Synthesis of 2,3,5-Trihydroxyphenylprop-1-ene and its 4-Chloro-, 6-Chloro-, and 4,6-Dichloro- Derivatives

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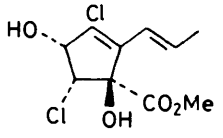
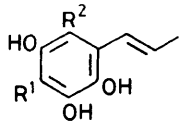
The synthesis of (*E*)-2,3,5-trihydroxyphenylprop-1-ene (**2**) and its 4-chloro-(**3**), 6-chloro-(**4**), and 4,6-dichloro- derivatives (**5**) is described. The routes involve the key intermediates, methyl 2,3,5-tribenzyloxybenzoate (**15**) and methyl 2,3,5-tribenzyloxy-4-chlorobenzoate (**41**) which were prepared from vanillin and 3,5-dimethoxytoluene (**33**), respectively. The benzoates (**15**) and (**41**) were treated with the anion from ethylphosphonic bis(dimethylamide) (**6**) to give the corresponding β-oxophosphonamides (**17**) and (**42**). These were reduced with sodium borohydride to the β-hydroxyphosphonamides (**19**) and (**29**), respectively. The benzyl protecting groups were removed by hydrogenolysis and subsequent treatment with acid gave the required phenylpropenes (**2**) and (**3**). The 6-chloro derivatives (**4**) and (**5**) were prepared *via* chlorination of the β-acetoxyphosphonamides (**27**) and (**44**), respectively.

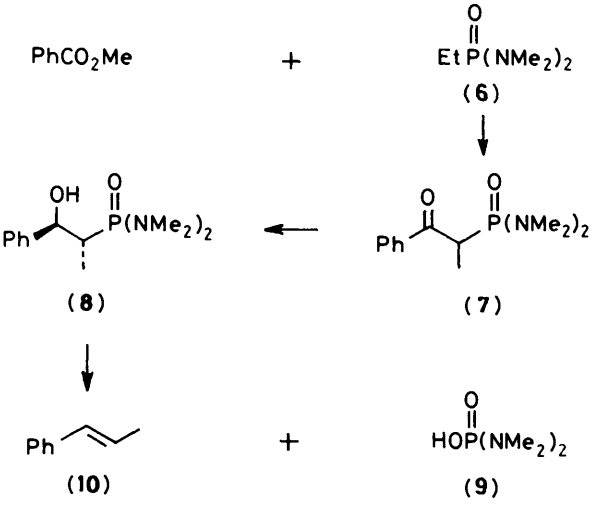
In connection with studies in this laboratory[1] on the biosynthesis of cryptosporiopsinol (**1**)[2] from *Periconia macrospinosa*, we required efficient syntheses of 2,3,5-trihydroxyphenylprop-1-ene (**2**) and its 4-chloro-(**3**), 6-chloro-(**4**), and 4,6-dichloro-derivatives (**5**). The dichloro derivative (**5**) has been proposed[3] as a potential precursor of cryptosporiopsinol (**1**). As the stereochemistry of the double bond in the natural product cryptosporiopsinol (**1**) is *E*, we required the potential precursors to have *E* double bonds. This paper describes the synthesis of these phenylpropenes.



(**1**)



(**2**) $R^1 = R^2 = H$
(**3**) $R^1 = Cl, R^2 = H$
(**4**) $R^1 = H, R^2 = Cl$
(**5**) $R^1 = R^2 = Cl$

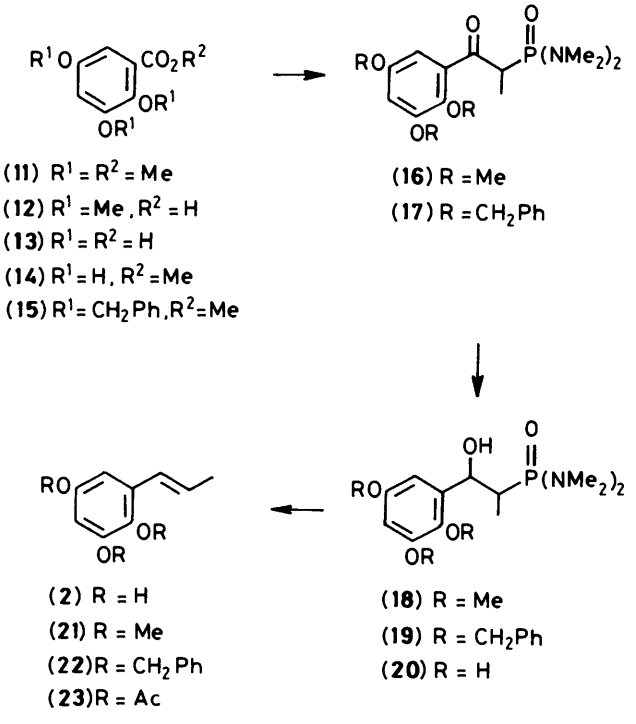


Scheme 1.

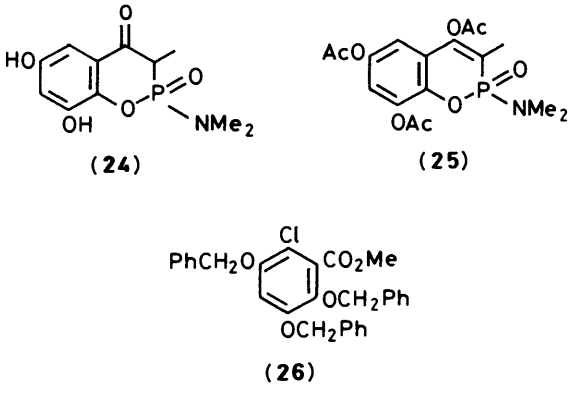
Results and Discussion

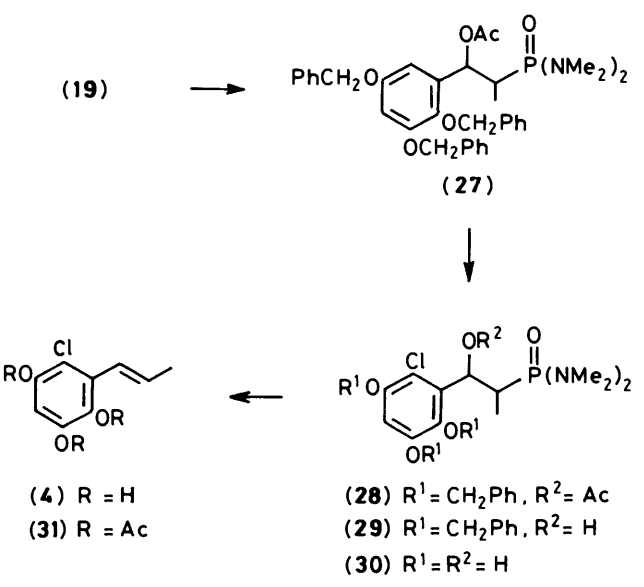
The synthesis is based on the synthesis of (*E*)-phenylprop-1-ene (**10**) by Corey.[4] Treatment of methyl benzoate with the anion from ethylphosphonic bis(dimethylamide) (**6**)[5] gave the β-oxophosphonamide (**7**). Reduction of the ketone with sodium borohydride occurred in a stereospecific manner and the resulting alcohol (**8**) undergoes acid-catalysed cycloelimination in a *syn*-manner to give specifically (*E*)-phenylprop-1-ene (**10**) and tetramethylphosphorodiamidic acid (**9**) (Scheme 1).

The initial approach to the synthesis of 2,3,5-trihydroxyphenylprop-1-ene (**2**) was to utilise methyl 2,3,5-trimethoxybenzoate (**11**) (Scheme 2). This benzoate (**11**) was prepared in good yield from vanillin *via* 2,3,5-trimethoxybenzoic acid (**12**).[6] The benzoate (**11**) reacted successfully with the anion of ethylphosphonic bis(dimethylamide) (**6**) to give the β-oxophosphonamide (**16**) in high yield. Reduction of the ketone with sodium borohydride gave the alcohol (**18**) which when refluxed in toluene, with silica gel gave 2,3,5-trimethoxyphenylprop-1-ene (**21**). Examination of the phenylpropene (**21**) by ^{1}H n.m.r. spectroscopy did not reveal the presence of any product with *Z*-stereochemistry. Since the β-hydroxyphosphonamide (**18**) and the phenylpropene (**21**) are both unstable under acidic conditions, the deprotection of the phenolic hydroxy groups was attempted on the β-oxophosphonamide (**16**). Treatment of the β-oxophosphonamide (**16**) with boron tribromide cleaved the methyl ethers; however, the product cyclised with elimination of dimethylamine to form the cyclic phosphonate (**24**). The phosphonate (**24**) readily gave a triacetate (**25**) on treatment with acetic anhydride. All attempts to convert the cyclic phosphonate (**24**) into the desired phenylpropene (**2**) failed. In view of these results the benzyl-protected β-oxophosphonamide (**17**) was prepared from 2,3,5-trihydroxybenzoic acid (**13**).[6] The methyl benzoate (**14**) was treated with benzyl bromide in butanone with anhydrous potassium carbonate to give the tribenzyloxybenzoate (**15**). The benzyl ether (**15**) was converted into 2,3,5-tribenzyloxyphenylprop-1-ene (**22**) by the same method as the methyl ether series. The phenylpropene (**22**) again showed no contamination with the *Z*-isomer indicating that the benzyl ethers had not affected the stereochemistry of the ketone reduction. Hydrogenolysis of the tribenzyloxy β-hydroxyphosphonamide (**19**) using palladium on charcoal as catalyst gave the trihydroxy β-hydroxyphosphonamide (**20**) without affecting the benzylic hydroxy group. Cycloelimination of this β-hydroxyphosphonamide (**20**) in methanol containing a catalytic



Scheme 2.





Scheme 3.

amount of trifluoroacetic acid gave the required 2,3,5-trihydroxyphenylprop-1-ene (**2**). Using this procedure the by-product, tetramethylphosphorodiamidic acid (**9**) was converted into its methyl ester. Since the trihydroxyphenylpropene (**2**) and the subsequent chlorinated derivatives (**3**), (**4**), and (**5**) are highly unstable, they were purified and characterised as their triacetates.

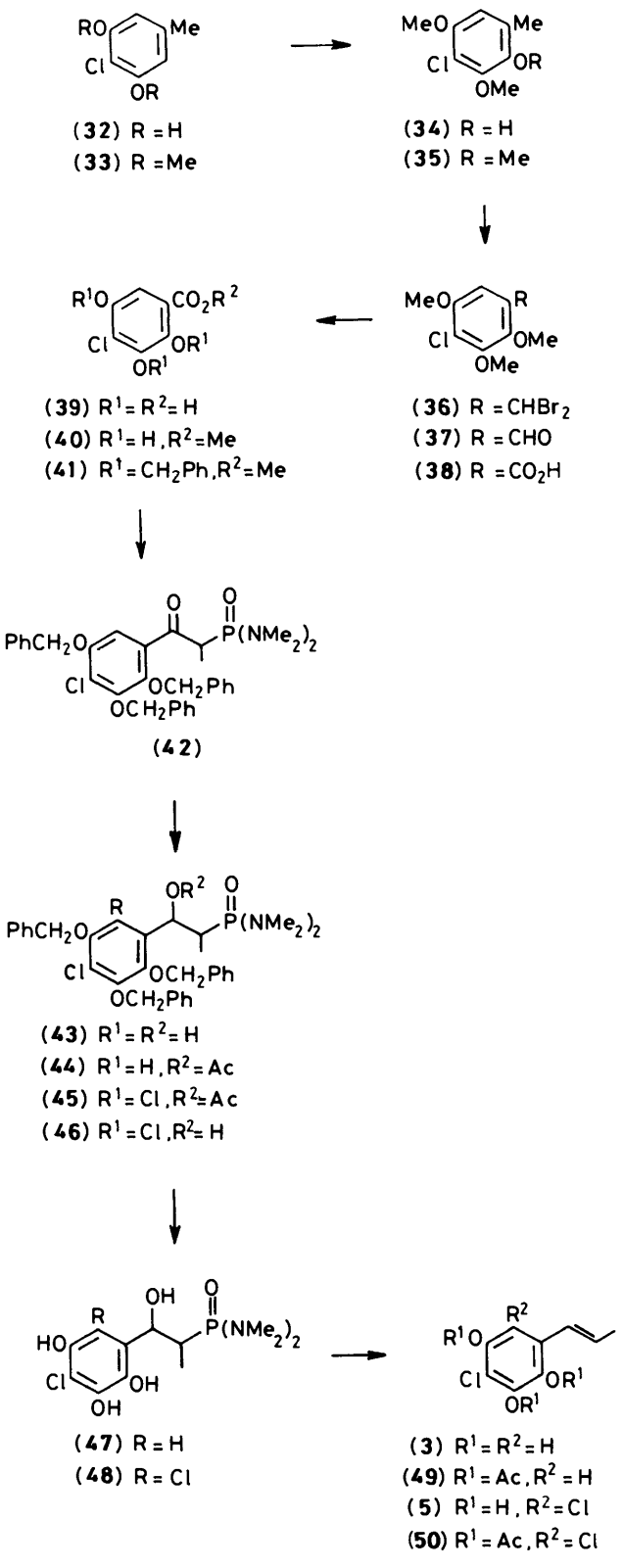
Attention was then turned to the synthesis of 6-chloro-2,3,5-trihydroxyphenylprop-1-ene (**4**). Reaction of the tribenzyloxybenzoate (**15**) with sulphuryl chloride resulted in the chlorination of the 6-position only. However, the 6-chlorobenzoate (**26**) proved to be too hindered for attack by the alkylphosphonate anion; therefore, the chlorine had to be introduced at the 6-position after β-oxophosphonamide formation. Treatment of the β-oxophosphonamide (**17**) with sulphuryl chloride led to chlorination α to the ketone and attempts at chlorination of the β-hydroxyphosphonamide (**19**) resulted in cycloelimination. The hydroxy group was thus protected as the acetate. Chlorination of the β-acetoxyphosphonamide (**27**) gave the required 6-chloro derivative (**28**). The acetate protecting group was removed using aqueous methanolic sodium hydroxide to give the chloro β-oxophosphonamide (**20**) which was converted into 6-chloro-2,3,5-trihydroxyphenylprop-1-ene (**4**) (Scheme 3).

In order to prepare 4-chloro-2,3,5-trihydroxyphenylprop-1-ene (**3**), methyl 4-chloro-2,3,5-tribenzyloxybenzoate (**41**) was required. This compound was made from 4-chloro-3,5-dimethoxytoluene (**33**) (Scheme 4). Methylation of 4-chloro-3,5-dihydroxytoluene (4-chloro-orcinol) (**32**)[7] with dimethyl sulphate gave the dimethyl ether (**33**) which could also be made from 3,5-dimethoxytoluene by treatment with butyl-lithium followed by 1,2-dichloroethane. The corresponding 4-bromo-derivative has been reported to be synthesized in a similar manner.[8] *O*-Alkylated orcinols have been hydroxylated by *m*-chloroperbenzoic acid.[9] Thus oxidation of the dimethyl ether (**33**) gave the hydroxylated derivative (**34**) and further methylation gave 4-chloro-2,3,5-trimethoxytoluene (**35**). Traditional oxidation of the toluene (**35**) to the benzoic acid (**38**) was not possible due to the electron-rich aromatic ring. Thus a milder method was used. The trimethoxytoluene (**35**) on reaction under radical-favouring conditions with *N*-bromosuccinimide gave the geminal dibromide (**36**). Hydrolysis using aqueous silver nitrate in methoxyethanol gave the aldehyde (**37**) which yielded the benzoic acid (**38**) on mild oxidation with tetrabutylammonium permanganate. Demethylation, followed by esterification and formation of the benzyl ethers, gave the desired benzylated methyl ester (**41**). This ester (**41**) was converted into 4-chloro-2,3,5-trihydroxyphenylprop-1-ene (**3**) by a series of reactions similar to the preparation of the phenylpropene (**2**).

4,6-Dichloro-2,3,5-trihydroxyphenylprop-1-ene (**5**) was prepared *via* chlorination of the 4-chloro β-acetoxyphosphonamide (**44**) in a related series of reactions (Scheme 4).

Experimental

M.p.s were determined with a Kofler hot-stage apparatus. I.r. spectra were recorded for potassium bromide discs with a Perkin-Elmer 580 spectrometer. ^{1}H N.m.r. spectra were recorded with a Perkin-Elmer RB 24 spectrometer for solutions in deuteriochloroform unless otherwise stated ($SiMe_4$ as internal standard). Evaporation was performed by rotary evaporator under reduced pressure; solutions in organic solvents were dried over magnesium sulphate.



Scheme 4.

Methyl 2,3,5-*Trimethoxybenzoate* (**11**).—A solution of 2,3,5-trimethoxybenzoic acid (**12**)[6] (2 g) in dry methanol (30 ml) was saturated with hydrogen chloride and heated under reflux for 4 h. The methanol was evaporated off and the residue dissolved in ether. The ether solution was washed with aqueous sodium hydrogen carbonate and water, dried, and evaporated to give the *title compound* as an oil (1.94 g, 85%) (Found: C, 58.4; H, 6.3%; M^+, 226. $C_{11}H_{14}O_5$ requires C, 58.4; H, 6.25%; *M*, 226); δ_H 6.67 (1 H, d, *J* 3 Hz, ArH), 6.61 (1 H, d, *J* 3 Hz, ArH), 3.91 (3 H, s, OMe), and 3.84 (9 H, s, OMe).

Methyl 2,3,5-*Trihydroxybenzoate* (**14**).—A solution of 2,3,5-trihydroxybenzoic acid (**13**)[6] (2 g) in dry methanol (30 ml) was saturated with hydrogen chloride and heated under reflux for 4 h. After being cooled, the mixture was evaporated to leave a gum which was triturated with hexane to give a *yellow crystalline solid* (2 g, 90%), m.p. 63—64 °C (from ethyl acetate–hexane) (Found: C, 48.6; H, 4.5%; M^+, 172. $C_7H_8O_5$ requires C, 48.8; H, 4.7%; *M*, 172); δ_H[$(CD_3)_2CO$] 6.77 (1 H, d, *J* 3 Hz, ArH), 7.65 (1 H, d, *J* 3 Hz, ArH), 5.30 (3 H, br s, OH), and 3.91 (3 H, s, OMe).

Methyl 2,3,5-*Tribenzyloxybenzoate* (**15**).—Benzyl bromide (4 ml), anhydrous potassium carbonate (5 g), and a few crystals of potassium iodide were added to a solution of methyl 2,3,5-trihydroxybenzoate (**14**) (1 g) in dry butanone (25 ml). The mixture was stirred and heated under reflux for 16 h. After cooling the mixture was filtered to remove the potassium carbonate which was washed with acetone (50 ml). The combined organic solutions were evaporated and the residue recrystallised from di-isopropyl ether to give the *title compound* (**15**) (1.95 g, 80%), m.p. 100—102 °C (Found: C, 76.9; H, 5.9%; M^+, 454. $C_{29}H_{26}O_5$ requires C, 76.6; H, 5.8%; *M* 454); $\nu_{max.}$ 3 090—2 880, 1 720, and 1 600 cm^{-1}; δ_H 7.38 (15 H, m, ArH), 6.98 (1 H, d, *J* 3 Hz, ArH), 6.82 (1 H, d, *J* 3 Hz, ArH), 5.09 (2 H, s, ArCH_2), 5.06 (2 H, s, ArCH_2), 5.02 (2 H, s, ArCH_2), and 3.86 (3 H, s, OMe).

Methyl 2,3,5-*Tribenzyloxy*-6-*chlorobenzoate* (**26**).—Sulphuryl chloride (0.27 ml) was added to a solution of methyl 2,3,5-tribenzyloxybenzoate (0.5 g) in dry ether (30 ml) with stirring at room temperature. After 1 h water (30 ml) was added and the organic layer was separated, dried, and evaporated to give the *title compound* (**26**), m.p. 105—108 °C (Found: C, 71.5; H, 5.2; Cl, 7.5%; M^+, 488/490. $C_{29}H_{25}ClO_5$ requires C, 71.2; H, 5.15; Cl, 7.25%; *M*, 488/490); $\nu_{max.}$ 3 090—2 880, 1 735, and 1 580 cm^{-1}; δ_H 7.37 (15 H, m, ArH), 6.67 (1 H, s, ArH), 5.04 (6 H, s, ArCH_2), and 3.87 (3 H, s, OMe).

4-*Chloro*-3,5-*dimethoxytoluene* (**33**).—*Method A.* Dimethyl sulphate (35 ml) was added during 2 min to a stirred mixture of 4-chloro-3,5-dihydroxytoluene (**32**)[7] (20 g), anhydrous potassium carbonate (100 g), and butanone (200 ml). The mixture was heated under reflux for 5 h after which it was allowed to cool. Concentrated ammonia solution (30 ml) was then added and the mixture was refluxed for a further 10 min. After cooling, the mixture was diluted with water (300 ml) and extracted with ether (200 ml). The ether extract was washed with aqueous sodium hydroxide (1M) until the washings were colourless, washed with water, dried, and evaporated to give the *title compound* (**33**) (20.25 g, 86%), m.p. 75—76 °C (from benzene) (Found: C, 57.9; H, 6.0; Cl, 19.15%; M^+, 186/188. $C_9H_{11}ClO_2$ requires C, 57.9; H, 5.95; Cl, 19.0%; *M*, 186/188); $\nu_{max.}$ 3 010—2 850 and 1 600 cm^{-1}; δ_H 6.40 (2 H, s, ArH), 3.84 (6 H, s, OMe), and 2.28 (3 H, s, Ar*Me*).

Method B. Butyl-lithium (1.655M; 4.36 ml) was added to a solution of 3,5-dimethoxytoluene (1.1 g) in dry ether (10 ml) at room temperature under nitrogen. The mixture was left in the dark at room temperature for 72 h after which it was cooled to 5 °C and a mixture of 1,2-dichloroethane (1.2 ml) and dry ether (5 ml) was added dropwise with stirring during 0.5 h. The mixture was heated under reflux for 1.5 h and then cooled. Dilute hydrochloric acid (1M; 10 ml) was added and the organic

layer was separated, washed with aqueous sodium hydroxide and water, dried, and evaporated to give the product (0.83 g, 62%) whose properties were identical with the earlier sample.

4-*Chloro*-3,5-*dimethoxytoluene*-2-*ol* (**34**).—A solution of 4-chloro-3,5-dimethoxytoluene (**33**) (5 g) in dry dichloromethane (20 ml) was added dropwise to a solution of *m*-chloroperbenzoic acid (5.12 g) in dry dichloromethane (150 ml) at 0 °C under nitrogen. The mixture was stirred for 5 h at 0 °C after which ether (100 ml) was added and the organic solution was washed thoroughly with aqueous sodium bisulphite (5%), aqueous sodium hydrogen carbonate, and water. The organic solution was dried and evaporated to give the *title compound* (**34**) (3.38 g, 62%), m.p. 68—69 °C (Found: C, 53.4; H, 5.45; Cl, 17.5%; M^+, 202/204. $C_9H_{11}ClO_3$ requires C, 53.35; H, 5.45; Cl, 17.5%; *M*, 202/204); $\nu_{max.}$ 3 450, 3 020—2 845, 1 600, and 1 485 cm^{-1}; δ_H 6.49 (1 H, s, ArH), 5.91 (1 H, s, OH), 3.87 (3 H, s, OMe), 3.79 (3 H, s, OMe), and 2.20 (3 H, s, Ar*Me*).

4-*Chloro*-2,3,5-*trimethoxytoluene* (**35**).—Dimethyl sulphate (20 ml) was added to a mixture of 4-chloro-3,5-dimethoxytoluene-2-ol (**34**) (10 g), anhydrous potassium carbonate (30 g), and butanone (200 ml) and the mixture was stirred and heated under reflux for 5 h. Concentrated ammonia solution (20 ml) was added dropwise and the mixture was refluxed for a further 10 min; it was then allowed to cool. After dilution with water (200 ml) the mixture was extracted with ether (200 ml). The organic extracts were washed with aqueous sodium hydroxide (1M) until the washings were colourless, washed with water, dried, and evaporated to give the title compound as an oil (9.1 g, 85%), b.p. 85 °C/0.03 mmHg (Found: C, 55.35; H, 6.1; Cl, 16.4%; M^+, 218/220. $C_{10}H_{13}ClO_3$ requires C, 55.45; H, 6.05; Cl, 16.35%; *M*, 218/220); $\nu_{max.}$ 3 010—2 845, 1 595, and 1 485 cm^{-1}; δ_H 6.54 (1 H, s, ArH), 3.93 (3 H, s, OMe), 3.82 (3 H, s, OMe), 3.78 (3 H, s, OMe), and 2.22 (3 H, s, ArMe).

4-*Chloro*-1-*dibromomethyl*-2,3,5-*trimethoxybenzene* (**36**).—*N*-Bromosuccinimide (1.22 g) was added to a solution of 4-chloro-2,3,5-trimethoxytoluene (**35**) (0.71 g) in carbon tetrachloride (40 ml) and the mixture was heated under reflux while being irradiated with a tungsten lamp for 1.5 h; it was then allowed to cool. The precipitated succinimide was removed and the solvent evaporated off. The *title compound* was purified by chromatography on silica gel using ethyl acetate as eluant to give an oil (1.18 g, 97%) (Found: M^+, 371.874. $C_{10}H_{11}{}^{79}Br_2{}^{35}ClO_3$ requires *M*, 371.876); $\nu_{max.}$ 3 020—2 840, 1 725, 1 595, and 1 470 cm^{-1}; δ_H 7.04 (1 H, s, ArH), 7.00 (1 H, s, $CHBr_2$), 3.91 (3 H, s, OMe), 3.90 (3 H, s, OMe), and 3.83 (3 H, s, OMe).

4-*Chloro*-2,3,5-*trimethoxybenzaldehyde* (**37**).—A solution of silver nitrate (1.18 g) in water (20 ml) was added dropwise during 20 min to a refluxing solution of 4-chloro-1-dibromomethyl-2,3,5-trimethoxybenzene (**36**) (1.18 g) in methoxyethanol (20 ml). A precipitate of silver bromide formed immediately. Heating was continued for a further 10 min after which the mixture was cooled and diluted with water (100 ml). Silver bromide was filtered off and the aqueous filtrate was extracted with ether. The extract was dried and evaporated to give the *title compound* (**37**) (0.72 g, 98%), m.p. 57—60 °C (Found: C, 51.85; H, 4.6; Cl, 15.5%; M^+, 230/232. $C_{10}H_{11}ClO_4$ requires C, 52.1; H, 4.8; Cl, 15.35%; *M*, 230/232); $\nu_{max.}$ 2 980—2 740, 1 690, and 1 590 cm^{-1}; δ_H 10.27 (1 H, s, CHO), 7.08 (1 H, s, ArH), 3.97 (3 H, s, OMe), 3.92 (3 H, s, OMe), and 3.89 (3 H, s, OMe).

4-*Chloro*-2,3,5-*trimethoxybenzoic Acid* (**38**).—A solution of tetrabutylammonium permanganate (3.81 g) in pyridine (25 ml) was added dropwise during 15 min to a stirred solution of 4-chloro-2,3,5-trimethoxybenzaldehyde (**37**) (1 g) in pyridine (35 ml) under nitrogen. After disappearance of the characteristic purple colour of the permanganate ion, the brown solution was poured into a cold solution of sodium metabisulphite (2.6 g) in hydrochloric acid (5M; 200 ml). The solution became clear instantly and was cooled for 16 h at 4 °C, during which time the *title compound*: (**38**) crystallised out. The acid was collected and washed with cold water to give needles (0.9 g, 84%), m.p. 148—150 °C (from ether) (Found: C, 48.6; H, 4.25; Cl, 14.8%; M^+, 246/248. $C_{10}H_{11}ClO_5$ requires C, 48.7; H, 4.5; Cl, 14.4%; *M*, 246/248); $\nu_{max.}$ 2 940, 1 695, and 1 595 cm^{-1}; δ_H 7.44 (1 H, s, ArH), 6.10 (3 H, s, OMe), and 3.94 (6 H, s, OMe).

4-*Chloro*-2,3,5-*trihydroxybenzoic Acid* (**39**).—Powdered anhydrous aluminium chloride (2.9 g) was added to a solution of 4-chloro-2,3,5-trimethoxybenzoic acid (1 g) in chlorobenzene (15 ml) with stirring and the mixture was heated under reflux for 45 min. The reaction mixture was allowed to cool and then poured onto ice (20 g) and the flask washed with water (50 ml). The solutions were filtered through Celite and the aqueous layer was separated and washed with ether. The clear brown aqueous layer was acidified with concentrated hydrochloric acid to give a voluminous yellow solid precipitate. This was collected after the mixture had been set aside at 0 °C for 2 h to afford the *title compound* (**39**) (0.7 g, 84%), m.p. 210 °C decomp. (from acetic acid) (Found: C, 41.1; H, 2.15; Cl, 17.2%; M^+, 204/206. $C_7H_5ClO_5$ requires C, 41.1; H, 2.45; Cl, 17.35%; *M*, 204/206); $\nu_{max.}$ 3 360, 1 680, and 1 470 cm^{-1}; $\delta_H[(CD_3)_2CO]$ 8.50 (4 H, s, OH) and 7.01 (1 H, s, ArH).

Methyl 4-*Chloro*-2,3,5-*trihydroxybenzoate* (**40**).—A solution of 4-chloro-2,3,5-trihydroxybenzoic acid (**39**) (2 g) in dry methanol (30 ml) was saturated with hydrogen chloride and heated under reflux for 4 h. After cooling, the mixture was evaporated to leave a yellow solid which was dissolved in ethyl acetate. The organic solution was washed with aqueous sodium hydrogen carbonate and water, dried, and evaporated to give the *title compound* (**40**) (1.7 g, 79%), m.p. 180—181 °C (from benzene) (Found: C, 44.1; H, 3.25; Cl, 16.4%; M^+, 218/220. $C_8H_7ClO_5$ requires C, 43.95; H, 3.25; Cl, 16.2%; *M*, 281/220); $\nu_{max.}$ 3 500, 3 450, 1 670, 1 480, and 1 445 cm^{-1}; $\delta_H[(CD_3)_2CO]$ 8.34 (1 H, s, OH), 8.26 (1 H, s, OH), 6.43 (1 H, s, ArH), and 3.92 (3 H, s, OMe).

Methyl 2,3,5-*Tribenzyloxy*-4-*chlorobenzoate* (**41**).—Benzyl bromide (4 ml), anhydrous potassium carbonate (5 g), and a few crystals of potassium bromide were added to a stirred solution of methyl 4-chloro-2,3,5-trihydroxybenzoate (**40**) (1 g) in dry butanone (25 ml). The mixture was then heated under reflux for 16 h. After cooling, the mixture was filtered to remove potassium carbonate which was washed with acetone. The combined organic solutions were evaporated and the excess of benzyl bromide was distilled off under reduced pressure (0.05 mmHg). The residue was recrystallised from di-isopropyl ether to give the *title compound* (**41**) (2.05 g, 86%), m.p. 98—100 °C (Found: C, 71.0; H, 5.05; Cl, 7.4%; M^+, 488.139. $C_{29}H_{25}ClO_5$ requires C, 71.25; H, 5.15; Cl, 7.25%; *M*, 488.139); $\nu_{max.}$ 3 090—2 860, 1 735, 1 705, and 1 587 cm^{-1}; δ_H 7.34 (15 H, m, ArH), 7.22 (1 H, s, ArH), 5.11 (2 H, s, $ArCH_2$), 5.04 (2 H, s, $ArCH_2$), 5.01 (2 H, s, $ArCH_2$), and 3.82 (3 H, s, OMe).

1-*Oxo*-1-(2,3,5-*trimethoxyphenyl*)*propan*-2-*ylphosphonic Bis*(*dimethylamide*) (**16**).—A solution of butyl-lithium in hexane (1.6M; 3.9 ml) was added to a stirred solution of ethylphosphonic bis(dimethylamide) (**6**)[5] (1 g) in dry tetrahydrofuran (15 ml) at −78 °C under nitrogen. The mixture was stirred at −50 °C for 3 h after which it was cooled to −78 °C; a solution of methyl 2,3,5-trimethoxybenzoate (**11**) (0.68 g) in dry tetrahydrofuran (10 ml) was then added. Stirring was continued for 2 h at

−78 °C after which the solution was allowed to warm to room temperature. Water (10 ml) was added and the organic solvents were evaporated. The aqueous solution was extracted with ethyl acetate and the combined organic extracts were washed thoroughly with aqueous sodium chloride (1M) to remove the unchanged ethylphosphonic bis(dimethylamide). The organic solution was dried and evaporated to give the β-*oxophosphonamide* (**16**) as an oil (0.97 g, 90%) (Found: C, 53.5; H, 7.55; N, 7.85; P, 8.8. $C_{16}H_{27}N_2O_5P$ requires C, 53.6; H, 7.6; N, 7.8; P, 8.65%); δ_H 6.60 (2 H, s, ArH), 4.53 (1 H, dq, J_{HH} 7 and J_{PH} 18 Hz, C*H*Me), 3.86 (3 H, s, OMe), 3.82 (3 H, s, OMe), 3.79 (3 H, s, OMe), 2.60 (6 H, d, J_{PH} 10 Hz, NMe), 2.58 (6 H, d, J_{PH} 10 Hz, NMe), and 1.49 (3 H, dd, J_{HH} 7 and J_{PH} 16 Hz, CHMe).

1-*Oxo*-1-(2,3,5-*tribenzyloxyphenyl*)*propan*-2-*ylphosphonic Bis*(*dimethylamide*) (**17**).—Methyl 2,3,5-tribenzyloxybenzoate (**15**) by the foregoing method gave the β-*oxophosphonamide* (**17**) (85%), m.p. 147—149 °C (from di-isopropyl ether) (Found: C, 69.5; H, 6.75; N, 4.6; P, 5.35. $C_{34}H_{39}N_2O_5P$ requires C, 69.6; H, 6.7; N, 4.75; P, 5.3%); $\nu_{max.}$ 3 090—2 800, 1 675, and 1 600 cm^{-1}; δ_H 7.38 (15 H, m, ArH), 6.79 (1 H, d, *J* 3 Hz, ArH), 6.71 (1 H, d, *J* 3 Hz, ArH), 5.12 (1 H, d, *J* 26.2 Hz, ArCH_2), 4.83 (1 H, d, *J* 26.2 Hz, ArCH_2), 5.09 (2 H, s, ArCH_2), 5.02 (2 H, s, ArCH_2), 4.55 (1 H, dq, J_{HH} 7 and J_{PH} 19 Hz, C*H*Me), 2.49 (6 H, d, J_{PH} 10 Hz, NMe), 2.44 (6 H, d, J_{PH} 10 Hz, NMe), and 1.31 (3 H, dd, J_{HH} 7 and J_{PH} 16 Hz, CH*Me*).

1-*Oxo*-1-(2,3,5-*tribenzyloxy*-4-*chlorophenyl*)*propan*-2-*ylphosphonic Bis*(*dimethylamide*) (**42**).—Methyl 2,3,5-Tribenzyloxy-4-chlorobenzoate (**40**) by the foregoing method gave the β-*oxophosphonamide* (**42**) (84%), m.p. 105—109 °C (from di-isopropyl ether) (Found: C, 65.65; H, 5.95; Cl, 5.6 N, 4.35; P, 5.0. $C_{34}H_{38}ClN_2O_5P$ requires C, 65.75; H, 6.15; Cl, 5.7 N, 4.5; P, 4.95%); $\nu_{max.}$ 3 050—2 800, 1 650, and 1 580 cm^{-1}; δ_H 7.26 (15 H, m, ArH), 7.04 (1 H, s, ArH), 5.14 (2 H, s, ArCH_2), 5.13 (1 H, d, *J* 23.2 Hz, ArCH_2), 5.09 (2 H, s, ArCH_2), 4.88 (1 H, d, *J* 23.2 Hz, ArCH_2), 4.48 (1 H, dq, J_{HH} 7 and J_{PH} 19 Hz, C*H*Me), 2.27 (12 H, d, J_{PH} 10 Hz, NMe), and 1.26 (3 H, dd, J_{HH} 7 and J_{PH} 16 Hz, CH*Me*).

1-*Hydroxy*-1-(2,3,5-*trimethoxyphenyl*)*propan*-2-*ylphosphonic Bis*(*dimethylamide*) (**18**).—Sodium borohydride (1 g) was added slowly to a stirred solution of the β-oxophosphonamide (**16**) (1 g) in methanol (30 ml) at 0 °C. After the mixture had been stirred for 1 h dilute hydrochloric acid (0.1M) was carefully added to it to destroy the excess of sodium borohydride, the pH being kept above 7.5. The solution was diluted with water and extracted with ethyl acetate. The extract was dried and evaporated to give the *title compound* (**18**) as an oil (0.93 g, 92%) (Found: C, 53.5; H, 8.3; N, 7.6; P, 8.65. $C_{16}H_{29}N_2O_5P$ requires C, 53.3: H, 8.1; N, 7.75; P, 8.6%); δ_H 6.62 (1 H, d, *J* 3 Hz, ArH), 6.42 (1 H, d, *J* 3 Hz, ArH), 6.04 (1 H, s, OH), 5.14 (1 H, dd, J_{HH} 9 Hz and J_{PH} 12 Hz, C*H*OH), 3.83 (3 H, s, OMe), 3.81 (3 H, s, OMe), 3.79 (3 H, s, OMe), 3.45 (1 H, m, C*H*Me), 2.82 (6 H, d, J_{PH} 10 Hz, NMe), 2.60 (6 H, d, NMe), and 0.84 (3 H, dd, J_{HH} 8 Hz and J_{PH} 16 Hz, CH*Me*).

1-*Hydroxy*-1-(2,3,5-*tribenzyloxyphenyl*)*propan*-2-*ylphosphonic Bis*(*dimethylamide*) (**19**).—The β-oxophosphonamide (**17**) by the foregoing method gave the *title compound* (**19**) (90%), m.p. 131—133 °C decomp. (from di-isopropyl ether) (Found: C, 69.1; H, 7.0; N, 4.6; P, 5.0. $C_{34}H_{41}N_2O_5P$ requires C, 69.35; H, 7.0; N, 4.75; P, 5.25%); $\nu_{max.}$ 3 300, 3 000—2 800, and 1 600 cm^{-1}; δ_H 7.42 (15 H, m, ArH), 6.82 (1 H, d, *J* 3 Hz, ArH), 6.66 (1 H, d, *J* 3 Hz, ArH), 5.40—4.96 (2 H, m, C*H*OHC*H*Me), 5.24 (1 H, d, *J* 32.5 Hz, ArCH_2), 5.15 (2 H, s, ArCH_2), 5.10 (2 H, s, ArCH_2), 4.81 (2 H, d, *J* 32.5 Hz, ArCH_2), 2.69 (6 H, d, J_{PH} 10 Hz, NMe), 2.57 (6 H, d, J_{PH} 10 Hz, NMe), and 0.83 (3 H, dd, J_{HH} 7 and J_{PH} 17 Hz, CH*Me*).

1-*Hydroxy*-1-(2,3,5-*tribenzyloxy*-4-*chlorophenyl*)*propan*-2-*ylphosphonic Bis*(*dimethylamide*) (**43**).—The β-oxophosphonamide (**42**) by the foregoing method gave the *title compound* (**43**) (91%), m.p. 156—159 °C (from acetone–hexane) (Found: C, 65.55; H, 6.2; Cl, 5.9; N, 4.55; P, 4.8. $C_{34}H_{40}ClN_2O_5P$ requires C, 65.55; H, 6.45; Cl, 5.7; N, 4.5; P, 4.95%); δ_H 7.36 (15 H, m, ArH), 6.96 (1 H, s, ArH), 5.24 (1 H, d, *J* 32.5 Hz, ArCH_2), 5.18 (2 H, s, ArCH_2), 5.10 (2 H, s, ArCH_2), 4.81 (1 H, d, *J* 32.5 Hz, ArCH_2), 2.64 (6 H, d, J_{PH} 10 Hz, NMe), 2.52 (6 H, d, J_{PH} 10 Hz, NMe), and 0.70 (3 H, dd, J_{HH} 7 and J_{PH} 17 Hz, CH*Me*).

1-*Acetoxy*-1-(2,3,5-*tribenzyloxyphenyl*)*propan*-2-*ylphosphonic Bis*(*dimethylamide*) (**27**).—The β-hydroxyphosphonamide (**19**) (2 g) was dissolved in acetic anhydride (20 ml) and pyridine (20 ml) and the solution was stirred for 16 h. The solution was then distilled under reduced pressure to give the *title compound* (**27**) as an oil (2.1 g, 98%) (Found: C, 68.6; H, 6.6; N, 4.45; P, 4.85%. $C_{36}H_{43}N_2O_6P$ requires C, 68.55; H, 6.85; N, 4.45; P, 4.9%); δ_H 7.37 (15 H, m, ArH), 6.62 (1 H, d, *J* 3 Hz, ArH), 6.56 (1 H, d, *J* 3 Hz, ArH), 5.30—4.82 (7 H, m, ArCH_2 and C*H*OAc), 2.58 (6 H, d, J_{PH} 10 Hz, NMe), 2.56 (6 H, d, J_{PH} 10 Hz, NMe), 2.06 (3 H, s, OAc), and 0.81 (3 H, dd, J_{HH} 7 and J_{PH} 15 Hz, CH*Me*).

1-*Acetoxy*-1-(2,3,5-*tribenzyloxy*-4-*chlorophenyl*)*propan*-2-*ylphosphonic Bis*(*dimethylamide*) (**44**).—The β-hydroxyphosphonamide (**43**) by the foregoing method gave the *title compound* (**44**) (97%) (Found: C, 65.0; H, 6.3; N, 4.1; P, 4.75; Cl, 5.1%. $C_{36}H_{42}ClN_2O_6P$ requires C, 65.0; H, 6.35; N, 4.2; P, 4.65; Cl, 5.35%); δ_H 7.33 (15 H, m, ArH), 6.24 (1 H, s, ArH), 5.15 (7 H, ArCH_2 and C*H*OAc), 2.57 (6 H, d, J_{PH} 10 Hz, NMe), 2.54 (6 H, d, J_{PH} 10 Hz, NMe), 1.99 (3 H, s, OAc), and 0.78 (3 H, dd, J_{HH} 7 and J_{PH} 16 Hz, CH*Me*).

1-*Acetoxy*-1-(2,3,5-*tribenzyloxy*-6-*chlorophenyl*)*propan*-2-*ylphosphonic Bis*(*dimethylamide*) (**28**).—Sulphuryl chloride (2.6 ml) was added to a solution of the β-acetoxyphosphonamide (**27**) (1 g) in ether (30 ml) and the mixture was stirred at room temperature for 3 h. The reaction mixture was poured onto ice, and the organic layer separated and washed with water, dried, and evaporated to give the *title compound* (**28**) as an oil (0.95 g, 90%) (Found: C, 65.1; H, 6.55; Cl, 5.25; N, 4.2; P, 4.6. $C_{36}H_{42}ClN_2O_6P$ requires C, 65.0; H, 6.35; Cl, 5.35;N, 4.2; P, 4.65%); δ_H 7.31 (15 H, m, ArH), 6.63 (1 H, s, ArH), 5.28—4.87 (2 H, m, C*H*OAcC*H*Me), 5.02 (6 H, s, ArCH_2), 2.60 (6 H, d, J_{PH} 10 Hz, NMe), 2.57 (6 H, d, J_{PH} 10 Hz, NMe), and 0.82 (3 H, dd, J_{HH} 7 and J_{PH} 15 Hz, CH*Me*).

1-*Acetoxy*-1-(2,3,5-*tribenzyloxy*-4,6-*dichlorophenyl*)*propan*-2-*ylphosphonic Bis*(*dimethylamide*) (**45**).—The β-acetoxyphosphonamide (**44**) by the foregoing method gave the *title compound* (**45**) (88%) (Found: C, 62.0; H, 5.9; Cl, 10.35; N, 3.95; P, 4.35. $C_{36}H_{41}Cl_2N_2O_6P$ requires C, 61.8; H, 5.9; Cl, 10.15; N, 4.0; P, 4.45%); δ_H 7.33 (15 H, m, ArH), 5.30—4.86 (2 H, m, C*H*OAcC*H*Me), 5.06 (6 H, m, ArCH_2), 2.66 (6 H, d, J_{PH} 10 Hz, NMe), 2.64 (6 H, d, J_{PH} 10 Hz, NMe), 2.07 (3 H, s, OAc), and 0.81 (3 H, dd, J_{HH} 7 and J_{PH} 15 Hz, CH*Me*).

1-*Hydroxy*-1-(2,3,5-*tribenzyloxy*-6-*chlorophenyl*)*propan*-2-*ylphosphonic Bis*(*dimethylamide*) (**29**).—A solution of the β-acetoxyphosphonamide (**28**) (0.5 g) in ethanol (10 ml) containing aqueous sodium hydroxide (5M; 2 ml) was heated under reflux for 2 h. After cooling, the solution was diluted with water (50 ml) and extracted with ethyl acetate. The organic solution was dried and evaporated to give the *title compound*

(**29**) (0.4 g, 85%) (Found: C, 65.45; H, 6.35; Cl, 5.9; N, 4.7; P, 4.7. $C_{34}H_{40}ClN_2O_5P$ requires C, 65.5; H, 6.45; Cl, 5.7; N, 4.5; P, 4.95%); δ_H 7.34 (15 H, m, ArH), 6.61 (1 H, s, ArH), 5.28—4.80 (2 H, m, C*H*OHC*H*Me), 5.03 (6 H, m, ArCH_2), 2.74 (6 H, d, J_{PH} 10 Hz, NMe), 2.53 (6 H, d, J_{PH} 10 Hz, NMe), and 0.72 (3 H, dd, J_{HH} 7 and J_{PH} 15 Hz, CH*Me*).

1-*Hydroxy*-1-(2,3,5-*tribenzyloxy*-4,6-*dichlorophenyl*)*propan*-2-*ylphosphonic Bis*(*dimethylamide*) (**46**).—The β-acetoxyphosphonamide (**45**) by the foregoing method gave the *title compound* (**46**) (83%) (Found: C, 62.2; H, 5.95; Cl, 10.85; N, 4.25; P, 4.45. $C_{34}H_{39}Cl_2N_2O_5P$ requires C, 62.1; H, 6.0; Cl, 10.8;N, 4.25; P, 4.7%); δ_H 7.33 (15 H, m, ArH), 5.25—4.80 (2 H, m, C*H*OHC*H*Me), 5.04 (6 H, m, ArCH_2), 2.76 (6 H, d, J_{PH} 10 Hz, NMe), 2.56 (6 H, d, J_{PH} 10 Hz, NMe), and 0.71 (3 H, dd, J_{HH} 7 and J_{PH} 17 Hz, CH*Me*).

(E)-1-(2,3,5-*Trimethoxyphenyl*)*prop*-1-*ene* (**21**).—Silica gel (2 g) was added to a solution of the β-hydroxyphosphonamide (**18**) (0.5 g) in toluene (15 ml) and the mixture was heated under reflux for 16 h. The silica was filtered off and the filtrate evaporated. Purification of the residue on silica gel using dichloromethane as eluant gave the *phenylpropene* (**21**) as an oil (0.26 g, 93%) (Found: C, 68.95; H, 7.75. $C_{12}H_{16}O_3$ requires C, 69.2; H, 7.75%); δ_H 6.90—6.00 (2 H, m, olefinic H), 6.53 (1 H, d, *J* 3 Hz, ArH), 6.37 (1 H, d, *J* 3 Hz, ArH), 3.82 (3 H, s, OMe), 3.78 (3 H, s, OMe), 3.74 (3 H, s, OMe), and 1.89 (3 H, dd, *J* 6.3 and 1.3 Hz, Me).

(E)-1-(2,3,5-*Tribenzyloxyphenyl*)*prop*-1-*ene* (**22**).—The β-hydroxyphosphonamide (**19**) by the foregoing method gave the *phenylpropene* (**22**) (95%), m.p. 72—74 °C (from acetone–hexane) (Found: C, 82.1; H, 6.85. $C_{30}H_{28}O_3$ requires C, 82.5; H, 6.45%); $\nu_{max.}$ 3 110—2 880 and 1 600 cm^{-1}; δ_H 7.36 (15 H, m, ArH), 6.63 (1 H, d, *J* 3 Hz, ArH), 6.51 (1 H, d, *J* 3 Hz, ArH), 6.45—5.90 (2 H, m, olefinic H), 5.03 (2 H, s, ArH), 4.98 (2 H, s, ArH), 4.88 (2 H, s, ArH), and 1.82 (3 H, dd, *J* 6.5 and 1 Hz, Me).

(E)-1-(2,3,5-*Triacetoxyphenyl*)*prop*-1-*ene* (**23**).—A solution of the β-hydroxyphosphonamide (**19**) (1 g) in methanol (20 ml) containing 10% palladium on charcoal (0.5 g) was hydrogenated at atmospheric pressure for 1 h. The catalyst was removed by filtration through Celite and the filtrate evaporated to give the β-hydroxyphosphonamide (**20**) as an unstable oil (0.48 g, 96%); $\delta_H(CD_3OD)$ 6.28 (2 H, s, ArH), 5.18—4.80 (2 H, m, C*H*OHC*H*Me), 2.67 (6 H, J_{PH} 10 Hz, NMe), 2.61 (6 H, d, J_{PH} 10 Hz, NMe), and 0.91 (3 H, dd, J_{HH} 7 and J_{PH} 17 Hz, CH*Me*). The β-hydroxyphosphonamide (**20**) (0.48 g) was dissolved in dry methanol (20 ml) containing trifluoroacetic acid (0.1 ml) and the mixture was stirred at room temperature under nitrogen for 16 h. The solvents were evaporated off under reduced pressure and the residue dissolved in acetic anhydride (20 ml) and pyridine (20 ml). After 5 h at room temperature, the reaction mixture was poured onto ice and the aqueous solution was extracted with ethyl acetate. The organic extracts were washed with dilute hydrochloric acid (0.1M), aqueous sodium hydrogencarbonate and water, and then dried and evaporated. The residue was purified by chromatography on silica gel using chloroform–ethyl acetate (4:1) as eluant to give the *phenylpropene* (**23**) (0.39 g, 72%), m.p. 89—91 °C (Found: C, 61.5; H, 5.7%; M^+, 292.095. $C_{15}H_{16}O_6$ requires C, 61.65; H, 5.5%; *M*, 292.095); $\nu_{max.}$ 3 015, 1 770, and 1 600 cm^{-1}; δ_H 7.10 (1 H, d, *J* 3 Hz, ArH), 6.89 (1 H, d, *J* 3 Hz, ArH), 6.28 (2 H, m, olefinic H), 2.28 (3 H, s, OAc), 2.23 (3 H, s, OAc), 2.22 (3 H, s, OAc), and 1.84 (3 H, d, *J* 5 Hz, Me).

(E)-1-(2,3,5-*Triacetoxy*-4-*chlorophenyl*)*prop*-1-*ene* (**49**).—The β-hydroxyphosphonamide (**43**) by the foregoing method gave the β-hydroxyphosphonamide (**47**) (95%); $\delta_H(CD_3OD)$ 6.48 (1 H, s, ArH), 5.18—4.80 (2 H, m, C*H*OHC*H*Me), 2.63 (6 H, d, J_{PH} 10 Hz, NMe), 2.59 (6 H, d, J_{PH} 10 Hz, NMe), and 0.90 (3 H, dd, J_{HH} 7 and J_{PH} 17 Hz, CH*Me*). The β-hydroxyphosphonamide (**47**) by the foregoing method gave the *phenylpropene* (**49**) (68%) (Found: C, 55.35; H, 4.75; Cl, 10.8. $C_{15}H_{15}ClO_6$ requires C, 55.15; H, 4.65; Cl, 10.85%); δ_H 7.19 (1 H, s, ArH), 6.26 (2 H, m, olefinic H), 2.27 (9 H, s, OAc), and 1.84 (3 H, d, *J* 5 Hz, Me).

(E)-1-(2,3,5-*Triacetoxy*-6-*chlorophenyl*)*prop*-1-*ene* (**31**).—The β-hydroxyphosphonamide (**29**) by the foregoing method gave the *phenylpropene* (**31**) (36%) (Found: C, 55.35; H, 4.5; Cl, 10.9. $C_{15}H_{15}ClO_6$ requires C, 55.15; H, 4.65; Cl, 10.85%); δ_H 6.97 (1 H, s, ArH), 6.23 (2 H, m, olefinic H), 2.29 (3 H, s, OAc), 2.22 (6 H, s, OAc), and 1.87 (3 H, d, *J* 5 Hz, Me).

(E)-1-(2,3,5-*Triacetoxy*-4,6-*dichlorophenyl*)*prop*-1-*ene* (**50**).—The β-hydroxyphosphonamide (**46**) by the foregoing method gave the phenylpropene (**50**) (40%) (Found: C, 49.75; H, 4.1; Cl, 19.85. $C_{15}H_{14}Cl_2O_6$ requires C, 49.9; H, 3.9; Cl, 19.65%); δ_H 6.25 (2 H, m, olefinic H), 2.32 (3 H, s, OAc), 2.27 (6 H, s, OAc), and 1.89 (3 H, d, *J* 5 Hz, Me).

2-*Dimethylamino*-6,8-*dihydroxy*-3-*methyl*-2H-1,2λ^5-*benzoxaphosphorin*-2,4(3H)-*dione* (**24**).—The β-oxophosphonamide (**16**) (0.23 g) was dissolved in dichloromethane (20 ml) at −78 °C under nitrogen and boron tribromide (0.5 ml) was added. After 15 min, the cooling bath was removed and the reaction left at room temperature for 16 h. Ether and then water were added and the aqueous layer was saturated with sodium chloride and extracted with ethyl acetate. The combined organic extracts were dried and evaporated. The residue was purified by chromatography on silica gel using ethyl acetate as eluant to give the *cyclic phosphonate* (**24**) (0.14 g, 82%) (Found: C, 48.65; H, 5.3; N, 5.35; P, 11.4. $C_{11}H_{14}NO_5P$ requires C, 48.7; H, 5.2; N, 5.15; P, 11.4%); $\delta_H[(CD_3)_2CO]$ 8.55 (2 H, s, OH), 6.76 (1 H, d, *J* 3 Hz, ArH), 6.64 (1 H, d, *J* 3 Hz, ArH), 3.63 (1 H, dq, J_{HH} 7 and J_{PH} 23.5 Hz, C*H*Me), 2.82 (6 H, d, J_{PH} 10 Hz, NMe), and 1.29 (3 H, dd, J_{HH} 7 and J_{PH} 17 Hz, CH*Me*).

4,6,8-*Triacetoxy*-2-*dimethylamino*-3-*methyl*-2H-1,2λ^5-*benzoxaphosphorin*-2-*one* (**25**).—The phosphonate (**24**) (0.14 g) was dissolved in acetic anhydride (5 ml) and pyridine (5 ml) and the solution was stirred at room temperature for 3 h. The reagents were removed by distillation under reduced pressure and the residue was purified by chromatography on silica gel using dichloromethane as eluant to give the *triacetate* (0.2 g, 97%) (Found: C, 51.35; H, 4.95; N, 3.75; P, 7.55. $C_{17}H_{20}NO_8P$ requires C, 51.4; H, 5.05; N, 3.55; P, 7.8%); $\delta_H(CD_3OD)$ 7.06 (2 H, s, ArH), 2.67 (6 H, d, J_{PH} 11 Hz, NMe), 2.38 (3 H, s, OAc), 2.30 (3 H, s, OAc), 2.24 (3 H, s, OAc), and 1.89 (3 H, d, J_{PH} 15 Hz, Me).

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