCl_3) 1.37 (Me), $^4\text{J}(\text{P},\text{CH}_3)$ 2.0 Hz, $^3\text{J}(\text{CH},\text{CH}_3)$ 6.4 Hz; m/e 55 (100%), 291 (71.4), 289 (37.7), 237 (36.8), 235 (18.4),

156 (36.6), and 93 (64.8) (Found: C, 41.5; H, 5.15; P, 10.05; N, 5.1%). Oxidation with 30% hydrogen peroxide in dioxan solution, as described in section (3a), gave pure (IIIa), m.p. 174–176°, in 94% yield.

(5) *Addition of Sulphur to the Anilino-derivative* (II).—(a) *trans-2-Anilino-4-methyl-1,3,2-dioxaphosphorinan 2-sulphide* (Vb). The procedure described in section (4a) was carried out with sulphur in place of selenium and gave an 82% yield of the *sulphide* (Va) as white crystals, m.p. 171–172° (from methanol), ^{31}P δ –59.5 p.p.m. (dioxan); δ_{H} (CDCl_3) 1.45 (Me), $^4\text{J}(\text{P},\text{CH}_3)$ 1.6 Hz, $^3\text{J}(\text{CH},\text{CH}_3)$ 6.6 Hz; m/e 189 (100%), 243 (92), 171 (23), 155 (18.6), and 93 (69) (Found: C, 48.9; H, 5.9; P, 12.4; N, 5.45. $\text{C}_{10}\text{H}_{14}\text{NO}_2\text{PS}$ requires C, 49.4; H, 5.8; P, 12.75; N, 5.75%).

(b) *cis-2-Anilino-4-methyl-1,3,2-dioxaphosphorinan 2-sulphide* (Va). The procedure described in section (4b) was carried out with sulphur in place of selenium and gave a 68% yield of pure (Va) as white crystals, m.p. 91–92° (benzene–hexane), ^{31}P δ –63.0 p.p.m. (benzene); δ_{H} (CDCl_3) 1.31 (Me), $^4\text{J}(\text{P},\text{CH}_3)$ 2.0 Hz, $^3\text{J}(\text{CH},\text{CH}_3)$ 6.4 Hz; m/e 243 (100%), 189 (65.8), 171 (25.8), 155 (16.2), and 93 (57.2) (Found: C, 49.3; H, 6.0; P, 12.45; N, 5.9%).

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