Synthesis of Substituted Dibenzophospholes. Part 4. Chemical Transformations of 4,6-Diaryl-3,7-dialkoxydibenzophosphole 5-Oxides †

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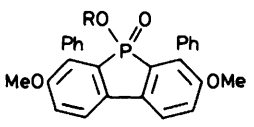
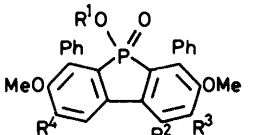
Studies of 4,6-diaryl-3,5,7-trimethoxydibenzophosphole 5-oxides reported here include (*a*) electrophilic substitution (chlorination, bromination, and nitration) in the dibenzophosphole ring system and in the aryl side-chains; (*b*) dealkylations of the ether groups at positions 3, 5, and 7; and (*c*) attachment of water-solubilizing groups to the oxygen atoms at positions 3 and 7.

WE described in Part 3 [1] a general synthesis of molecules of type (1). For the elaboration of substances designed to catalyse the hydration of olefins in an enzyme-like manner, it was desirable to explore the possibilities

All R^n = H unless stated otherwise

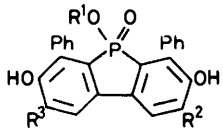


(1)



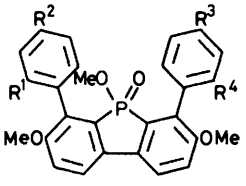
(2)

a; R^1 = Me
b; R^1 = Me, R^2 = Br
c; R^1 = Me, R^2 = Cl
d; R^1 = Me, R^3 = Cl
e; R^1 = Me, R^2 = R^4 = Cl
f; R^1 = Me, R^3 = R^4 = Cl
g; R^1 = Me, R^2 = R^3 = R^4 = Cl
h; R^1 = Me, R^2 = NO_2
i; R^1 = Me, R^2 = R^4 = NO_2
j; R^1 = Me, R^2 = NO_2, R^3 = R^4 = Cl
k; R^1 = Ac
l; R^1 = CH_2CH_2OH



(3)

a; R^1 = Me
b; R^1 = Me, R^2 = R^3 = Cl



(4)

a; R^2 = R^3 = NO_2
b; R^2 = R^4 = NO_2
c; R^1 = R^4 = NO_2

for chemical modification of substances of this type. The explorations in this paper concern (i) electrophilic substitution; (ii) modification of functional groups generally to confer solubility of the whole molecule in water.

Electrophilic Substitution.—Bromination of 3,5,7-trimethoxy-4,6-diphenylbenzophosphole (2a) in chloroform gave, smoothly and somewhat unexpectedly, the 1-bromo-derivative (2b). The assignment of structures to this and other substitution products was made easier by the characteristic J 4.5 Hz splitting, due to the phosphorus atom, of the n.m.r. signals for hydrogen at positions 1 and 9. Since these resonances are also coupled (J 8—9 Hz) with those of the 2 and 8 hydrogens respectively, the presence or absence of hydrogen at any of these four positions was generally simple to deduce. In addition, the chemical shift of the 3- and 7-methoxy-group hydrogens was altered significantly by substitution at positions 2 and 8. A halogen at position 1 caused a marked downfield shift in the signal for 9-H; this effect was much less for the nitro-derivatives (below).

The bromination was always incomplete (*ca.* 50%) when compound (2a) and bromine were mixed in chloroform, and the high yield (88%) eventually attained was the result of subsequent slow addition of sodium acetate. Evidently, salt formation between the product hydrogen bromide and a basic centre of compound (2a) (probably the P=O group; see later) can inhibit bromination.

The reaction of (2a) with chlorine was more complex and it depended on the solvent used. In chloroform, mixtures too difficult to separate were formed; but the presence of the 1- and 2-monochloro-derivatives (2c) and (2d), the 1,8- and 2,8-dichloro-derivatives (2e) and (2f), and the 1,2,8-trichloro-derivatives (2g) was inferred from the n.m.r. spectra of different mixtures produced by different proportions of chlorine. Chlorination at −10 °C in trifluoroacetic acid gave a similar range of products, but with much larger proportions of material chlorinated at positions 2 or 8, or both. No completely pure product was isolated and these chlorinations have little preparative value. In this and in the other substitutions, no indication of 1,9-disubstitution was observed. This is not surprising since two substituents larger than fluorine would obstruct each other. Demethylation (see below) of compound (2a) gave, after re-esterification, the 3,7-diol (3a). Reaction of this with chlorine was apparently complicated by oxidation, probably to diphenoquinones, and mixtures were again formed. Chlorination in acetic acid and methylation of the product obtained, sometimes after reduction with dithionite, gave a product analysed as a mixture of compound (2f) and (2g), from which the latter (and major) component was obtained pure. In acetic acid–hydrochloric acid chlorination of compound (3a) with toluene-4-sulphonyldichloroamide (Dichloramine-T) proceeded smoothly without significant oxid-

† No reprints available.

ation and the 2,8-dichloro-derivative (3b) [from which compound (2f) was made by methylation] was isolated in 80—85% yield.

Nitration of (2a) by the usual reagents (acetyl nitrate; nitric acid–sulphuric acid) proceeded rapidly to give complex mixtures; but cautious addition of fuming nitric acid to a solution of compound (2a) in acetic acid allowed isolation of the 1-nitro-derivative (2h) in 82% yield. Further nitration of (2h), in trifluoroacetic acid at −15 °C with potassium nitrate, gave a 90% yield of the 1,8-dinitro-derivative (2i), also obtainable directly (73% yield) from (2a) and the same reagent. Again with the same reagent, the 2,8-dichloro-derivative (2f) readily afforded the 2,8-dichloro-1-nitro-derivative (2j).

In contrast, when potassium nitrate (2 equiv.) was dissolved in a mixture of dichloromethane and trifluoromethanesulphonic acid, and the ester (2a) (1 equiv.) was added to this mixture at −40 °C, a product was formed from which three components were separated with some difficulty. These were identified as the dinitro-derivatives (4a), (4b), and (4c), resulting from mononitrations of both the benzene rings attached at positions 4 and 6.

This complete switch in the type of substitution can again be attributed to salt formation. It would appear that the positions 1, 2, 8, and 9 of (2a) are intrinsically the most susceptible to electrophilic substitution, but that in the presence of a strong enough acid the concentration of free (2a) can be depressed sufficiently to allow substitution at the 2, 4, and 6 positions of the phenyl substituents, less reactive intrinsically but less affected in their reactivity by salt formation.

Comparison of the recorded basicities of methyl diphenylphosphinate (pK_{BH^+} −4.8 [2]) and phenolic ethers (pK_{BH^+} *ca.* −6.5 [3]) suggests that the primary site of protonation in (2a) is the P=O group rather than the methoxy-groups at positions 3 and 7. The effects (see Table) on the chemical shifts in the n.m.r. spectra of

Chemical shifts (δ) of n.m.r. signals of protons of 3,5,7-trimethoxy-4,6-diphenyldibenzophosphole 5-oxide

Solvent	1-,9-H	2-,8-H	Ph	P(O)OMe	3-, 7-OMe
$CDCl_3$	7.55	7.00	7.37	2.60	3.73
CF_3CO_2H	7.82	7.38 [a]	7.40	3.10	3.95
Δδ (p.p.m.)	−0.27	−0.38	−0.03	−0.50	−0.22

[a] Approximate value: signal partially obscured.

compound (2a) on changing the solvent from chloroform to trifluoroacetic acid support the view that in the more acidic solvent protonation or strong hydrogen bonding has affected the whole dibenzophosphole system without having much effect on the attached phenyl groups. Addition of hydrogen bromide to a chloroform solution of compound (2a) caused complete precipitation of a solid, presumably a phospholium salt. Incidentally, aluminium chloride was found to form a chloroform-soluble complex with compound (2a) and, perhaps because of complex formation, the ester could not be acylated in normal Friedel–Crafts conditions.

Modification of Functional Groups.—As mentioned in Part 3,[1] conversion of the phosphinic esters (2a) and (5a) into the corresponding acids was conveniently effected by treatment with a chloroform solution of iodotrimethylsilane at room temperature (method of Jung and Lyster [4]), or with lithium iodide in dimethylformamide (DMF);[5] the latter reagent with the ester (5a) gave a lithium salt crystallizable from acetone–diethyl ether. For demethylation of the 3 and 7 methoxy-groups in compound (2a), prolonged heating with iodotrimethylsilane in chloroform or with lithium ethanethiolate in hexamethylphosphoramide [6] were effective, but it was quicker and easier to use boron tribromide in dichloromethane.[7] For convenience in handling the phenolic derivatives the phosphinic acid group was generally re-esterified [*e.g.* to compound (3a)] after demethylations: treatment with lithium carbonate and methyl iodide in cold DMF or acetone was found a convenient and selective method.

The presence of t-butyl groups and of two additional methoxy-groups in (5a) complicated the problem of

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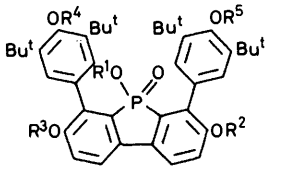
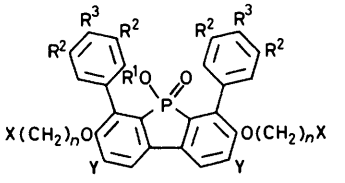


(5b)

a; $R^1 = R^2 = R^3 = R^4 = R^5$ = Me
c; $R^4 = R^5$ = Me
d; $R^1 = R^4 = R^5$ = Me
e; $R^1 = R^5$ = Me



(6)

a; R^1 = Me, X = OH, Y = Cl, n = 2
b; R^1 = CH_2CH_2OH, X = OH, Y = Cl, n = 2
c; R^1 = Me, X = OTs, Y = Cl, n = 2
d; R^1 = Me, X = I, Y = Cl, n = 2
e; R^1 = Me, X =  , Y = Cl, n = 2
f; X = SO_3H, Y = H, n = 3
g; R^1 = Me, X = $P(O)(OMe)_2$, Y = H, n = 4
h; R^1 = Me, R^2 = Bu^t, R^3 = OMe, X = P(O)(OEt)(OMe), Y = H, n = 3
i; R^2 = Bu^t, R^3 = OMe, X = P(O)(OEt)OH, Y = H, n = 3
j; R^2 = Bu^t, R^3 = OMe, X = $P(O)(OH)_2$, Y = H, n = 3

demethylation. Sodium ethanethiolate in DMF gave total demethylation to (5b), and pyridine hydrochloride removed some of the t-butyl groups as well. Better selectivity was obtained with methylmagnesium iodide, when the 3,7-diol (5c) [ester (5d)] could be obtained in reasonable yield; an impure specimen of the triol (5e)

was obtained in the course of these experiments. Gentle treatment with boron tribromide gave an impure monophenol, identified only by mass spectroscopy, and iodotrimethylsilane was unselective, giving a mixture of (5d) and (5e).

The oxygen substitution at positions 3 and 7 was designed for carrying water-solubilizing groups, and some orienting experiments were made in this direction. Reaction of the phenolic ester (3b) with an ionizing base (usually potassium carbonate) and 2-chloroethyldimethylamine, 2-(methoxymethoxy)ethyl iodide, 2-(2-tetrahydropyranyloxy)ethyl iodide, 3,5-8-trioxanonyl iodide, 2-chloroethanol, and ethylene oxide (with ethyldi-isopropylamine) gave uniformly incomplete and unsatisfactory conversion. It was therefore surprising to find that the phenol (3b) was smoothly converted into its di-2-hydroxyethyl ether (6a) by heating it with 2-iodoethanol and potassium carbonate in glyme. The product was accompanied by some of the 2-ethoxyethyl ester (6b), presumably formed by demethylation (by iodide ion) and esterification of the resulting potassium salt. Ethylene oxide could not replace 2-iodoethanol in this procedure. From the ether (6a) the di-iodide (6d) was prepared without difficulty *via* the toluene-4-sulphonate (6c), and it reacted easily with morpholine (as it does with other secondary amines) to yield, after re-esterification, the bis-morpholinoethyl ester (6e) which formed water-soluble salts.

Attachment of acidic groups (sulphonic or phosphonic acids) at positions 3 and 7 was also studied. The disodium salt of compound (3a) in methanol with propane sultone gave, after hydrolysis, the water-soluble disulphonic acid (6f), isolated as the crystalline barium salt. Again, compound (3a), by successive reactions with 1,4-dibromobutane, sodium iodide, and trimethyl phosphite, gave the diphosphonate (6g), and another diphosphonate (6h) was prepared from compound (5d) by condensation with di-3-bromopropyl phosphonate followed by hydrolysis.

Among miscellaneous transformations effected in the course of this work were the preparation of the mixed anhydride (2k) and the 2-hydroxyethyl ester (2l), and the reduction of the nitro-compound (2h) to the corresponding amine.

EXPERIMENTAL

For general directions see Part 2.[8]

1-Bromo-3,5,7-trimethoxy-4,6-diphenyldibenzophosphole 5-Oxide (2b).—To a rapidly stirred solution of the phosphinic ester (2a) (221 mg) in chloroform (10 ml) was added bromine (160 mg) in chloroform (5 ml). After 15 min, sodium acetate (0.5 g) was added gradually during 1 h. The mixture was diluted (10% aqueous $NaHSO_3$; 20 ml) and the chloroform layer was washed (water), dried, and evaporated. Crystallization of the residue from methanol gave colourless prisms, m.p. 238—240 °C, which remained solvated after drying *in vacuo* at room temperature; after drying at 110 °C for 2 days the unsolvated *monobromide* (2b) (230 mg) was obtained, m.p. 224—225 °C (Found: C, 61.9; H, 4.2; Br, 15.3. $C_{27}H_{22}BrO_4P$ requires C, 62.2; H, 4.2; Br, 15.3%); δ 2.48 (3 H, d, *J* 11.5 Hz, 5-OMe), 3.72 and 3.74 (6 H, 2 s, 3-,7-OMe), 7.13br (1 H, d, *J* 9 Hz, 8-H), 7.26br (1 H, s, 2-H), 7.42br (10 H, s, 2 × Ph), and 8.89 (1 H, dd, *J* 9, 4.5 Hz, 9-H); $\lambda_{max.}$ ($\varepsilon_{max.}$) 360 (1 500), 305 (9 700), 289 (9 600), 250sh (15 000), and 236 nm (18 000).

2,8-Dichloro-3,5,7-trimethoxy-4,6-diphenyldibenzophosphole 5-Oxide (2f).—3,7-Dihydroxy-5-methoxy-4,6-diphenyldibenzophosphole 5-oxide (3a) (107 mg) (see below for preparation) was suspended in acetic acid (4 ml) and 2M hydrochloric acid (0.2 ml); the mixture was warmed briefly, cooled, and treated with toluene-4-sulphonyldichloroamide (63.5 mg) in acetic acid (4 ml) very slowly (0.5 h) dropwise with stirring. Water (1 ml) was added and sulphur dioxide was passed briefly to discharge a dark colour; then more water (50 ml) was added. The product was collected, dried (106 mg), and methylated in dichloromethane (ethereal diazomethane; overnight). The *dichloride* (2f) crystallized from methanol as colourless needles, m.p. 217—221 °C (Found: C, 63.3; H, 4.1; Cl, 14.0. $C_{27}H_{21}Cl_2O_4P$ requires C, 63.4; H, 4.1; Cl, 13.9%); δ 2.63 (3 H, d, *J* 11.5 Hz, 5-OMe), 3.50 (6 H, s, 3-,7-OMe), 7.3—7.6 (10 H, m), and 7.73 (2 H, d, *J* 4.5 Hz, 1-,9-H); $\lambda_{max.}$ ($\varepsilon_{max.}$) 351 (1 600), 310sh (8 630), 298 (11 200), 277 (25 750), and 261 nm (32 700).

2,8-Dichloro-3,7-dihydroxy-5-methoxy-4,6-diphenyldibenzophosphole 5-Oxide (3b).—To a vigorously stirred suspension of the 3,7-diol (3a) (1.656 g) in acetic acid (40 ml) containing 1M hydrochloric acid (4 ml) was added at room temperature a solution of toluene-4-sulphonyldichloroamide (1.01 g) in acetic acid (40 ml) dropwise over 1 h. After 0.5 h more, sodium hydrogensulphite (4 ml, 10% aqueous) was added and the mixture was diluted with water to 400 ml). The precipitate, when solid, was collected, washed with water, sucked dry, and boiled with ethanol (120 ml) and activated charcoal (0.25 g) for 2 h. The mixture was filtered hot and concentrated to 50 ml when the *dichloro-compound* (3b) crystallized slowly. Two crops were collected to give a total yield of 1.797 g (93%). The analytical sample, very pale yellow cubes (from methanol), had m.p. 276—279 °C (Found: C, 62.0; H, 3.5; Cl, 14.9. $C_{25}H_{17}Cl_2O_4P$ requires C, 62.1; H, 3.6; Cl, 14.7%); *m/e* 484 (M^+, 68%), 482 (M^+, 100), 451 (22), and 449 (28); $\lambda_{max.}$ ($\varepsilon_{max.}$) 375i (1 620), 350sh (2 800), 315sh (15 600), 304 (18 000), 276 (23 800), and 265 nm (26 100); $\nu_{max.}$ 3 400—3 100, 1 585, 1 428, 1 310, 1 165, 1 130, 1 037, 968, and 702 cm^{-1}. The *diacetate* (3,7-diacetoxy-2,8-dichloro-5-methoxy-4,6-diphenyldibenzophosphole 5-oxide) obtained by treatment with acetic anhydride and pyridine, formed as prisms, m.p. 227—229 °C (Found: C, 61.4; H, 3.7; Cl, 12.7. $C_{29}H_{21}Cl_2O_6P$ requires C, 61.4; H, 3.7; Cl, 12.5%); δ 2.00 (6 H, s, 2 × Ac), 2.64 (3 H, d, *J* 11.5 Hz, 5-OMe), 7.40br (10 H, s, 2 × Ph), and 7.80 (2 H, d, *J* 3.5 Hz, 1-,9-H); $\nu_{max.}$ 1 768, 1 190, 1 036, 882, 870, and 706 cm^{-1}.

1,2,8-Trichloro-3,5,7-trimethoxy-4,6-diphenyldibenzophosphole 5-Oxide (2g).—The diol (3a) (83 mg) (see below for preparation) was suspended and stirred in acetic acid (15 ml). Chlorine was bubbled gently into the mixture for 5 min. The clear, golden solution was heated to boiling and most of the acetic acid was boiled off. Chloroform was added and the chloroform solution was washed (aqueous $NaHCO_3$), dried, and evaporated. The residue was methylated in dichloromethane (ethereal diazomethane, overnight). The product in chloroform was passed through alumina when a colourless fore-run containing the product and the eluate from a following yellow band were collected and combined. Crystallization from ethanol gave the *trichloride*

(2g) (34 mg) as very pale yellow cubes, m.p. 246—249 °C (Found: C, 59.5; H, 3.7; Cl, 19.7. $C_{27}H_{20}Cl_3O_4P$ requires C, 59.4; H, 3.7; Cl, 19.5%); *m/e* 544, 546, 548, and 550 (M^+, 100%, trichloro-pattern); δ 2.50 (3 H, d, *J* 12 Hz, 5-OMe), 3.53 (6 H, s, 3-,7-OMe), 7.45br (10 H, s, 2 × Ph) and 8.85 (1 H, d, *J* 4.5 Hz, 9-H); $\lambda_{max.}$ ($\varepsilon_{max.}$) 348 (2 540), 311sh (6 960) 300 (9 400), 276 (21 700), and 263 nm (28 300).

Chlorinations of 3,5,7-*Trimethoxy*-4,6-*diphenyldibenzophosphole* 5-*Oxide* (2a).—(a) *In chloroform.* To a solution of the phosphinic ester (0.44 g; 1 mmol) in chloroform (1 ml) at 0 °C was added a solution of chlorine in chloroform (1M). The mixture, after 4 h at 0 °C, was diluted with aqueous sodium hydrogensulphite (10%). The organic layer was washed (water), dried, and evaporated and the residue was examined (n.m.r.).

With 1 mmol of chlorine the product was deduced to be a mixture of *ca.* equal amounts of the monochloro-derivatives (2c) and (2d); δ 2.50 [d, *J* 11.5 Hz, 5-OMe in (2c)], 2.68 [d, *J* 11.5 Hz, 5-OMe in (2d)], 3.45 [s, 3-OMe in (2d)], 3.73 [3 unresolved s; 3-,7-OMe in (2d) and 7-OMe in (2c)], 7.00br [s, 2-H in (2c)], 7.4br (s), and 8.77 [dd, *J* 9.0, 5.5 Hz, 9-H in (2c)]. The integrations at δ 8.77 and 3.45, and the peak heights of signals at δ 2.68 and 2.50, decided the proportions assigned.

With 6 mmol of chlorine the product was deduced similarly to be a mixture of (2e), (2f), and (2g) in the proportions *ca.* 1 : 2 : 3.

(b) *In trifluoroacetic acid.* To a stirred solution of the phosphinic ester (2a) (1 g) in trifluoroacetic acid (10 ml) at −10 °C was added a solution of chlorine (0.47 g) in trifluoroacetic acid (5 ml). The mixture, initially fluorescent green, was colourless after 2 h. It was poured into ice–water (200 ml) in which sodium pyrosulphite (2 g) had been dissolved. The mixture was extracted with dichloromethane (2 × 100 ml) which was then washed [water (100 ml) saturated $NaHCO_3$ (100 ml), brine (100 ml)], dried, and evaporated. Recrystallization from ethanol then gave colourless needles (0.61 g, m.p. 215—220 °C, then 0.41 g, m.p. 216—219 °C); a second crystallization gave 0.84 g, m.p. 218—220 °C. The n.m.r. spectrum was that of a 9 : 1 mixture of the 2,8-dichloro- (2f) and the 1,2,8-trichloro- (2g) derivatives.

3,5,7-*Trimethoxy*-1-*nitro*-4,6-*diphenyldibenzophosphole* 5-*Oxide* (2h).—To a stirred solution of the phosphinic ester (2a) (0.5 g) in acetic acid (25 ml) was added nitric acid (1 ml, *d* 1.5) dropwise during 5 min. The mixture was stirred at room temperature for 1.5 h, then poured into ice–water, and extracted with dichloromethane. The washed (saturated $NaHCO_3$, water) and dried extract was evaporated and the residue, in dichloromethane, was passed through alumina. Trituration with diethyl ether then gave the yellow 1-*nitro-derivative* (2h) which crystallized from dichloromethane–ethanol as yellow prisms (0.45 g, 82%), m.p. 272—276 °C (superficially discoloured with time in air) (Found: C, 66.5; H, 4.5; N, 2.8. $C_{27}H_{22}NO_6P$ requires C, 66.5; H, 4.5; N, 2.9%); δ 2.50 (3 H, d, *J* 11.5 Hz, 5-OMe), 3.74 and 3.76 (6 H, 2s, 3-, 7-OMe), 7.00br (1 H, d, *J* 8.5 Hz, 8-H), 7.15br (1 H, s, 2-H), 7.40br (10 H, s), and 7.44 (1 H, dd, *J* 8.5, 4.5 Hz, 9-H); $\nu_{max.}$ 1 529 (NO_2), 1 039, 877, 794, and 700 cm^{-1}. On hydrogenation in ethyl acetate over platinum (from the oxide), this compound was converted almost quantitatively into 1-amino-3,5,7-trimethoxy-4,6-diphenyldibenzophosphole 5-oxide, obtained as plates (from dichloromethane–methanol), m.p. 245—246 °C; δ 2.55 (3 H, d, *J* 11.5 Hz, 5-OMe), 3.63 and 3.70 (6 H, 2 s, 3-, 7-OMe), 6.33br (1 H, s, 2-H), 7.00br (1 H, d, *J* 8.5 Hz, 8-H), 7.40br (10 H, s, 2 × Ph), and 7.73 (1 H, dd, *J* 8.5, 4.5 Hz, 9-H).

3,5,7-*Trimethoxy*-1,8-*dinitro*-4,6-*diphenyldibenzophosphole* 5-*Oxide* (2i).—(*a*) The phosphinic ester (2a) (221 mg) in trifluoroacetic acid (10 ml) was stirred at −14 °C during addition (15 min) of potassium nitrate (126 mg). After 2 h at −5 °C the solution, at first deep green and then brown-black, was poured into ice–water and the product was worked up as in the preceding experiment. The eluate from alumina gave a residue that crystallized directly from dichloromethane–methanol to yield the *dinitro-compound* (2i) (194 mg) as yellow cubes, m.p. 198—199 °C (Found: C, 60.8; H, 4.0; N, 5.1. $C_{27}H_{21}N_2O_8P$ requires C, 60.9; H, 4.0; N, 5.3%); δ 2.53 (3 H, d, *J* 11.5 Hz, 5-OMe), 3.47 (3 H, s, 7-OMe), 3.87 (3 H, s, 3-OMe), 7.40 (11 H, m), and 7.80 (1 H, d, *J* 4.5 Hz, 9-H).

(*b*) The 1-nitro-compound (2h) (100 mg), nitrated in the same manner (−5 °C overnight) with potassium nitrate (1.2 equiv.), gave the same dinitro-compound (2i) (98 mg; 90%), m.p. 198—199 °C. The substance, like the mononitro-compound, became discoloured when kept.

2,8-*Dichloro*-1-*nitro*-3,5,7-*trimethoxy*-4,6-*diphenyldibenzophosphole* 5-*Oxide* (2j). The dichlorophosphinic ester (2f) (0.6 g) in trifluoroacetic acid (10 ml) was nitrated at 0 °C (16 h) with potassium nitrate (0.24 g). The mixture was worked up as in the previous example to yield the 2,8-*dichloro*-1-*nitro-derivative* as almost colourless cubes, m.p. 245—247 °C (from dichloromethane–methanol) (Found: C, 58.1; H, 3.6; Cl, 13.1; N, 2.2. $C_{27}H_{20}Cl_2NO_6P$ requires C, 58.3; H, 3.6; Cl, 12.8; N, 2.5%); δ 2.53 (3 H, d, *J* 11.5 Hz, 5-OMe), 3.50 and 3.53 (6 H, 2 s, 3-,7-OMe), and 7.50br (11 H, s); $\lambda_{max.}$ ($\varepsilon_{max.}$) 317 (1 200), 285sh (4 300), 274sh (5 000), and 215 nm (23 000).

Nitration of the Phosphinic Ester (2a) *in Trifluoromethanesulphonic Acid.*—Potassium nitrate (0.23 g) was stirred at room temperature with a mixture of dichloromethane (50 ml) and trifluoromethanesulphonic acid (5 ml) until it dissolved (*ca.* 10 min). The mixture was stirred at −40 °C and the phosphinic ester (2a) (0.442 g) in dichloromethane (0.5 ml) was added. The mixture became discoloured and a black oil was formed. After 6 h at −30 °C iced water (100 ml) and dichloromethane (100 ml) were added. The organic layer was washed (water, aqueous $NaHCO_3$, brine), dried, and put through a small alumina column. The pale yellow eluate on evaporation left a pale yellow powder (0.35 g), which appeared homogeneous in all t.l.c. systems except ethyl acetate–dichloromethane (3 : 17) which gave partial separation of three components. Preparative t.l.c. (twice) with this solvent gave eluates from the three bands, and these were recrystallized. The most mobile component was 3,5,7-*trimethoxy*-4,6-*di*-(4-*nitrophenyl*)*dibenzophosphole* 5-*oxide* (4a) which crystallized from dichloromethane–acetone, m.p. 288—291 °C (Found: C, 60.9; H, 4.4; N, 5.3. $C_{27}H_{21}N_2O_8P$ requires C, 60.9; H, 4.0; N, 5.3%); δ 2.78 (3 H, d, *J* 11.5 Hz, 5-OMe), 3.78 (6 H, s, 3-,7-OMe), 7.20br (2 H, d, *J* 8.5 Hz, 2-,8-H), 7.73 (4 H, d, *J* 9 Hz, 2-, 6-H of 4-nitrophenyl), 7.80 (2 H, dd, *J* 8.5, 4.5 Hz, 1-,9-H), and 8.31 (4 H, d, *J* 9 Hz, 3-,5-H of 4-nitrophenyl); $\lambda_{max.}$ ($\varepsilon_{max.}$) 376 (3 400), 293 (35 000), 259 (33 000), and 247 nm (30 000); $\nu_{max.}$ 1 603, 1 531, 1 516, 1 035, 822, and 692 cm^{-1}.

The middle band yielded 3,5,7-*trimethoxy*-4-(2-*nitrophenyl*)-6-(4-*nitrophenyl*)*dibenzophosphole* 5-*oxide* (4b), m.p. 163—166 °C (from dichloromethane–methanol) (Found: C, 60.7; H, 4.0; N, 5.2. $C_{27}H_{21}N_2O_8P$ requires C, 60.9; H, 4.0; N, 5.3%); δ 2.82 (3 H, d, *J* 11.5 Hz, 5-OMe), 3.82 (6 H,

s, 3-,7-OMe), 7.21br (2 H, d, *J* 8.5 Hz, 2-,8-H), and 7.6—8.4 (10 H, m); $\lambda_{max.}$ ($\varepsilon_{max.}$) 376 (3 200), 294 (31 000), and 258 nm (34 000); $\nu_{max.}$ 1 530, 1 515, 1 030, 820, and 700 cm^{-1}.

The least mobile band gave 3,5,7-*trimethoxy*-4,6-*di*-(2-*nitrophenyl*)*dibenzophosphole* 5-*oxide* (4c), m.p. 254—257 °C (from dichloromethane–diethyl ether) (Found: C, 60.6; H, 4.1; N, 5.3. $C_{27}H_{21}N_2O_8P$ requires C, 60.9; H, 4.0; N, 5.3%); δ 2.82 (3 H, d, *J* 11.5 Hz, 5-OMe), 3.78 (6 H, s, 3-,7-OMe), and 7.18br (2 H, d, *J* 8.5 Hz, 2-,8-H); the remaining aromatic protons formed two groups of multiplets (total 10 H) at δ 8.36—8.15 and 7.95—7.50; amid the latter the characteristic double doublet (*J* 8.5, 4.5 Hz) of 1-,9-H occurred at δ 7.78. Three atropisomers are possible for this compound, but no indication of heterogeneity was seen; $\lambda_{max.}$ ($\varepsilon_{max.}$) 377 (2 600), 306sh (21 000), 296 (23 000), 255 (45 000), and 216 nm (39 000); $\nu_{max.}$ 1 532, 1 516, 1 039, and 705 cm^{-1}.

3,7-*Dihydroxy*-5-*methoxy*-4,6-*diphenyldibenzophosphole* 5-*Oxide* (3a).—(*a*) A stirred solution of the phosphinic ester (2a) (4.42 g) in dichloromethane (100 ml) was cooled under nitrogen to −78 °C and treated with boron tribromide (5 ml; 13.1 g). After 15 min the cooling bath was removed and the mixture was stirred for 48 h, then poured on ice (200 g). Some solid product was collected and united with the residue from evaporation of the dichloromethane layer in the filtrate. The whole was dried (100 °C/0.1 mmHg) for 0.5 h, dissolved in DMF (70 ml), and stirred with lithium carbonate (2 g) and methyl iodide (4 ml) at room temperature for 24 h. The mixture was poured into water (400 ml), acidified with 2M hydrochloric acid (50 ml), and the solid was collected and dried as before (3.97 g; 96%). Crystallization from methanol–chloroform (3 : 1) gave the *ester diol* (3a) as pale yellow needles which, after drying (120 °C/0.1 mmHg for 2 h), had m.p. 303—305 °C (Found: C, 72.3; H, 4.7; P, 7.2. $C_{25}H_{19}O_4P$ requires C, 72.5; H, 4.6; P, 7.5%); *m/e* 414 (M^+, 100%) and 381 (28); $\lambda_{max.}$ ($\varepsilon_{max.}$) 385 (2 470), 309 (19 200), 301 (19 500), 277 (13 300), and 259 nm (17 400); $\nu_{max.}$ 3 160br, 1 605, 1 585, 1 430, 1 290, 1 270, 1 175, 1 140, 1 075, 1 045, 780, and 700 cm^{-1}.

(*b*) The phosphinic ester (2a) (3.3 g) in alcohol-free chloroform (50 ml) was heated in a sealed tube with iodotrimethylsilane (6.5 g) at 60 °C for 8 days. Methanol (5 ml) was added and next day the mixture was evaporated. The red-brown solid was dissolved in DMF (100 ml) and stirred for 3 days at room temperature with lithium carbonate (2.76 g) and iodomethane (8 ml). The solution was poured into stirred, iced 2M hydrochloric acid (500 ml) to which had been added sodium pyrosulphite (5 g). After 1 h a pale yellow solid had formed; it was collected and dried at 100 °C for 2 days. The yield of diol (3a), m.p. 298—300 °C, was 3.01 g (97%).

(*c*) 5-Hydroxy-3,7-dimethoxy-4,6-diphenyldibenzophosphole 5-oxide (428 mg) was dissolved in a 0.5M solution (10 ml) of lithium ethanethiolate in hexamethylphosphoramide (the thiolate was made by adding butyl-lithium in hexane to ethanethiol, in diethyl ether containing a little 2,2′-bipyridyl, until a pink colour appeared; the mixture was then evaporated) and the solution was heated under nitrogen; first at 85—90 °C for 24 h, then at 120 °C for 16 h, and finally at 150 °C for 16 h. The mixture was diluted with water and acidified with sulphuric acid to give a precipitate which was methylated as above. Crystallization of the product from methanol–chloroform gave the diol (3a) (243 mg, 60%), m.p. 300—301 °C.

3,7-*Dihydroxy*-5-*methoxy*-4,6-*di*-(4-*methoxy*-3,5-*di*-*t*-*butylphenyl*)*dibenzophosphole* 5-*Oxide* (5d).—To the phosphinic ester (5a) (144 mg), suspended in diethyl ether (2 ml), was added ethereal methylmagnesium iodide (0.75 ml of 1.4M). The green solution was evaporated and the residue was heated under nitrogen, first at 185 °C for 0.25 h, then at 150 °C for 18 h. Progress was monitored by t.l.c. (ethyl acetate–hexane, 3 : 2). The cooled mixture was decomposed by stirring it with 2M hydrochloric acid (15 ml) and the yellowish solid obtained was collected, dried, and purified by preparative t.l.c. in the above system. The major band was eluted (methane–chloroform, 1 : 4) yielding a yellowish residue that gave, on trituration with diethyl ether, a cream solid (37 mg) which appeared to be the phosphinic acid, 3,5,7-*trihydroxy*-4,6-di-(4-*methoxy*-3,5-*di*-*t*-*butylphenyl*)-*dibenzophosphole* 5-*oxide* (5c) δ[(CD_3COCD_3) 1.39 (36 H, s, 4 × Bu^t), 3.62 (6 H, s, 2 × OMe in side chains), 7.00 (2 H, d, *J* 8 Hz, 2-,8-H), 7.40 (2 H, dd, *J* 8, 4 Hz, 1-,9-H), and 7.80 (4 H, s, 2-,6-H in side chains); the phenolic OH signal appeared at δ 3.1 and the phosphinic acid signal at δ 8.6 (br)]. The residue from the ether (47 mg) was methylated with lithium carbonate and methyl iodide in DMF as above. The product was purified by t.l.c. (ethyl acetate–hexane, 1 : 1) and gave the *ester diol* (5d) (21 mg) as needles (from acetone–hexane), m.p. 272—273 °C (Found: C, 73.6; H, 7.9; P, 4.4. $C_{43}H_{55}O_6P$ requires C, 73.9; H, 7.9; P, 4.4%); *m/e* 698.4 (M^+, 100%); δ 1.42 (36 H, s), 2.60 (3 H, d, *J* 11 Hz, 5-OMe), 3.67 (6 H, s, 2 × OMe in side chains), 5.55br (2 H, s, exchanged with D_2O, 2 × OH), 7.07 (2 H, d, *J* 8.5 Hz, 2-,8-H), and 7.42 (s) overlapping 7.36—7.55 (dd) (total 6 H).

In another experiment, when twice as much methylmagnesium iodide was used and the mixture was heated for 1.75 h at 165—170 °C, the product, isolated as above and purified by preparative t.l.c. (ethyl acetate–hexane, 1 : 1, twice developed) both before and after methylation as above, gave a crystalline compound (41 mg) which crystallized from chloroform or chloroform–hexane as prisms, m.p. 293—295 °C. This product, not quite pure, was principally the *ester triol* (5e) (Found: C, 73.31; H, 7.65. $C_{42}H_{53}O_6$ requires C, 73.66; H, 7.80%); *m/e* 684.4 (M^+, 100%), with small similar groups at 670 and 698, indicating contamination with more and less highly demethylated products; δ 1.42 (36 H, s), 2.57 (3 H, d, *J* 11 Hz, 5-OMe), 3.65 (3 H, s, OMe in side chain), 5.30 (1 H, sharp s, exchanged in D_2O, OH in side-chain), 5.4br (2 H, s, exchanged in D_2O, 3-,7-OH), 7.03 (2 H, d, *J* 8.5 Hz, 2-,8-H), and 7.28—7.60 (6 H, m). The structure, and hence that of compound (5d), is defined by the sharp signal at δ 5.0 (hindered OH, not hydrogen-bonded) and the absence of a 4-proton singlet from the 2,6-hydrogen atoms in the side-chains, as in (5d).

3,5,7-*Trihydroxy*-4,6-*bis*-(4-*hydroxy*-3,5-*di*-*t*-*butylphenyl*)-*dibenzophosphole* 5-*Oxide* (5b).—Demethylation of the phosphinic ester (5a) (88 mg) with lithium iodide (160 mg) in DMF (2.5 ml) at 100—120 °C for 44 h gave, when the mixture was poured into water, a solid product that crystallized from acetone–diethyl ether as needles, m.p. 346—348 °C (decomp.), of the lithium salt of the phosphinic acid. This product (61 mg) was added to a solution of sodium ethanethiolate (from 160 mg sodium hydride and an excess of ethanethiol in DMF at −10 °C) in DMF (5 ml). The mixture was heated at 90 °C for 66 h, then at 125 °C for 24 h; then it was poured into 2M hydrochloric acid and extracted with chloroform. The extracted product was purified by preparative t.l.c. (dichloromethane–methanol, 99 : 1) and the

major band, on elution, gave a white solid (16 mg) which crystallized from acetone–hexane as needles consisting of the tetrahydroxyphosphinic acid (5b); δ (on crude product) 1.40 (36 H, s), 2.70 and 2.76 (3 H, 3-,7-OH + PO_2H?), 5.30 (2 H, sharp s, 2 × OH in side-chains), 7.00 (2 H, d, *J* 8.5 Hz, 2-, 8-H), 7.30 (4 H, s, 2-,6-H in side chains), and 7.70 (2 H, dd, *J* 8.5, 4 Hz, 1-,9-H); *m/e* 656 (M^+, 100%).

2,8-*Dichloro*-3,7-*bis*-(2-*hydroxyethoxy*)-5-*methoxy*-4,6-*diphenyldibenzophosphole* 5-*Oxide* (6a).—The dichlorodihydroxy-ester (3b) (1.208 g), dry potassium carbonate (1.21 g), 1,2-dimethoxyethane (70 ml, freshly purified), and 2-iodoethanol (4.0 ml; 8.82 g) were stirred under nitrogen at 90—95 °C (bath) for 2.5 h, after which t.l.c. (methanol–dichloromethane, 1 : 19) showed a major product and no starting material. Water (50 ml) was added to the cold mixture which was then evaporated to small bulk. Acidification with 1M hydrochloric acid (2 ml) and dilution to *ca.* 100 ml with water gave a solid which was collected, washed, dried, and put on a column of alumina (80 g, 16 × 2.5 cm). Elution with 1% methanol in chloroform gave a colourless fore-run which was evaporated. The residue, on crystallization from ethanol, gave the *diether* (6a) in four crops (1.07 g, 75%) which were dried at 100 °C/0.1 mmHg. The analytical sample, colourless prisms from ethanol, had m.p. 215—217 °C (Found: C, 60.9; H, 4.4; Cl, 12.4. $C_{29}H_{25}Cl_2O_6P$ requires C, 61.0; H, 4.4; Cl, 12.4%); *m/e* 572 (M^+, 31%), 570 (M^+, 38), 528 (21), 526 (29), 484 (66), 482 (100), 451 (34), 449 (48), 417 (14), and 415 (16); δ 1.71br (2 H, s, 2 × OH), 2.64 (3 H, d, *J* 12 Hz, 5-OMe), 3.4—3.9 (8 H, m, 4 × CH_2), 7.3—7.6 (10 H, m, 2 × Ph), and 7.74 (2 H, d, *J* 4 Hz, 1-, 9-H). Further elution of the column yielded the 2-*hydroxyethyl ester* (6b) which, after purification twice by preparative t.l.c. (methanol–chloroform, 1 : 19) formed crystals (from ethanol), m.p. 226—227 °C (Found: C, 59.8; H, 4.5. $C_{30}H_{27}Cl_2O_7P$ requires C, 59.9; H, 4.5%); *m/e* 600 (M^+, 100%); δ 1.61br (3 H, s, 3 × OH), 2.7—3.0 (4 H, m, P–O–CH_2–CH_2–), 3.4—3.7 (4 H, m, $ArOCH_2CH_2OH$), 3.7—4.0 (4 H, m, $ArOCH_2CH_2OH$), 7.4—7.7 (10 H, m, 2 × Ph), and 7.76 (2 H, d, *J* 4 Hz, 1-,9-H).

2,8-*Dichloro*-3,7-*bis*-(2-*iodoethoxy*)-5-*methoxy*-4,6-*diphenyldibenzophosphole* 5-*Oxide* (6d).—To the above diether (6a) (1.142 g) in pyridine (20 ml) at 0 °C was added toluene-4-sulphonyl chloride (2.29 g) in portions. The mixture was kept for 5 days at 0—5 °C and then poured onto ice (100 g). The mixture was diluted to *ca.* 200 ml with cold water; the solid product was collected and dissolved in dichloromethane (100 ml) which was washed (0.5M HCl, water, brine), dried, and evaporated leaving the crude ditosylate (6c). This was dissolved, along with sodium iodide (3 g), in acetone (80 ml) and the stirred mixture was heated (reflux) for 16 h. To correct demethylation by iodide ion, methyl iodide (5 ml) was then added and the mixture was stirred at room temperature for 24 h. Water (50 ml) was added and the acetone was evaporated. The residue was extracted with chloroform (3 × 40 ml), and the extract was washed (2 × 100 ml water, 100 ml brine), dried, and evaporated. The residue, in chloroform, was put through a short column of alumina; the fore-run contained the *bis*-(2-*iodoethyl*) *ether* (6d) which crystallized as colourless needles (0.81 g, 2 crops) (from ethanol). The analytical sample had m.p. 203—205 °C (Found: C, 44.2; H, 2.9; I, 31.9. $C_{29}H_{23}Cl_2I_2O_4P$ requires C, 44.0; H, 2.9; I, 32.1%); *m/e* 792 (M^+, 33%), 790 (M^+, 46), 637 (71, 635 (100), 484 (25), 483 (42), 482 (62), 481 (62), 480 (50), 451 (29), 449 (50), and 447 (25); δ 2.62 (3 H, d, *J* 12 Hz, 5-OMe), 2.98 (4 H, t, *J* 7.5 Hz, CH_2I), 3.6—4.0 (4 H, m, $-OCH_2CH_2I$), 7.3—7.6 (10 H, m, Ph), and 7.70 (2 H, d, *J* 4 Hz, 1-,9-H).

2,8-*Dichloro*-5-*methoxy*-3,7-*bis*-(2-*morpholinoethoxy*)-4,6-*diphenyldibenzophosphole* 5-*Oxide* (6e).—The above iodoethyl ether (396 mg) and dry morpholine (5 ml) were stirred together at 70 ± 5 °C for 3 h. Morpholine and *N*-methylmorpholine were removed by steam distillation. The residue was extracted with chloroform (3 × 20 ml) and the extract was washed (brine), dried, and evaporated. The oily residue, in dichloromethane (15 ml), was stirred overnight with an excess of ethereal diazomethane. The residue from evaporation was crystallized from ethanol (5 ml); the *morpholino-derivative* (6e), after brief washing with ethanol, then with diethyl ether, and drying at 100 °C/0.1 mmHg, formed colourless needles (295 mg, 83%), m.p. 188—189 °C (Found: C, 62.3; H, 5.6; Cl, 10.0; N, 4.1. $C_{37}H_{39}Cl_2N_2O_6P$ requires C, 62.6; H, 5.5; Cl, 10.0; N, 4.0%).

5-*Hydroxy*-4,6-*diphenyl*-3,7-*bis*-(3-*sulphopropoxy*)*dibenzophosphole* 5-*Oxide* (6f).—The diol ester (3a) (82.8 mg) was added to sodium methoxide in methanol (0.45 ml of 0.893M) under nitrogen. 1,2-Oxathiolan 2,2-dioxide (propane sultone; 50 mg) in methanol (0.5 ml) was added and the mixture was heated (reflux) for 1 h. Since t.l.c. then indicated incomplete reaction the addition of methoxide and of sultone and the heating were repeated twice. Methanol was added to dissolve the precipitate and, on cooling, the product [presumably the disodium salt of 5-methoxy-4,6-diphenyl-3,7-bis-(3-sulphopropoxy)dibenzophosphole 5-oxide], separated and was recrystallized from 90% ethanol [yield 80 mg; δ(D_2O) 1.9 (4 H, m), 2.4—2.8 (7 H, m, including a doublet, *J* 12 Hz, 5-OMe), 3.9 (4 H, m), and 6.9—7.5 (14 H, m)]. This compound, in water, was passed through a column of Dowex 50W-X8 and the filtrate, after concentration, was boiled with barium hydroxide (10 ml of 0.05M) and concentrated to *ca.* 5 ml. Addition of ethanol (0.1 ml) caused crystallization of the *barium salt* of compound (6f) (78 mg; 71%) (Found: C, 40.8; H, 3.3. $C_{30}H_{26}Ba_{1.5}O_{10}PS_2 \cdot 2H_2O$ requires C, 40.7; H, 3.4%); δ(D_2O) 2—2.22 (4 H, m), 2.9—3.1 (4 H, m), 4.1—4.2 (4 H, t, *J* 9 Hz), and 7.3—8.1 (14 H, m). This salt was dissolved in water and put through a Dowex 50 column to yield, after evaporation of the filtrate and drying over phosphorus pentoxide, the acid (6f) as an almost colourless glass, soluble in water and in methanol.

5-*Methoxy*-3,7-*Bis*-(4-*dimethylphosphonobutoxy*)-4,6-*diphenyldibenzophosphole* 5-*Oxide* (6g).—The diol ester (3a) (100 mg), 1,4-dibromobutane (2.16 g), potassium carbonate (0.5 g), and acetone (10 ml) were stirred and heated under reflux for 48 h. After evaporation of acetone, water (10 ml) was added. The product extracted by dichloromethane was put on alumina (25 g) and light petroleum eluted 1,4-dibromobutane. The product, a pale yellow oil eluted by dichloromethane–methanol (25 : 1), was dissolved in acetone (10 ml) and heated for 60 h under reflux with sodium iodide (1 g). The solvent was removed, the residue was diluted with hydrochloric acid (50 ml of 5M) and extracted with dichloromethane. The extract was treated with a slight excess of ethereal diazomethane at 0 °C. Evaporation then gave a yellow oil which was subjected to preparative t.l.c. (ethyl acetate–hexane, 1 : 1, thrice developed) to give 3,7-di-(4-iodobutoxy)-5-methoxy-4,6-diphenyldibenzophosphole 5-oxide, which crystallized from methanol as large prisms (72 mg), m.p. 149—150 °C; δ 1.73 (8 H, m), 2.67 (3 H, d, *J* 12 Hz), 3.00 (4 H, m), 3.90 (4 H, m), 7.07 (2 H, d, *J* 8.5 Hz), 7.40 (10 H, m), and 7.57 (2 H, dd, *J* 8.5, 4.5 Hz).

This compound (30 mg) was boiled under reflux for 24 h with trimethyl phosphite (1 ml). The mixture was evaporated and hydrochloric acid (1 ml of 5M) was added. The suspension was shaken vigorously and evaporated; the residue in dichloromethane (5 ml) was treated (without apparent change) with diazomethane. Evaporation then gave the phosphinic ester (6g) as a pale yellow oil (28 mg); δ 1.67br (12 H, s), 2.63 (3 H, d, *J* 11.5 Hz), 3.67 [12 H, d, P(O)OMe], 3.93 (4 H, m), 7.06 (2 H, d, *J* 8.5 Hz), 7.37 (10 H, m), 7.53 (2 H, dd, *J* 8.5, 4.5 Hz).

3,7-*Bis*-(3-*ethylmethylphosphonopropoxy*)-5-*methoxy*-4,6-*bis*-(3,5-*di*-*t*-*butyl*-4-*methoxyphenyl*)-*dibenzophosphole* 5-*oxide* (6h).—The diol ester (5d) (190 mg), potassium carbonate (190 mg), diethyl 3-bromopropylphosphonate [9] (260 mg), and acetone (7 ml) were stirred and boiled together under reflux for 1.5 h, stirred overnight before heating for a further 4 h, and finally stirred for 48 h. After dilution with water, acidification (2M hydrochloric acid), and extraction with ethyl acetate the extract was washed (water), dried, and evaporated. The yellow oil was boiled under reflux for 12 h with potassium hydroxide (2 g) in methanol (10 ml) and water (1 ml). The cooled mixture was brought to pH 1 (5M hydrochloric acid) and the precipitated solid was collected and dissolved in chloroform, which on evaporation left a yellow residue (230 mg). On trituration with acetone (25 ml) this afforded a white solid (101 mg). A sample purified by precipitation from chloroform with acetone gave an n.m.r. spectrum (in CD_3OD) suggestive of the phosphinic acid bis-monoethylphosphonate (6i). The crude product (101 mg) was dissolved in chloroform (8 ml) and methylated with an excess of ethereal diazomethane. The product by preparative t.l.c. (methanol–chloroform, 1 : 9) gave a major band which was eluted to give the *bis-ethylmethylphosphonate ester* (6h) (82 mg) which crystallized from diethyl ether–hexane (1 : 1) as clusters of needles, m.p. 159 °C (Found: C, 64.2; H, 7.9. $C_{55}H_{81}O_{12}P$ requires C, 64.3; H, 8.0%); *m/e* 1 026 (M^+) and 1 012 (100%); δ 1.25 (6 H, t, *J* 7 Hz), 1.42 (36 H, s), 1.7—2.0 (8 H, m), 2.48 (3 H, d, *J* 11 Hz), 3.58 (d, *J* 11.5 Hz) and 3.65 (s) (total 12 H), 3.8—4.15 (8 H, m), 7.05 (2 H, d, *J* 8.5 Hz), and 7.42br (s) overlapping 7.57 (dd, *J*, 8.5, 4 Hz) (total 6 H). The mass spectrum showed minor peaks at *m/e* 998 and 1 054; probably indicating ester interchange (probe at 350 °C) on evaporation.

This ester (6h) (90 mg) was treated in chloroform with iodotrimethylsilane (8 equiv.) at room temperature for 1 h. Methanol (10 ml) was added and the mixture was stirred overnight. The methanol was evaporated and the residue was taken up in ethyl acetate which was washed (aqueous $NaHSO_3$) and then extracted with aqueous sodium hydroxide (10 ml of 2M, 10 ml of 1M). Acidification gave a white solid (50 mg) which, after trituration with acetone, was reduced to 14 mg. This substance dissolved in deuterium oxide on addition of sodium hydroxide (2 equiv.). The n.m.r. spectrum indicated complete removal of ester groups and was consistent with the structure (6j).

5-*Acetoxy*-3,7-*dimethoxy*-4,6-*diphenyldibenzophosphole* 5-*Oxide* (2k).—5-Hydroxy-3,7-dimethoxy-4,6-diphenyldibenzophosphole 5-oxide (428 mg) was boiled under reflux with acetic anhydride (10 ml) for 3 h. Next day the yellow crystals were collected and washed with diethyl ether. The *mixed anhydride* (433 mg, 92%), recrystallized from acetic anhydride, had m.p. 230—245 °C (decomp.) (Found: C, 71.2; H, 5.0. $C_{28}H_{23}O_5P$ requires C, 71.5; H, 4.9%); *m/e* 470 (M^+, 8%), 429 (29), and 428 (100); δ 1.48 (3 H, d, *J* 1 Hz, Ac), 3.71 (6 H, s), 7.12 (2 H, d, *J* 8.5 Hz), 7.3—7.5 (10 H, m), and 7.67 (2 H, dd, *J* 8.5, 4 Hz); $\lambda_{max.}$ ($\varepsilon_{max.}$) (dioxan) 372 (2 860), 308 (23 200), 297.5 (25 100), and 270 nm (21 900); $\nu_{max.}$ 1 763 cm^{-1} (C=O).

5-(2-*Hydroxyethoxy*)-3,7-*dimethoxy*-4,6-*diphenyldibenzophosphole* 5-*Oxide* (2l).—5-Hydroxy-3,7-dimethoxy-4,6-diphenyldibenzophosphole 5-oxide (67 mg) was boiled under reflux for 20 h in acetone (8 ml) with potassium carbonate (0.3 g) and 2-iodoethanol (0.3 ml). Water was added and the solid was collected. It was dissolved in chloroform and put on a column of alumina. Chloroform–methanol (99 : 1) eluted the *ester* (2l) (53.5 mg) which was recrystallized twice from methanol to give the analytical sample, m.p. 265—266 °C (Found: C, 71.1; H, 5.3. $C_{28}H_{25}O_5P$ requires C, 71.2; H, 5.3%); *m/e* 472 (M^+, 100%), 442 (18), 429 (38), 428 (90), 427 (15), 403 (20), 402 (17), 401 (28), 399 (12), 396 (15), and 395 (40); δ 2.7—3.0 (4 H, m), 1.63br (1 H, s, OH), 3.73 (6 H, s), 7.11 (2 H, d, *J* 8.5 Hz), 7.35—7.65 (10 H, m), and 7.66 (2 H, dd, *J* 8.5, 4 Hz).

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