

Synthesis of Diethyl Alkoxyethylphosphonates *via* Lewis Acid Promoted Regiospecific Cleavage of Alkoxy-4-Chlorophenoxymethanes

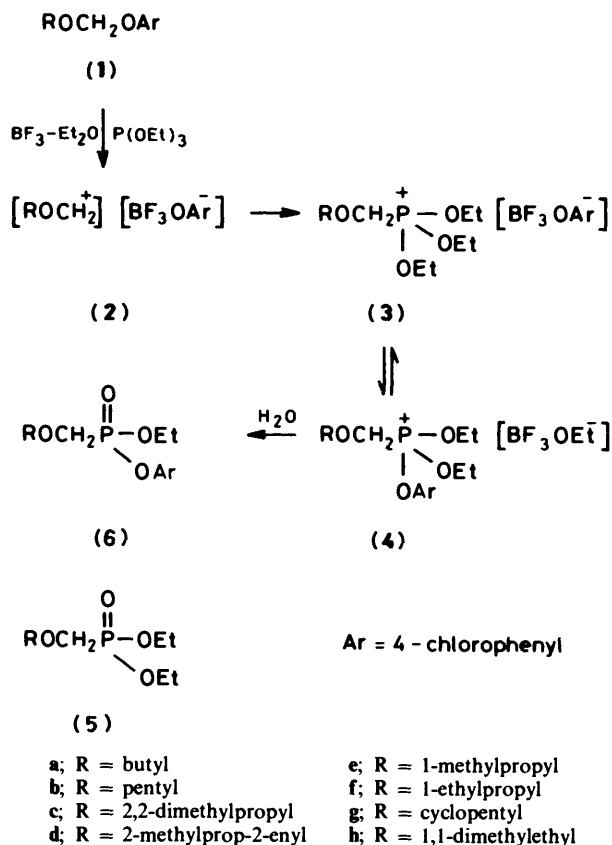
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Alkoxy-4-chlorophenoxymethanes, readily prepared from 1-chloro-4-chloromethoxybenzene and sodium alkoxide, generate alkoxyethyltriethoxyphosphonium ions in a regiospecific reaction with triethyl phosphite and titanium tetrachloride or boron trifluoride. Precise reaction conditions are necessary since the phosphonium ions can undergo disproportionation. Subsequent addition of water gives diethyl alkoxyethylphosphonates; if disproportionation has been permitted these contain 4-chlorophenyl ethyl alkoxyethylphosphonates. Under the preferred conditions (titanium tetrachloride, -78°C , 15 min, dichloromethane) yields of *ca.* 80% of diethyl alkoxyethylphosphonates have been obtained from primary, secondary, tertiary, and allylic alcohols.

An Arbuzov reaction between a chloromethyl alkyl ether and a trivalent phosphorus compound is the most commonly used method for the preparation¹ of alkoxyethylphosphonates. However, this procedure has several drawbacks. The preparation of chloromethyl alkyl ethers is awkward, wasteful in alcohol, and lacks applicability to more complex alcohols. Also, the Arbuzov reaction is restricted to simple alkyl phosphites unless vigorous conditions are employed. Current interest in the applications¹⁻³ of alkoxyethylphosphonates calls for new methods for the preparation of these important compounds. Zimmer⁴ and Shono⁵ have prepared 1-ethoxy-1-arylmethylphosphonates and derivatives of α -amino-methylphosphonates by the interaction of arylaldehyde diethyl acetals and α -methoxyurethanes, respectively with triethyl phosphite and boron trifluoride-diethyl ether. This evidence suggested that an aryl alkyl acetal might react in a similar fashion to give diethyl alkoxyethylphosphonates.

The alkoxy-4-chlorophenoxymethanes (1) were prepared by treating the appropriate sodium alkoxides in THF with an equivalent amount of the readily available 1-chloro-4-chloromethoxybenzene.⁶ Treatment of (1a-h) with titanium tetrachloride and triethyl phosphite at -78°C for 15 min in dichloromethane gave regiospecifically the diethyl alkoxyethylphosphonates (5a-h) in 80-90% yields from the alcohol. Use of triphenyl phosphite and titanium tetrachloride (-78°C , 15 min), (1f) gave diphenyl 1-ethylpropoxymethylphosphonate in 82% yield. However, as the Table illustrates, careful choice of the Lewis acid and the reaction conditions are required in order to avoid disproportionation, a secondary process leading to mixtures of diethyl- and ethyl aryl-alkoxyethylphosphonates (5) and (6) (Scheme). Reaction of the alkoxy 4-chlorophenoxymethanes (1) with the Lewis acid generates regiospecifically, presumably *via* the more stable oxonium ion (2), the alkoxyethyltriethoxyphosphonium ion (3). ³¹P N.m.r. spectroscopy of the reaction mixture of (1a) or (1b) in CD₂Cl₂ with triethyl phosphite in the presence of either titanium tetrachloride or boron trifluoride-ether at room temperature showed that no diethyl or ethyl aryl alkoxyethylphosphonates [(5a), (5b), or (6a), (6b)] were formed until the reaction mixture was quenched with water. ¹H N.m.r. analysis (360 MHz, CD₂Cl₂) of the reaction mixture of (1a) with triethyl phosphite in the presence of boron trifluoride-ether indicated



Scheme.

the presence of two phosphonium ions. A double quartet at δ 4.58 (*J* 7,7 Hz, POCH₂) and a doublet at δ 4.45 (*J* 7.5 Hz, OCH₂P) in a ratio of 3:1 was assigned to (3a), and another double quartet at δ 4.51 (*J* 7,7 Hz) and a doublet at δ 4.57 (*J* 7 Hz) in a ratio of 2:1 was assigned to (4a). For (1a) or (1b) with triethyl phosphite and boron trifluoride-ether in CD₂Cl₂, the ³¹P n.m.r. spectra showed one major product peak at δ +33.2 or δ +35.1, respectively and these were assigned to the alkoxyethyltriethoxyphosphonium aryloxytrifluoroborates (3a) and (3b). This assignment was based on the similarity of their ³¹P

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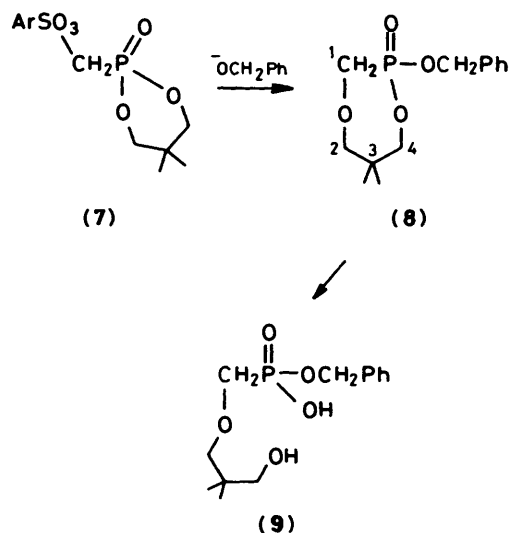
Table. Preparation of diethyl alkoxymethylphosphonates (5)

ROCH ₂ OAr ^a (1)	Lewis acid	Reaction conditions	Ratio of (5):(6) ^b
(1a)	TiCl ₄	-78 °C, 15 min	100:0
(1a)	TiCl ₄	-78 °C, then 20 °C, 16 h	92:8
(1a)	BF ₃ -Et ₂ O	-78 °C, 2 h	No reaction
(1a)	BF ₃ -Et ₂ O	-35 °C, 15 min	100:0 ^c
(1a)	BF ₃ -Et ₂ O	-35 °C, 45 min	100:0 ^d
(1a)	BF ₃ -Et ₂ O	-20 °C, then 20 °C, 16 h	80:20
(1f)	BF ₃ -Et ₂ O	-20 °C, then 20 °C, 16 h	87:13
(1h)	BF ₃ -Et ₂ O	-20 °C then 20 °C, 16 h	95:5

^a Ar = 4-chlorophenyl. ^b Ratio by ³¹P n.m.r. ^c 30% Reaction. ^d 50% Reaction.

chemical shifts with the values reported by Hudson⁷ for alkyltriphenoxyphosphonium halides (δ +30—+41) and by Schmidpeter and Brecht⁸ for aryltriethoxyphosphonium hexachloroantimonates (δ +35). Quasiphosphonium intermediates exist essentially as ion pairs⁷ in poorly ionizing media such as CH₂Cl₂ and have been observed to undergo disproportionation.⁹ For example, Westheimer has reported¹⁰ that there is a rapid redistribution of phenoxy and 4-nitrophenoxy groups between methyl tetraphenoxyposphorane and methyl tetra-4-nitrophenoxyphosphorane involving all possible phosphorane and aryloxyphosphonium intermediates. Redistribution of the 4-chlorophenoxy and ethoxy groups of triethoxy-1-butoxy-methylphosphonium 4-chlorophenoxytrifluoroborate (3a) followed by hydrolysis of the two phosphonium ions (3a) and (4a) accounts for both (5a) and (6a).

Petrov¹¹ investigated the reaction of sodium alkoxides with alkyl and arylsulphonyloxymethylphosphonates. However this method is of limited use because only poor yields of dialkyl alkoxymethylphosphonates are obtained due to transesterification and dealkylation of the ester groups at the phosphorus atom. 2-(4-Chlorophenylsulphonyloxymethyl)-5,5-dimethyl-1,3,2-dioxaphosphorinan-2-one (7) was synthesized from 2-hydroxy-5,5-dimethyl-1,3,2-dioxaphosphorinan¹² using the procedures of Stannett¹³ and Holy.³ Reaction of sodium benzyl oxide with (7) in DMSO led to numerous products. In



contrast, slow addition of sodium benzyl oxide to (7) in THF at room temperature afforded only the benzyl ester (8) in 80% yield, presumably by initial transesterification followed by intramolecular displacement of 4-chlorobenzenesulphonate by the anion derived from the 1,3-diol. The structure of (8) followed from its ¹³C and ¹H n.m.r. spectra. The former gave 11 peaks, thus eliminating the possibility of straightforward displacement of 4-chlorobenzenesulphonate by the benzyl oxide anion in its reaction with (7). Two n.o.e. difference experiments helped to assign the resonances in the ¹H n.m.r. spectrum. Irradiation at one of the methyl groups at δ 0.91 caused a 4% enhancement in the signals at δ 3.93 (*J* 12, 15.6 Hz), 3.83 (*J* 1.1, 12.0, 18.6 Hz), 3.56 (*J* 1.1, 12.6 Hz), and 3.38 (*J* 12.6 Hz) and so these peaks were assigned to the protons on C-4 and C-2. The resonances at δ 3.56 and 3.38 were assigned to the protons on C-2 as they were not coupled to the phosphorus. A 6% enhancement of the signals at δ 3.93 and δ 3.56 was obtained on irradiation at δ 1.0 ('axial' methyl group) and these resonances were assigned to the 'equatorial' protons on C-4 and C-2 respectively. There was also long range (*J* 1.1 Hz), *W* coupling between these 'equatorial' protons. The remaining peaks at δ 4.08 (*J* 5.6, 15.6 Hz) and δ 3.99 (*J* 0.9, 15.6 Hz) were assigned to the protons on C-1. Mild basic hydrolysis of (8) gave the acyclic mono ester (9).

Experimental

M.p.s were determined on a Kofler hot-stage apparatus and are uncorrected. ¹H N.m.r. spectra were recorded on Bruker WH360 or Varian T60 spectrometers as solutions in CDCl₃, unless otherwise stated, and with SiMe₄ as internal standard. ¹³C N.m.r. spectra were determined at 90.56 MHz on a Bruker WH360 spectrometer as solutions in CDCl₃. ³¹P N.m.r. spectra were obtained at 32.43 MHz using a Bruker WP80 spectrometer as solutions in CDCl₃ and shifts are quoted in p.p.m. downfield from 85% phosphoric acid. Mass spectra were recorded on a Kratos MS 80RF instrument. Merck Kieselgel 60 (Art 9395) was used for column chromatography. Petroleum refers to light petroleum (b.p. 60—80 °C) and ether to diethyl ether. Solvents were routinely purified by standard techniques. Sodium hydride was obtained as a 50% dispersion in mineral oil and washed with petroleum before use.

General Procedure for the Preparation of Diethyl or Diphenyl Alkoxymethylphosphonates.—The alcohol (5 mmol) dissolved in THF (10 ml) was added to sodium hydride (5 mmol). The resulting mixture was stirred for 4 h at ambient temperature and then treated with a solution of 1-chloro-4-chloromethoxybenzene⁶ (0.89 g, 5 mmol) in THF (5 ml). The resulting mixture was stirred for 14 h, and water and ether were then added. The organic layer was separated, washed with saturated aqueous sodium chloride, dried, and evaporated to leave the acetal as a colourless oil. The crude acetal and triethyl phosphite (1.4 ml) or triphenyl phosphite (1.5 ml) were dissolved in dichloromethane (10 ml) and then cooled to -78 °C. Titanium tetrachloride (0.6 ml) was added and the mixture was stirred for 15 min and then quenched with water (20 ml). The mixture was allowed to warm to room temperature and then extracted with ether. The organic extract was washed with saturated aqueous sodium chloride, dried, concentrated and the residue was chromatographed on silica, using ethyl acetate-petroleum (1:2) as eluant to remove 4-chlorophenol and then ethyl acetate to give the desired phosphonate. All the diethyl alkoxymethylphosphonates (5a—h), and diphenyl 1-ethylprooxymethylphosphonate, were colourless liquids, and were analysed as salts of their corresponding monoethyl or phenyl alkoxymethylphosphonate esters, obtained through basic hydrolysis [2M KOH, ethanol-water (1:1), 40 °C].

Diethyl butoxymethylphosphonate (5a) (1.0 g, 90%), b.p. 74 °C/0.04 mmHg (lit.,¹⁴ 115 °C/3 mmHg); δ_{H} (360 MHz, CD_2Cl_2) 4.10 (4 H, dq, J 7.8 Hz), 3.70 (2 H, d, J 8.6 Hz), 3.51 (2 H, t, J 6.5 Hz), 1.53 (2 H, m), 1.35 (2 H, m), 1.30 (6 H, dt, J 0.3, 8 Hz), and 0.9 (3 H, t, J 7.3 Hz); δ_{P} +20.5; 4-nitrobenzylisothiuronium ethyl butoxymethylphosphonate, m.p. 164 °C (from ethyl acetate-petroleum) (Found: C, 44.1; H, 6.2; N, 10.3. $\text{C}_{15}\text{H}_{26}\text{N}_3\text{O}_6\text{PS}$ requires C, 44.2; H, 6.4; N, 10.3%).

4-Chlorophenyl ethyl butoxymethylphosphonate (6a) (Found: M^+ , 306.0787. $\text{C}_{13}\text{H}_{20}\text{ClO}_4\text{P}$ requires 306.0768. Found: $M\text{H}^+$, 307.0866. $\text{C}_{13}\text{H}_{21}\text{ClO}_4\text{P}$ requires 307.0852); δ_{H} (60 MHz) 7.2 (4 H, br s), 4.21 (2 H, dq, J 7, 7 Hz), 3.84 (2 H, d, J 8 Hz), 1.46 (4 H, m), 1.34 (3 H, t, J 7 Hz), and 0.9 (3 H, t, J 6 Hz); δ_{P} +17.80; m/z 307 ($M\text{H}^+$, 20%), 234 (30), 206 (85), 141 (40), 128 (90), and 111 (40).

Diethyl pentoxymethylphosphonate (5b) (1.07 g, 90%); δ_{H} (60 MHz) 4.13 (4 H, dq, J 7, 7 Hz), 3.72 (2 H, d, J 9 Hz), 3.50 (2 H, t, J 6 Hz), 1.33 (6 H, t, J 7 Hz), 1.33 (6 H, m), and 0.90 (3 H, t, J 6 Hz); δ_{P} +20.9; 4-nitrobenzylisothiuronium ethyl pentoxymethylphosphonate, m.p. 134 °C (from chloroform-petroleum) (Found: C, 45.2; H, 6.3; N, 10.0. $\text{C}_{16}\text{H}_{28}\text{N}_3\text{O}_6\text{PS}$ requires C, 45.6; H, 6.7; N, 10.0%).

Diethyl 2,2-dimethylpropoxymethylphosphonate (5c) (1.06 g, 89%); δ_{H} (60 MHz) 4.15 (4 H, dq, J 7, 7 Hz), 3.75 (2 H, d, J 8 Hz), 3.19 (2 H, s), 1.38 (6 H, t, J 7 Hz), and 0.93 (9 H, s); δ_{P} +20.6; diphenylmethylammonium ethyl 2,2-dimethylpropoxymethylphosphonate, m.p. 139 °C (from CCl_4 -petroleum) (Found: C, 64.0; H, 8.15; N, 3.3. $\text{C}_{21}\text{H}_{32}\text{NO}_4\text{P}$ requires C, 64.1; H, 8.2; N, 3.55%).

Diethyl 2-methylprop-2-enyloxymethylphosphonate (5d) (0.84 g, 76%); δ_{H} (60 MHz) 4.88 (2 H, br s), 4.12 (4 H, dq, J 7, 7 Hz), 3.93 (2 H, s), 3.67 (2 H, d, J 9 Hz), 1.72 (3 H, s), and 1.33 (6 H, t, J 7 Hz); δ_{P} +20.75; 4-nitrobenzylisothiuronium ethyl 2-methylprop-2-enyloxymethylphosphonate, m.p. 155 °C (from ethyl acetate-petroleum) (Found: C, 44.3; H, 5.7; N, 10.2. $\text{C}_{15}\text{H}_{24}\text{N}_3\text{O}_6\text{PS}$ requires C, 44.4; H, 6.0; N, 10.4%).

Diethyl 1-methylpropoxymethylphosphonate (5e) (1.02 g, 91%); δ_{H} (60 MHz) 4.13 (4 H, dq, J 7, 7 Hz), 3.62 (2 H, d, J 9 Hz), 3.35 (1 H, sext., J 6 Hz), 1.33 (2 H, m), 1.33 (6 H, t, J 7 Hz), 1.13 (3 H, d, J 6 Hz), and 0.88 (3 H, t, J 6 Hz); δ_{P} +21.05; diphenylmethylammonium ethyl 1-methylpropoxy methylphosphonate, m.p. 122 °C (from CCl_4 -petroleum) (Found: C, 63.4; H, 7.95; N, 3.9. $\text{C}_{20}\text{H}_{30}\text{NO}_4\text{P}$ requires C, 63.3; H, 8.0; N, 3.7%).

Diethyl 1-ethylpropoxymethylphosphonate (5f) (1.0 g, 84%) (Found: $M\text{H}^+$, 239.1412. $\text{C}_{10}\text{H}_{24}\text{O}_4\text{P}$ requires 239.1411. Found: M^+ - C_2H_5 , 209.0943. $\text{C}_8\text{H}_{18}\text{O}_4\text{P}$ requires 209.0930); δ_{H} (60 MHz), 4.15 (4 H, dq, J 7, 7 Hz), 3.73 (2 H, d, J 9 Hz), 3.21 (1 H, quint., J 6 Hz), 1.47 (4 H, m), 1.33 (6 H, t, J 7 Hz), and 0.9 (6 H, t, J 7 Hz); δ_{P} +21.05; m/z 209 (84%), 153 (100), 125 (90), 111 (55), 99 (100), and 81 (80); diphenylmethylammonium ethyl 1-ethylpropoxymethylphosphonate, m.p. 105 °C (from CCl_4 -petroleum) (Found: C, 63.95; H, 8.1; N, 3.65. $\text{C}_{21}\text{H}_{32}\text{NO}_4\text{P}$ requires C, 64.1; H, 8.2; N, 3.6%).

4-Chlorophenyl ethyl 1-ethylpropoxymethylphosphonate (6f) (Found: M^+ - C_2H_5 , 291.0548. $\text{C}_{12}\text{H}_{17}\text{ClO}_4\text{P}$ requires 291.0553); δ_{H} (60 MHz) 7.17 (4 H, br s), 4.2 (2 H, dq, J 7, 7 Hz), 3.86 (2 H, d, J 9 Hz), 3.20 (1 H, quint., J 6 Hz), 1.5 (4 H, m), 1.34 (3 H, t, J 7 Hz), and 0.9 (6 H, t, J 6 Hz); δ_{P} +17.9.

Diethyl cyclopentoxymethylphosphonate (5g) (0.96 g, 81%) (Found: $M\text{H}^+$, 237.1255. $\text{C}_{10}\text{H}_{22}\text{O}_4\text{P}$ requires 237.1268); δ_{H} (60 MHz) 4.18 (4 H, dq, J 7, 7 Hz), 4.1 (1 H, m), 3.73 (2 H, d, J 9 Hz), 1.66 (8 H, br s), and 1.35 (6 H, t, J 7 Hz); δ_{P} +20.5; m/z 237 ($M\text{H}^+$, 5%), 169 (10), 152 (84), and 125 (100); diphenylmethylammonium ethyl cyclopentoxymethylphosphonate, m.p. 137 °C (from CCl_4 -petroleum) (Found: C, 64.5; H, 7.8; N, 3.25. $\text{C}_{21}\text{H}_{30}\text{NO}_4\text{P}$ requires C, 64.4; H, 7.7; N, 3.6%).

Diethyl 1,1-dimethylethoxymethylphosphonate (5h) (0.99 g,

88%) (Found: M^+ , 224.1183. $\text{C}_9\text{H}_{21}\text{O}_4\text{P}$ requires 224.1177); δ_{H} (60 MHz) 4.17 (4 H, dq, J 7, 7 Hz), 3.67 (2 H, d, J 11 Hz), 1.38 (6 H, t, J 7 Hz), and 1.26 (9 H, s); δ_{P} +21.9; m/z 225 ($M\text{H}^+$, 72%), 209 (45), 194 (34), 151 (58), 138 (100), 123 (48), and 111 (92); diphenylmethylammonium ethyl 1,1-dimethylethoxymethylphosphonate, m.p. 147 °C (from CCl_4 -petroleum) (Found: C, 63.45; H, 7.75; N, 3.5. $\text{C}_{20}\text{H}_{30}\text{NO}_4\text{P}$ requires C, 63.3; H, 8.0; N, 3.7%).

4-Chlorophenyl ethyl 1,1-dimethylethoxymethylphosphonate (6h) (Found: M^+ , 306.0797. $\text{C}_{13}\text{H}_{20}\text{ClO}_4\text{P}$ requires 306.0787. Found: M^+ - Me, 291.0553. $\text{C}_{12}\text{H}_{17}\text{ClO}_4\text{P}$ requires 291.0553); δ_{H} (60 MHz) 7.2 (4 H, br s), 4.23 (2 H, dq, J 7, 7 Hz), 3.74 (2 H, d, J 9 Hz), 1.34 (3 H, t, J 7 Hz), and 1.21 (9 H, s); δ_{P} +19.7; m/z 306 (M^+ , 25%), 291 (30), 251 (20), 205 (40), 141 (40), and 128 (100).

Diphenyl 1-ethylpropoxymethylphosphonate (1.37 g, 82%) (Found: $M\text{H}^+$, 335.1412. $\text{C}_{18}\text{H}_{24}\text{O}_4\text{P}$ requires 335.1419); δ_{H} (60 MHz) 7.2 (10 H, s), 3.96 (2 H, d, J 8 Hz), 3.25 (1 H, quint., J 5 Hz), 1.4 (4 H, m), and 0.9 (6 H, t, J 6 Hz); δ_{P} +14.7; m/z 335 ($M\text{H}^+$, 50%), 305 (70), 265 (70), 247 (75), 141 (58), and 107 (67); 4-nitrophenylmethylisothiuronium phenyl 1-ethylpropoxymethylphosphonate, m.p. 163 °C (from ethyl acetate-petroleum) (Found: C, 51.1; H, 5.9; N, 8.9. $\text{C}_{20}\text{H}_{28}\text{N}_3\text{O}_6\text{PS}$ requires C, 51.2; H, 6.0; N, 8.95%).

2-(4-Chlorophenylsulphonyloxymethyl)-5,5-dimethyl-1,3,2-dioxaphosphorinan-2-one (7).—To a stirred solution of 5,5-dimethyl-2-hydroxy-1,3,2-dioxaphosphorinan¹² (30 g, 0.2 mol) and aqueous formaldehyde (37%; 20 ml, 0.25 mol) at 0 °C was added dropwise triethylamine (4 ml) during 1 h. The reaction mixture was stirred for a further 2 h at room temperature and then at 100 °C/0.1 mmHg for 1 h. The residue was dissolved in ether (500 ml), triethylamine (21 ml, 0.2 mol) was added, and the reaction mixture was cooled to -5 °C and treated with a solution of 4-chlorobenzenesulphonyl chloride (42.0 g, 0.2 mol) in ether (150 ml). The mixture was stirred at 0 °C for 2 h then at room temperature overnight, whereupon the precipitate was filtered off and washed well with ether (200 ml). The filtrate was then concentrated and the residue was chromatographed on silica gel with ethyl acetate-petroleum (1:2) as eluant to give the title compound (7) (32 g, 45%), m.p. 118 °C (from CHCl_3 -petroleum) (Found: C, 40.6; H, 4.4. $\text{C}_{12}\text{H}_{16}\text{ClO}_6\text{PS}$ requires C, 40.6; H, 4.5%); δ_{H} (360 MHz) 7.86 (2 H, d, J 9 Hz), 7.58 (2 H, d, J 9 Hz), 4.38 (2 H, d, J 10 Hz, CH_2P), 4.22 (2 H, dd, J 7, 11 Hz, POCH_{ax}), 4.11 (2 H, dd, J 11, 13.5 Hz, POCH_{eq}), 1.22 (3 H, s, Me_{ax}), and 1.0 (3 H, s, Me_{eq}); δ_{C} 141.1, 133.0, 129.7, 129.3, 77.8 (d, J 7.1 Hz, POCH_2), 62.4 (d, J 165.3 Hz, PCH_2), 32.2 (d, J 7.9 Hz, CMe_2), 21.4, and 20.5; δ_{P} +6.12; m/z 355 (M^+ , 2%), 290 (74), 269 (56), 208 (50), 175 (80), 133 (90), and 111 (100).

2-Benzyloxy-6,6-dimethyl-1,4,2-dioxaphosphepan-2-one (8).—To 2-(4-chlorophenylsulphonyloxymethyl)-5,5-dimethyl-1,3,2-dioxaphosphorinan-2-one (7) (1.42 g, 4 mmol) dissolved in THF (10 ml) was added a solution of sodium benzyl oxide (4 mmol) in THF (30 ml) during 2 h and the resultant mixture was stirred overnight. Water was added and the reaction mixture was extracted with ether. The ether extract was washed with saturated aqueous sodium chloride, dried, and evaporated. Chromatography on silica gel with ethyl acetate-petroleum (1:1) as eluant gave 2-benzyloxy-6,6-dimethyl-1,4,2-dioxaphosphepan-2-one (8) (0.87 g, 80%), m.p. 58 °C (from CCl_4 -petroleum) (Found: C, 57.8; H, 6.85. $\text{C}_{13}\text{H}_{19}\text{O}_4\text{P}$ requires C, 57.8; H, 7.1%); δ_{H} (360 MHz) 7.39 (5 H, m), 5.14 (1 H, dd, J 11.8, 17.4 Hz), 5.12 (1 H, dd, J 11.8, 17.4 Hz), 4.08 (1 H, dd, J 5.6, 15.6 Hz), 3.99 (1 H, dd, J 0.9, 15.6 Hz), 3.93 (1 H, dd, J 12, 15.6 Hz, POCH_{ax}), 3.83 (1 H, ddd, J 1.1, 12, 18.6 Hz, POCH_{eq}), 3.56 (1 H, dd, J 1.1, 12.6 Hz, $\text{PCH}_2\text{OCH}_{\text{eq}}$), 3.38 (1 H, d, J 12.6 Hz, $\text{PCH}_2\text{OCH}_{\text{ax}}$), 1.0 (3 H, s, Me_{ax}), and 0.91 (3 H, s, Me_{eq}); δ_{C} 135.8 (d, J 5.5 Hz, *ipso* carbon), 128.4, 128.3, 127.8, 83.5 (PCH_2OCH_2), 73.5 (d, J 4.4 Hz, $\text{POCH}_2\text{CMe}_2$), 68.8 (d,

J 144.9 Hz, PCH₂), 67.1 (d, J 6.9 Hz, POCH₂Ph), 37.5 (d, J 1.8 Hz, CMe₂), 22.0, and 21.6; δ_P +25.84. Mild basic hydrolysis of (8) gave benzyl 3-hydroxy-2,3-dimethylpropoxymethylphosphonate (9) as a colourless liquid (Found: M^+ , 288.1127. C₁₃H₂₁O₅P requires 288.1116); δ_H (360 MHz, CD₃OD), 7.36 (5 H, m), 5.09 (2 H, d, J 8 Hz), 3.77 (2 H, d, J 8.3 Hz, PCH₂), 3.34 (2 H, s), 3.31 (2 H, s), and 0.86 (6 H, s); δ_P +21.70.

Acknowledgements

The author expresses his sincere gratitude to Professor Sir John Cornforth F.R.S. for his constant support, interest, and encouragement. The S.E.R.C. is also thanked for support via Professor Sir John Cornforth F.R.S.

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Received 10th September 1985; Paper 5/1551