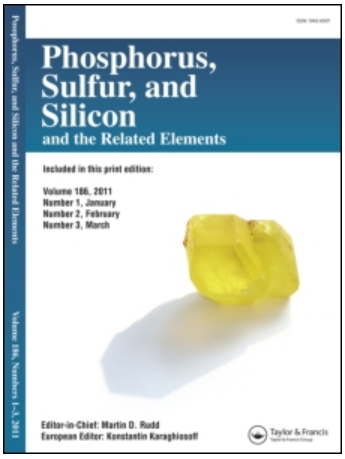

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DERIVATIVES OF CYCLOHEXANE-1,2-DIOL-PHOSPHOROCHLORIDATE AND 1-CHLOR-4,5-BENZ-2,6-DIOXAPHOSPHORINANONE-(3) 1-OXIDE

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DERIVATIVES OF CYCLOHEXANE-1,2-DIOL-PHOSPHORO-CHLORIDATE AND 1-CHLOR-4,5-BENZ-2,6-DIOXAPHOS-PHORINANONE-(3) 1-OXIDE

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Cyclohexane 1,2-diol (**1**) has been phosphorylated to the cyclic phosphorochloridate (2; X = O) and chloridothioate (2; X = S). Hydrolysis of the former with boiling aqueous acetone gave 2-hydroxycyclohexyl dihydrogen phosphate (3; X = O, R = H) and excess isopropyl alcohol gave the diisopropyl phosphate (3; X = O, R = $(CH_3)_2CH$). Reaction of the chloridate (2; X = O) with aniline, diethylamine, and morpholine gave the corresponding amidates (**4–6**). The chloridothioate (2; X = S) similarly gave amidates (**8**, **9**) with morpholine and aniline, but with isopropyl alcohol the cyclic isopropyl phosphate (**10**) was obtained. Attempted hydrolysis (aqueous acetone) of the chloridothioate (2; X = S) resulted in decomposition. Salicylic acid (**11**) with phosphorus oxychloride gave the cyclic phosphorochloridate (**12**) which reacted with ethanol, propanol, isopropyl alcohol and benzyl alcohol to give the alkoxy derivatives (**13–16**). The highly sterically hindered alcohols, t-butanol and benzhydrol did not react. The alkoxy derivatives were hydrolyzed to the corresponding 2-carboxyphenyl phosphates (**17–20**). Attempted reaction of the chloridate (**12**) with aniline gave complex mixtures of unidentified products. The proton n.m.r., i.r. and ms. of the compounds (**12–20**) are briefly discussed.

INTRODUCTION

A wide variety of organophosphorus compounds have attained importance as insecticides,[1] and more recently several have been developed as fungicides and herbicides.[2] The present paper represents an extension of previous studies[3–6] on the phosphorylation of alicyclic compounds as candidate pesticides: cyclohexane-1,2-diol and salicyclic acid have been converted to phosphorochloridates and derivatives.

DISCUSSION

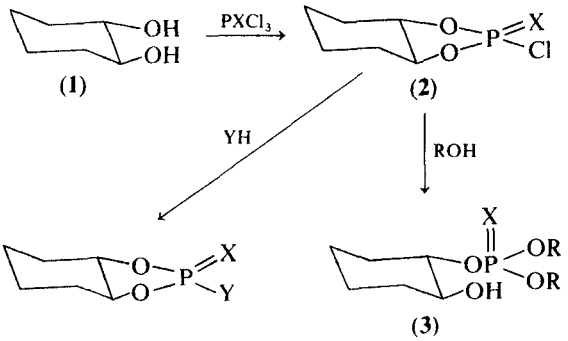
1,2-Diols can be phosphorylated to cyclic phosphates which can sometimes be isolated, but they are sensitive to hydrolysis to the diol monophosphate. In contrast, the cyclic phosphorothioates are quite stable to hydrolysis.[7] Brown and Higson[8] reacted *cis* and *trans*-cyclohexane-1,2-diol (**1**) with phosphorus oxychloride and on hydrolysis obtained 2-hydroxycyclohexyl dihydrogen phosphate

Attempted reactions of the chloridate (2; X = O) with *p*-chloro- and 2,4-dichloro-aniline in boiling tetrahydrofuran (4h) failed. Reactions with aqueous sodium azide or hydrazine hydrate did not give (3; X = O, R = H), although the intermediate cyclic phosphate was not isolated (Scheme 1).

Phosphorylation of the diol (**1**) with boiling thiophosphoryl chloride gave the cyclic phosphorochloridothioate (2; X = S) as an oil.[9]† Phosphorylation of cyclohexane-1,2-diol with phosphorus oxychloride occurred readily at room temperature (3h) but with thiophosphoryl chloride the reaction required prolonged boiling (8h) in benzene. The difference in the phosphorylation conditions reflects the greater polarization of the P=O bond in comparison with the P=S bond.

Cyclohexane-1,2-diol phosphorochloridate (2; X = O) was characterized by condensation with aniline, diethylamine and morpholine to give the amidates (**4–6**). Hydrolysis (boiling aqueous dioxan) afforded 2-hydroxycyclohexyl phosphate (3; X = O, R = H). Isopropyl alcohol (2 mol. equivs.) in boiling acetone similarly gave the diisopropyl phosphate (3; X = O, R = $CH(CH_3)_2$), presumably formed by ring opening of the intermediate cyclic isopropyl phosphate (**7**) by the excess isopropyl alcohol.

† Previous workers[7] obtained a solid, m.p. 54–56°, but they used *cis*-cyclohexane-1,2,-diol whereas our work was with the *trans*-diol (**1**).



X	Y
(4) O	NHC_6H_5
(5) O	$N(C_2H_5)_2$
(6) O	N O
(7) O	$CH(CH_3)_2$
(8) S	N O
(9) S	NHC_6H_5
(10) S	$CH(CH_3)_2$

SCHEME 1

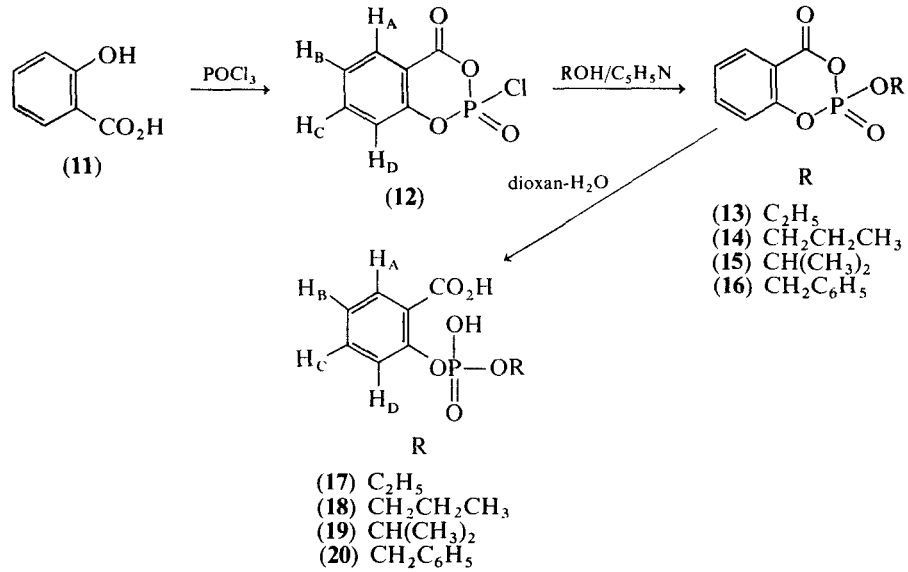
the azide or hydrazide, possibly due to competing base-catalysed hydrolysis.

Cyclohexane-1,2-diol phosphorochloridothioate (2; X = S) was converted to the morpholidate[9] (**8**), phenylamidate (**9**) and the O-isopropyl derivative (**10**).

The latter was obtained by reacting the chloridothioate (2: X = S) with isopropyl alcohol under identical conditions to those used with the oxygen analogue; presumably the stability of the product (**10**) is a consequence of the lower polarity of the thiophosphoryl bond.

Attempted hydrolysis of the chloridothioate (2; X = S) (boiling acetone, 2h) caused decomposition (loss of hydrogen sulfide); the mass spectrum of the oil obtained showed ions at 259, 228, 196, 159, 97, 81, and the ion at 196 corresponds to 2-hydroxycyclohexyldihydrogen phosphate (3, X = O, R = H) resulting from ring opening and sulfur-oxygen exchange.

Salicylic acid (11) was heated with phosphorus oxychloride as previously described[10] to give 1-chloro-4,5-benz-2,6-dioxaphosphorinanone (3)-1-oxide (**12**) (Scheme 2). The phosphorochloridate (**12**) was treated with various alcohols (ethanol, propanol, isopropyl alcohol, benzyl alcohol, *t*-butanol and benzhydrol) following the procedure used by Atherton[11-12] for the reaction with ethanol and butanol. The reactions of the chloridate (**12**) with ethanol and propanol gave the alkoxy derivatives (**13**, **14**) in qualitative yield and the reactions with isopropyl alcohol and benzyl alcohol gave 94% and 78% yields of (**15**, **16**) respectively. On the other hand, highly sterically hindered *t*-butanol and benzhydrol failed to react; suggesting that the reaction follows the S_N2 (P) mechanism since this would be highly sensitive to



(**13**) C_2H_5
(**14**) $CH_2CH_2CH_3$
(**15**) $CH(CH_3)_2$
(**16**) $CH_2C_6H_5$

(**17**) C_2H_5
(**18**) $CH_2CH_2CH_3$
(**19**) $CH(CH_3)_2$
(**20**) $CH_2C_6H_5$

SCHEME 2

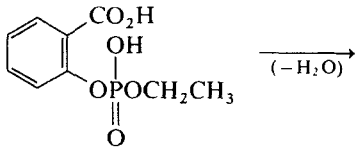
steric factors, which appear to be more important than the nucleophilicity of the alcohol as Atherton[12] found that the chloridate (**12**) reacted with phenol.

Hydrolysis (aqueous dioxan) of the alkoxy derivatives (**13–16**) afforded the corresponding alkyl 2-carboxyphenyl phosphates (**17–20**) in yields of 58, 21, 66 and 43% respectively. Attempts to precipitate the phosphates (**17–20**) as their barium salts failed, although they did show effervescence with aqueous sodium hydrogen carbonate confirming the presence of the carboxylic acid group.

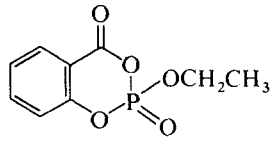
The infrared spectra of the alkyl derivatives (**13–16**) showed the carbonyl stretching band at 1790–1780; the phosphoryl band at 1285–1280; and the P-O-C vibration at 1000–990 cm^{-1} (cf. Ref. 13). After hydrolysis to the 2-carboxyphenyl phosphates (**17–20**), the carbonyl and phosphoryl bands moved to appreciably lower frequencies (1720–1710 and 1235–1220 cm^{-1}) respectively, whereas the P-O-C vibration is at a slightly higher frequency (1040–1020 cm^{-1}).

The n.m.r. spectrum of the phosphorochloridate (**12**) must be determined in $CDCl_3$ and not in CD_3OH or $(CD_3)_2SO$ as the latter nucleophilic solvents react causing ring opening. The aromatic protons (H_A, H_B, H_C and H_D) show as a complex multiplet in the 8.4–7.1 ppm region. Proton H_A which is *ortho* to the carbonyl group is the most deshielded and signals as a doublet at the lowest field (8.3 ppm). Proton H_C is deshielded as it is *para* to the carbonyl group and signals as a triplet at 7.95 ppm. The remaining protons (H_B and H_D) signal in the region 7.7–7.2 ppm as a complex pattern. In the alkoxy derivatives (**13–16**), the interesting feature is the methylene signal at δ 4.40 which appears as a multiplet (8 lines) and not as a quartet due to coupling with phosphorus. By a spin decoupling experiment the multiplet collapses to a doublet and the coupling constant J_{P-O-CH} was measured as 10.7 Hz, which is in good agreement with the value of 10–11 Hz reported by Thomas.[14] The alkyl-2-carboxyphenyl phosphates (**17–20**) show the CO_2H and P-OH protons as broad singlets in the region 9.7–8.9 ppm and these signals were removed by D_2O treatment.

The mass spectra of the alkoxy derivatives (**13–16**) showed the molecular ions followed by loss of the alkyl group, proton exchange, and further fragmentation down to a base peak of 92 (C_6H_4O). The alkyl 2-carboxyphenyl phosphates (**17–20**) showed the molecular ion, followed by loss of water, probably involving cyclisation to the corresponding alkoxy compound (e.g. **17** → **13**):

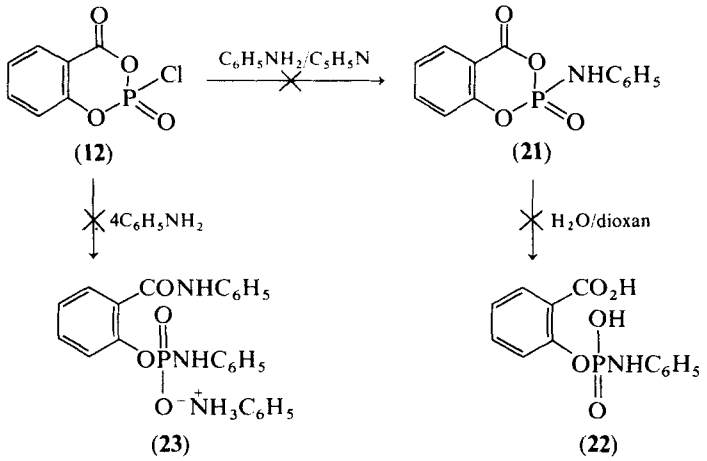


(**17**)



(**13**)

Consequently the mass spectra of the alkyl 2-carboxyphenyl phosphates (**17–20**) are virtually identical to those of the corresponding alkoxy derivatives (**13–14**) except for the presence of the M–18) fragment ion.



SCHEME 3

The reaction of the phosphorochloridate (**12**) with aniline (1 mol. equiv.) in benzene and pyridine (1 mol. equiv.) for 4h gave a semi-solid which could not be purified, and hydrolysis (aqueous dioxan, 1 week) gave an uncrystallizable oil.

These reactions should give the amidates (**21**) and (**22**) (Scheme 3), but the products appeared to be complex mixtures and the mass spectra gave no indication of the presence of the expected compounds. Reaction of the chloridate (**12**) with an excess of aniline (4 mol. equivs.) did not yield the expected amidic amide (**23**).

EXPERIMENTAL

I.r. spectra were recorded as Nujol mulls using a Perkin–Elmer 237 spectrophotometer. N.m.r. spectra were measured with a Varian HA 100 spectrometer using tetramethylsilane as internal standard. Mass spectra were determined with an AEI MS9 spectrometer at 70 eV. Melting points were determined with a Kofler hot-stage apparatus and are uncorrected. Microanalyses were carried out by Butterworth Microanalytical Consultancy Limited, Teddington, England and I.C.I. Limited, Pharmaceuticals Division, Alderley Park, Cheshire, England. T.l.c. was carried out on silica gel G plates developed with iodine vapour.

Cyclohexane-1,2-diol Phosphorochloridate (*2*; X=O)

Cyclohexane-1,2-diol (**1**) (12 g; 1 mol. equiv.) and pyridine (16.6 ml; 2 mol. equiv.) in dry benzene (100 ml) was added dropwise to a stirred solution of phosphorus oxychloride (9.6 ml; 1 mol. equiv.) in dry benzene (50 ml) at 0°. After 3 h at room temperature, pyridine hydrochloride was filtered off and the filtrate evaporated under reduced pressure to give the *phosphorochloridate* as a pale yellow oil (16 g). (Found: C, 36.4; H, 4.9; P, 16.0 $C_6H_{10}ClO_3P$ requires C, 36.6; H, 5.1; P, 15.8%).

ν_{max} (liquid film) 1300 (P=O), 990 (P—O—C), 670 (P—Cl) cm^{-1}. Ms. showed the molecular ions (M^+ 197, 196) and fragment ions at 168, 155, 97, 80, 79.

Cyclohexane-1,2-diol Phosphorochloridothioate (*2*; X=S)

Cyclohexane-1,2,-diol (**1**) reacted with thiophosphoryl chloride (1 mol. equiv.) in boiling benzene (8 h) as previously described[9] to give the *chlorodiothioate* as a yellow oil (80%). (Found: C, 33.7; H, 4.7; P, 14.8. $C_6H_{10}ClO_2PS$ requires C, 33.9; H, 4.7; P, 14.6%). ν_{max} (liquid film) 1000 (P—O—C), 720 (P=S), 685 (P—Cl). Ms. showed the molecular ions (M^+ 213, 212) and fragment ions at 177 (M—Cl), 133, 112, 81, 79.

2-Hydroxycyclohexyl Dihydrogen Phosphate (*3*; X=O, R=H)

Method A Cyclohexane-1,2,-diol phosphorochloridate (2; X=O) (1.98 g, 1 mol. equiv.) was refluxed with acetone (10 ml) containing distilled water (0.9 g; 5 mol. equivs.) for 2 h. The solution was concentrated and cooled (0°) to give the dihydrogen phosphate as a solid (0.45 g, 23%), m.p. 159–162°. (lit.[8] 164–168°). (Found: C, 36.5; H, 6.8; P, 16.0. Calc. for $C_6H_{13}O_5P$: C, 36.7; H, 6.6; P, 15.8%). ν_{max} 3250 (br, OH), 2300 (br, P—OH), 1260 (P=O) cm^{-1}. Ms. showed the molecular ion (M^+, 196) and fragment ions at 178 (M—H_2O), 137, 99, 80. T.l.c. (EtOAc-light petroleum (60–80°) 1:1) showed two spots R_F 0.85, 0.94.

Method B A similar reaction at room temperature for 3 weeks gave the *dihydrogen phosphate* (3: X=O, R=H) (10%), m.p. 160–163°.

Reactions of Cyclohexane-1,2-diol Phosphorochloridate (*2*: X=O) *with Nucleophiles*

i) Aniline The phosphorochloride (2 g) was stirred with aniline (1.89 g; 2 mol. equivs.) in ether (40 ml) at room temperature for 3 h. Aniline hydrochloride was filtered off, and the filtrate evaporated to give a gum. Trituration (petroleum ether 40–60°) afforded the phenylamidate (**4**) (30%), m.p. 133–135°. (Found: C, 56.6; H, 6.5; N, 5.3. $C_{12}H_{16}NO_3P$ requires C, 56.9; H, 6.3; N, 5.5%). Ms. showed the molecular ion (M^+ 253) and fragment ions at 174, 173, 155, 137, 108, 93. T.l.c. (EtOAc-light petroleum 60–80° 1:1) showed one spot, R_F 0.72). ν_{max} (KBr) 1260 (P=O), 1015 (P—O—C), 1605, 1505 (arom C=C), 820 (P—N) cm^{-1}.

ii) *Diethylamine* The phosphorochloridate (2 g) was similarly reacted with diethylamine (3.14 ml; 2 mol. equivs.) in benzene (2 h) to give the diethylamidate (**5**) as an oil (60%). (Found: C, 51.6; H, 8.8; N, 5.8. $C_{10}H_{20}NO_3P$ requires C, 51.5; H, 8.6; N, 6.0%). ν_{max} (liquid film) 1260 (P=O), 1020, 990 (P—O—C), 820 (P—N) cm^{-1}. Ms. showed the molecular ion (M^+, 233) and fragment ions at 218, 179, 138. T.l.c. (EtOAc-light petroleum 60–80° 1:1) showed one spot, R_F 0.23.

iii) *Morpholine* (2 mol. equivs.) afforded the *morpholidate* (**6**) (20%), m.p. 140–141° (from ethyl acetate). (Found: C, 48.5; H, 7.2; N, 5.5. $C_{10}H_{18}NO_4P$ requires C, 48.6; H, 7.3; N, 5.7%). Ms. showed the molecular ion (M^+ 247) and fragment ions at 216, 204, 190, 168, 152, 138, 124, 118, 86 (morpholine). T.l.c. (EtOAc-light petroleum 60–80° 1:1) showed one spot, R_F 0.10.

iv) *Isopropyl alcohol* The phosphorochloridate (2 g) was refluxed with isopropyl alcohol (1.95 ml, 2 mol. equivs.) in dry acetone (20 ml) and triethylamine (1.8 ml; 1 mol. equiv.) for 1 h. After 12 h at room temperature, evaporation *in vacuo* gave an oil, which was extracted with ether (250 ml), washed with water (3 × 20 ml), dried (Na_2SO_4), and evaporated to give the 0,0′-diisopropylphosphate (3; X=O; R=$(CH_3)_2CH$) as an oil (3.4 g). (Found: C, 51.6; H, 9.1; P, 10.8. $C_{12}H_{25}O_5P$ requires C, 51.4; H, 8.9; P, 11.1%). ν_{max} 3480 (br, OH), 1250 (P=O), 1020 P—O—C) cm^{-1}. Ms. showed the molecular ion (M^+, 280) and fragment ions at 266, 222 (M—$OCH(CH_3)_2$), 127, 99, 45.

Cyclohexane 1,2-diol Phosphorochloridothioate (*2*; X=S) was reacted with the following nucleophiles:

i) *Morpholine* (2 mol. equivs.) in ether (20 h) gave the *morpholidate* (**8**) (25%), m.p. 117–119° (lit.[9] 122–124°). (Found: C, 45.4; H, 7.0; N, 5.2. $C_{10}H_{18}NO_3PS$ requires C, 45.6; H, 6.8; N, 5.3%). ν_{max} (KBr) 1260, 1120 (C—O—C), 970 (P—O—C), 800 (P—N), 740 (P=S) cm^{-1}. Ms. showed the molecular ion (M^+, 263) and fragment ions at 230, 145, 86 (morpholino).

ii) *Aniline* (2 mol. equivs.) in tetrahydrofuran at 50° (5 h) gave the *phenylamidate* (**9**) (30%), m.p. 138–140° (from ether). (Found: C, 53.8; H, 6.2; N, 5.5. $C_{12}H_{16}NO_2PS$ requires C,

53.5; H, 6.0; N, 5.4%) ν_{max} 1600, 1580, 1500 (arom C=C), 1020 (P—O—C), 820 (P—N), 740 (P=S) cm^{-1}. Ms. showed the molecular ion (M^+, 269) and fragment ions at 194, 93 (aniline).

iii) *Isopropyl alcohol* The chloridothioate (2; X=S) (3 g) was refluxed with isopropanol (2.2 ml, 2 mol. equivs.) and triethylamine (1.97 ml; 1 mol. equiv.) in dry acetone (30 ml) for 2 h. After 2 h at room temperature, evaporation gave the *O-isopropyl-thioate* (**10**) as a pale yellow oil (3.2 g). (Found: C, 45.6; H, 7.4; P, 13.3. $C_9H_{17}O_3PS$ requires C, 45.8; H, 7.2; P, 13.1). ν_{max} (liquid film) 1000, 975 (P—O—C), 780 (P=S) cm^{-1}. Ms. showed the molecular ion (M^+, 236) and fragment ions at 222 ($M-CH_3$), 212, 208, 195, 194 ($M-CH(CH_3)_2$), 145, 143, 80.

1-Chloro-4,5-Benz-2,6-Dioxaphosphorinanone-(3) 1-Oxide (**12**)

A mixture of salicyclic acid (**11**) (20 g) was heated with phosphorus oxychloride (22.24 g; 1 mol. equiv.) at 140–150° for 2 h. After cooling to room temperature, distillation under reduced pressure afforded *the oxide* (**12**) (14.35 g, 45%), bp. 0.1 mm 114–120° (lit.[10] 116–125°), m.p. 85–88° (lit.[10] 90–93°). (Found: C, 38.8; H, 2.2; P, 14.0. Calc. for $C_7H_4ClO_4P$: C, 38.5; H, 1.9; P, 14.2%). ν_{max} ($CHCl_3$ solution) 1790 (CO), 1605 (arom C=C), 1280 (P=O) cm^{-1}. N.m.r. ($CDCl_3$) δ: 8.4–7.1, m, 4H (4ArH). Ms. showed the molecular ions (M^+, 220, 218 in ratio of 3:1) and fragment ions at 183 (M—Cl), 120 ($C_6H_4CO_2$), 92 (C_6H_4O).

Preparation of 1-Alkoxy-4,5-Benz-2,6-Dioxaphosphorinanone-(3)1-Oxide Derivatives (**13–16**)

The phosphorochloridate (**12**) was stirred with the appropriate alcohol (1 mol. equiv.) in dry benzene containing pyridine (1 mol. equiv.) at room temperature for 2 h. The precipitate of pyridine hydrochloride was filtered off and the filtrate evaporated (<35°) under reduced pressure. Trituration with light petroleum (b.p. 30–40°) and refiltration afforded the following alkoxy compounds:

i) *Ethoxy* (**13**) (100%), m.p. 50–52° (lit.[11] 55–56°). (Found C, 47.6; H, 4.3; P, 13.4. Calc. for $C_9H_9O_5P$: C, 47.4; H, 4.0; P, 13.6%). ν_{max} 1780 (C=O), 1605 (arom C=C), 1380 (P=O), 1000 (br P—O—C) cm^{-1}. N.m.r. ($CDCl_3$) δ: 8.35–7.05, m, 4H (4ArH); 4.40, m, 2H (OCH_2); 1.45, t, 3H (CH_3). Ms. showed the molecular ion (M^+, 228) and fragment ions at 213 ($M-CH_3$), 201, 200 ($M-C_2H_5$), 183 ($M-OC_2H_5$), 120 ($C_6H_4CO_2$), 92 C_6H_4O).

ii) *Propoxy* (**14**) (100%), yellow oil. (Found: C, 49.8; H, 4.6; P, 13.1. $C_{10}H_{11}O_5P$ requires: C, 49.6; H, 4.55; P, 12.8%). ν_{max} (liquid film) 1780 (C=O), 1605 (arom C=C), 1280 (P=O), 1000 (br, P—O—C) cm^{-1}. N.m.r. ($CDCl_3$) δ: 8.5–7.2, m, 4H (4ArH); 4.5, m, 2H (OCH_2); 1.9, m, 2H (CH_2); 1.1, t, 3H (CH_3). Ms. showed the molecular ion (M^+, 242), and fragment ions at 227 ($M-CH_3$), 213 ($M-C_2H_5$), 201, 200 ($M-C_3H_7$), 183 ($M-OC_3H_7$), 120, 92.

iii) *Isopropoxy* (**15**) (94%), pale yellow oil. (Found: C, 49.4; H, 4.3; P, 12.5. $C_{10}H_{11}O_5P$ requires C, 49.6; H, 4.55; P, 12.8%). ν_{max} (liquid film) 1780 (CO), 1606 (arom C=C), 1285 (P=O), 990 (br, P—O—C). N.m.r. ($CDCl_3$) δ: 8.4–7.1, m, 4H (4ArH); 5.1, m, 1H ($(CH_3)_2CH$); 1.5, d, 6H ($(CH_3)_2CH$). Ms. showed the molecular ion (M^+, 242) and fragment ions at 227 ($M-CH_3$), 201, 200, 183, 120, 92.

iv) *Benzyloxy* (**16**) (78%) oil. (Found: C, 47.6; H, 3.9; P, 10.4. $C_{14}H_{11}O_5P$ requires C, 57.9; H, 3.8; P, 10.7%). ν_{max} (liquid film) 1780 (CO), 1606 (arom C=C), 1280 (P=O), 1000 (br, P—O—C) cm^{-1}. Ms. showed the molecular ion (M^+, 290) and fragment ions at 228, 210, 201, 200, ($M-CH_2C_6H_5$), 120, 92.

Preparation of the Alkyl 2-Carboxyphenyl Phosphates (**17–20**)

The 1-alkoxy-4,5-benz-2,6-dioxaphosphorinanone-(3)1-oxide (**13–16**) was reacted with 30% aqueous dioxan at room temperature for 1 week. Evaporation *in vacuo* followed by dilution with benzene, azeotropic distillation and extraction with ether afforded the following alkyl 2-carboxyphenyl phosphates:

i) *Ethyl* (**17**) (58%), m.p. 112–115° (lit.[11] 120–121°). (Found: C, 44.2; H, 4.4; P, 12.3. Calc. for $C_9H_{11}O_6P$: C, 43.9; H, 4.5; P, 12.6%). ν_{max} 3400 (br OH), 1710 (CO), 1603 (arom C=C), 1220 (P=O), 1040 (br, P—O—C). N.m.r. $(CD_3)_2SO$ δ: 9.7, brs, 2H, (CO_2H, P—OH); 8.1–7.1, m, 4H (4ArH); 4.2, m, 2H (OCH_2); 1.3, t, 3H(CH_3). D_2O treatment removed the signal at δ 9.7. Ms. showed the molecular ion (M^+, 246) and fragment ions at 228 ($M-H_2O$), 213 ($M-H_2O-CH_3$), 201, 200, 183, 167, 120, 92.

ii) *Propyl* (**18**) (21%), m.p. 123–126°. (Found: C, 46.0; H, 4.7, P, 11.7. $C_{10}H_{13}O_6P$ requires: C, 46.2; H, 5.0; P, 11.9%). ν_{max} 3300 (br OH), 1710 (CO), 1603 (arom C=C), 1235 (P=O), 1020 (br, P—O—C) cm^{-1}. N.m.r. $((CD_3)_2SO)$ δ: 8.9, brs, 2H (CO_2H, P—O—H); 8.0–7.2, m, 4H (4ArH); 4.1, m, 2H (OCH_2); 1.6, q, 2H ($-CH_2-$); 0.9, t, 3H (CH_3). Treatment with D_2O removed the signal at δ 8.9. Ms. did not show the molecular ion (M^+, 260) but fragment ions were shown at 242 ($M-H_2O$), 227 ($M-H_2O-CH_3$), 213, 201, 200, 183 167, 120, 92.

iii) *Isopropyl* (**19**) (66%), m.p. 115–118°. (Found: C, 45.9; H, 4.9; P, 11.8. $C_{10}H_{13}O_6P$ requires C, 46.2; H, 5.0; P, 11.9%). ν_{max} 3300 (br, OH), 1710 (CO), 1605 (arom C=C), 1220 P=O), 1040 (br, P—O—C) cm^{-1}. N.m.r $((CD_3)_2SO)$ δ: 9.3, brs, 2H(CO_2H), P—OH), 8.2–7.1, m, 4H (4ArH); 4.9, m, 1H (OCH); 1.45, d, 6H ($(CH_3)_2C$). D_2O treatment removed the signal at δ 9.3. Ms. showed the molecular ion (M^+, 260) and fragment ions at 242 ($M-H_2O$), 227, 201, 200, 183, 120, 92.

iv) *Benzyl* (**20**) (43%), yellow oil. (Found: C, 54.2: H. 4.4; P, 9.8, $C_{14}H_{13}O_6P$ requires: C, 54.5; H, 4.3; P, 10.05%). ν_{max} (liquid film) 3500 (br, OH), 1720 (CO), 1610 (arom C=C), 1220 (P=O), 1020 br, P—O—C). N.m.r. $((CD_3)_2SO)$ δ: 9.0, brs, 2H (CO_2H, P—OH); 8.0–7.0, m, 9H (9ArH): 5.2, d, 2H (CH_2). D_2O treatment removed the signal at δ 9.0. Ms. did not show the molecular ion (M^+, 308), but there were fragment ions at 290 ($M-H_2O$), 273, 228, 210, 200 ($M-H_2O-CH_2C_6H_5$), 120, 91.

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