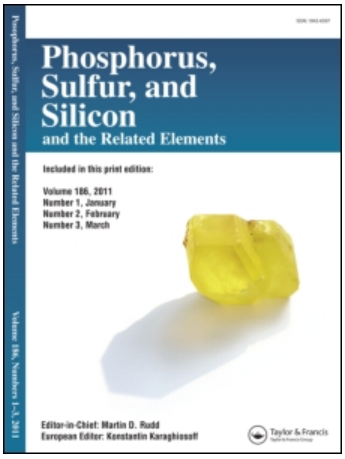

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DIMETHYL 3-CHLOROPROP-1-EN-2-YLPHOSPHONATE. PART 3. ALKYLATION OF ANIONIC O AND C NUCLEOPHILES AND PREPARATION OF 1-ALKENYL-2-PHOSPHONATES

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Under suitable reaction conditions 2-phosphorylated 3-chloropropene **1** monoalkylates methoxide, ethoxide, thiocyanate, methyl and allyl Grignard reagents and acetamidomalonate – the latter reactions leading to 2-phosphorylated 1-butene, 1,5-hexadiene and C-alkylated α-aminoacids. Diethyl malonate and ethyl acetoacetate give mixtures of mono and dialkylated products whereas ethyl cyanoacetate gives only dialkylated product. Acetylacetone gives a dialkylated product – the monoalkylated intermediate undergoing acyl cleavage to give 2-phosphorylated 5-hexene-2-one as the major product. A new simple route for the preparation of 2-phosphorylated 3-halopropenes via a Horner-Wittig reaction between formaldehyde and methylene diphosphonate is described.

Keywords: Alkenylphosphonates; alkenonephosphonates; aminophosphonopentenoic acids; aminophosphonopentanoic acid; cyanoalkenylphosphonates; haloalkenylphosphonates; 3-hydroxypropen-2-phosphonate

INTRODUCTION

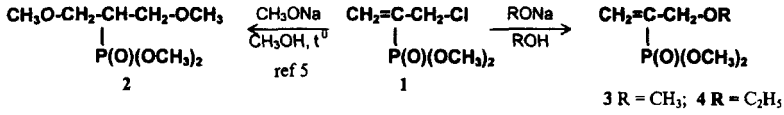
3-Chloroprop-1-en-2-ylphosphonate esters and their analogues are synthetically useful compounds and have been studied in organozinc reactions[1,2] and nucleophilic substitution reactions.[3] With respect to their reactions with anionic nucleophiles, Clarke and co-workers have

* Correspondence Authors.

described[4] the reaction of diethyl 3-bromoprop-1-en-2-ylphosphonate with lithiated methyl 1,4-dihydrobenzoate and diethyl 2,5-cyclohexadienyl-1-phosphonate whilst Belykh *et al*[5] have investigated the reaction of dimethyl 3-chloroprop-1-en-2-ylphosphonate with sodium methoxide and potassium iodide. As a part of our program on the synthesis of unsaturated compounds with a phosphonate group at C-2, we have undertaken a study of the reactions of dimethyl 3-chloroprop-1-en-2-ylphosphonate with a wider range of anionic nucleophiles and investigated their synthetic applications.

RESULTS AND DISCUSSION

It has been reported,[5] that the reaction of phosphonate **1** with an excess of sodium methoxide in methanol at elevated temperature leads to substitution of allylic chlorine followed by addition of methanol across the double bond (Scheme 1) – the only product isolated being dimethyl 1,3-dimethoxypropane-2-phosphonate **2.** We have found, that under mild conditions, it is possible to restrict the reaction to the formation of 3-methoxy propene-2-phosphonate **3** exclusively. Similarly, the reaction with sodium ethoxide under mild conditions gave 3-ethoxy propene-2-phosphonate **4** as the final product. No prototropic isomerisation had occurred.

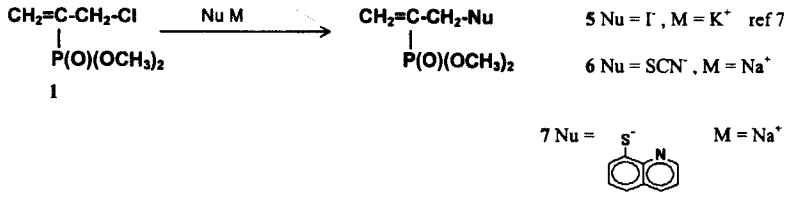


SCHEME 1 Interaction of dimethyl 3-chloroprop-1 -en-2-ylphosphonate with sodium alkoxides

The above results demonstrate, that despite activation of the double bond in phosphonates **3, 4** towards addition of nucleophilic agents, it is possible to carry out selective substitution of the allylic chlorine in phosphonate **1.** On the other hand, reaction of dimethyl 3-chloropropen-2-phosphonate **1** with potassium t-butoxide proceeded in a different manner. The isolated product of the reaction was a small amount of 3-methoxy propene-2-phosphonate **3.** This unexpected result can be

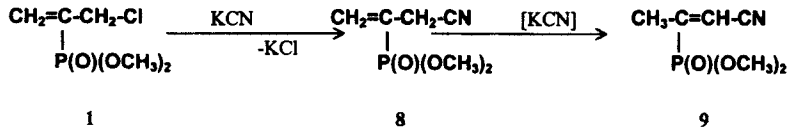
explained by trans-esterification (exchange of the phosphonate ester methoxy group by t-butoxy group) followed by substitution of the allylic chlorine in phosphonate **1** only by the released methoxide anion. Similar trans-esterification followed by addition of the released ethoxide ion occurred in the reaction of diethyl 2-propenylphosphonate with one molar equivalent of t-butoxide in t-butanol.[6]

Selective substitution of the allylic chlorine of dimethyl 3-chloropropen-2-phosphonate **1** could also be achieved using nucleophiles of quite low basicity to give iodide **5,** isocyanate **6** and quinoline **7** (Scheme 2).



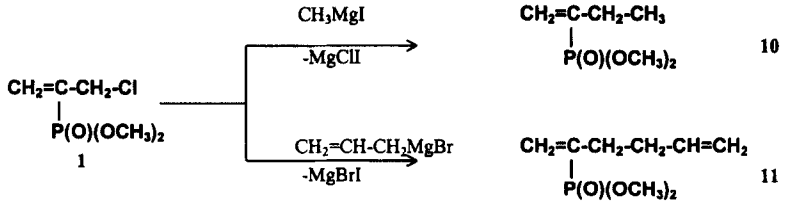
SCHEME 2 Reaction of dimethyl 3-chloroprop-1-en-2-ylphosphonate with low basicity nucleophiles

The reaction of phosphonate **1** with potassium cyanide was more complex. When the reaction was carried out in an aprotic solvent such as acetonitrile, selective allylic substitution to give the allyl nitrile **8** was accompanied by tautomerism to the crotononitrile isomer **9** (Scheme 3). The ratio of the products depended on the quantity of KCN used and the extent of the reaction. A low concentration of KCN and low degree of conversion favoured formation of the allylic nitrile **8.** Whereas when the reaction was carried out in a protic solvent such as methanol, only the isomeric crotononitrile **9** was isolated. These results are attributed to increased acidity of the methylene group in the allylic nitrile **8** – base catalysed prototropy occurring rapidly under the action of cyanide anion in the presence of a proton source. The formation of the least sterically strained E-isomer of phosphonate **9** supports this explanation.



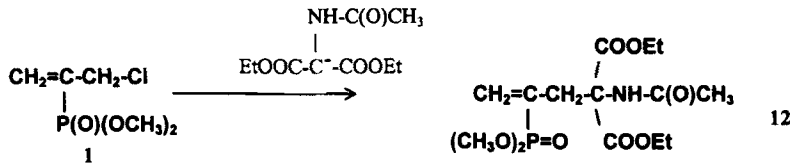
SCHEME 3 Reaction of dimethyl 3-chloroprop-1-en-2-ylphosphonate with KCN

The selectivity can be extended to the reactions of Grignard reagents. Thus dimethyl 3-chloropropen-2-phosphonate **1** reacted with methyl or allyl magnesium halides to give 2-butenyl and 2-hexadienyl phosphonates **10** and **11** respectively (Scheme 4). This reaction opens a new general approach for the synthesis of 1-alkenyl-2-phosphonates.



SCHEME 4 Reaction of dimethyl 3-chloroprop-1-en-2-ylphosphonate with Grignard reagents

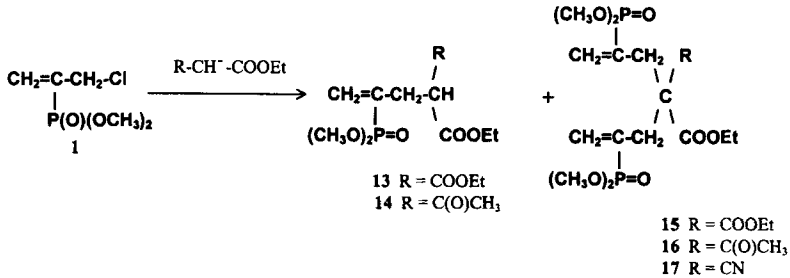
The ester **1** underwent facile reactions with the enolates of various malonates, β-ketoesters and β-diketones opening up the synthetic horizons further still. Thus the anion of diethyl acetamidomalonate reacted with phosphonate **1** to give 64% of the amidodiester **12** (Scheme 5).



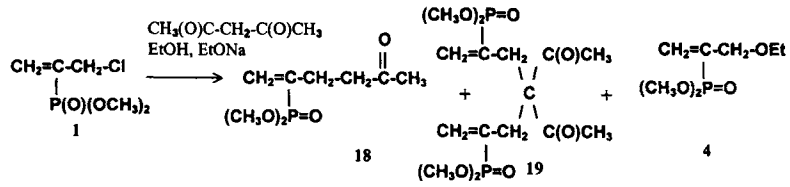
SCHEME 5 Reaction of dimethyl 3-chloroprop-1-en-2-ylphosphonate with the enolate derived from diethyl acetamidomalonate

On the other hand, reaction of the phosphonate **1** with enolates derived from diethyl malonate, ethyl acetoacetate and ethyl cyanoacetate all gave products of both mono- and dialkylation **13**, **14** and **15**, **16**, **17** respectively (Scheme 6). The reactions were carried out under the same conditions using one equivalent of the enolate. The ratio of products of mono to disubstitution was 1: 0.35 for diethyl malonate and 1: 1.2 for ethyl acetoacetate. The disubstituted compound **17** was the sole product in the case of ethyl cyanoacetate. Whilst no product of monosubstitution was detected

with the anion derived from acetylacetone, the reaction led to the formation of three organophosphorus compounds: the product of base-induced cleavage of the product of monoalkylation **18,** the product of dialkylation **19** and 3-ethoxy propene-2-phosphonate **4** in the ratio 1: 1.3: 1.7, respectively (Scheme 7). Formation of phosphonate **4** can be avoided by the use of sodium carbonate instead of sodium ethoxide, in which case the ketone **18** is the main product. The ratio of ketone **18** and dialkylation product **19** was 4.7: 1. Thus the ester **1** reacts readily with a range of relatively stable bulky enolates – the reaction products being determined more by nucleophilicity and thus the ease of formation of the enolates rather than their basicity.



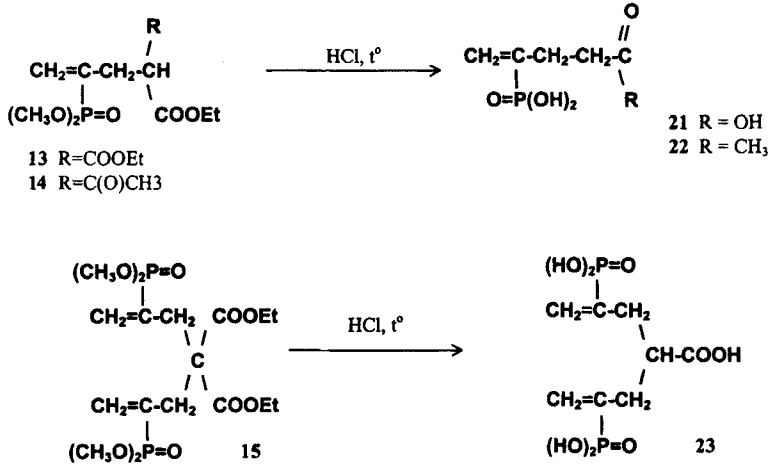
SCHEME 6 Reaction of dimethyl 3-chloroprop-1-en-2-ylphosphonate with the diethyl malonate, ethyl acetoacetone and ethyl cyanoacetate derived anions



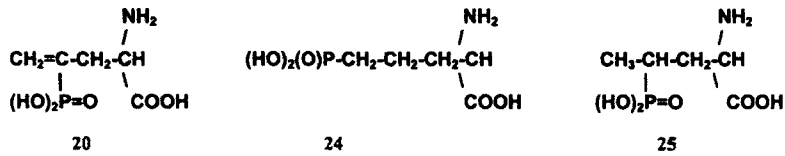
SCHEME 7 Reaction of dimethyl 3-chloroprop-1-en-2-ylphosphonate with anions derived from acetylacetone

Acidic hydrolysis of compounds **12** – **16** afforded aminophosphonocarboxylic acid **20** and phosphonocarboxylic acids **21**– **23** which were separated as cyclohexylammonium salts (Scheme 8). Many members of these classes of compounds possess biological activity.[7–10] Thus amino-

phosphonocarboxylic acid **20** is related to 2-amino-5-phosphonovaleric acid **24,** an antagonist for the N-methyl-D-aspartate sub-type of glutamate receptors.[8,9] Whilst hydrogenation of the alkenyl phosphonates would produce the corresponding saturated compounds 2-amino-4-phosphonovaleric acid **25** was obtained by the addition reaction of diethyl acetamidomalonate to dimethyl propene-2-phosphonate[12] followed by acidic hydrolysis.

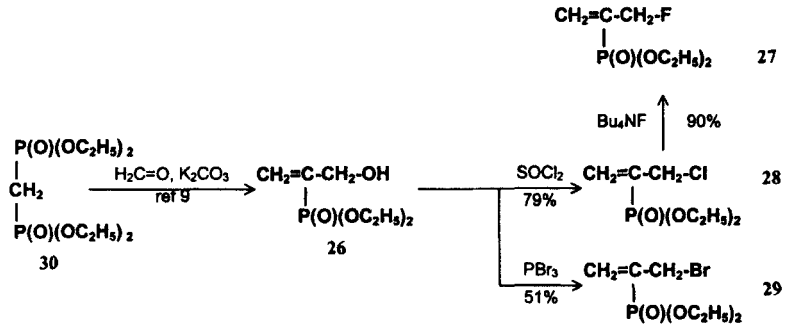


SCHEME 8 Syntheses of phosphoncarboxylic acids through acidic hydrolysis



It was considered that by analogy with the syntheses of ethyl α-halogenomethylacrylates from ethyl α-hydroxymethylacrylates,[14] it might be possible to obtain 3-halogenoprop-1-en-2-ylphosphonates from 3-hydroxyprop-1-en-2-ylphosphonate **26**. This possibility was realised and the 3-fluoro-, 3-bromo-, and 3-iodoprop-1-en-2-ylphosphonates **27**, **28** and **29** were produced as shown in Scheme 9. 3-Hydroxyprop-1-en-2-ylphospho-

nate **26** was prepared by the Wittig-Horner reaction of tetraethyl methylene diphosphonate **30** with formaldehyde in boiling water using potassium carbonate as a base.[15]



SCHEME 9 Syntheses of 3-halogenoprop-1-en-2-ylphosphonates

In conclusion, 3-halogenopropene-2-phosphonates react readily with various anionic nucleophiles providing an effective route to a variety of compounds with potential biological or synthetic interest. Although several different methods for the preparation of such type compounds have been reported,[1,13] they are laborious and more limited in their applications.

EXPERIMENTAL

NMR spectra were determined on TESLA BS497 (100 MHz), JEOL FX90Q, GSX270 and Bruker AC500 instruments; the solvent was $CDCl_3$. J Values recorded in Hz. GC-MS analysis was performed on a VG Trio 1000 HS linked to a Carlo Erba Mega GC using a DB 17 0.32 mm capillary column. The mass spectroscopy conditions were as follows: electron energy 70 eV, source temperature 200 °C, resolution 1 a.m.u.

Dimethyl 3-chloroprop-1-ene-2-ylphosphonate 1

This was prepared as described previously.[13]

Dimethyl 3-methoxyprop-1-ene-2-ylphosphonate 3

To a stirred solution of the ester **1** (1 g) in methanol (5 ml), sodium methoxide (0.88 g) was added. The stirring was continued for 2 h at room temperature. Addition of ether (50 ml), gave a precipitate which was removed and the filtrate evaporated. To a stirred solution of the residue in ether (2 ml), triethylamine (1 ml) was added dropwise (to convert unreacted chloride **1** to its ammonium salt).[13] The stirring was continued for 10 min at room temperature, after which the solution was passed through silica gel column (10 g), using ether as eluent. After evaporation of the solvent, vacuum distillation gave the phosphonate **3** (0.6 g, 61 %), bp 75 °C (1.5 mm Hg); δ_H 5.97 (CH_AH_B=, $^3J_{AP}$ 47, J_{AB} 1.7, J_{AH} 1.7); 6.03 (CH_AH_B=, $^3J_{BP}$ 23, J_{BH} 1.7); 3.89 (CH_2, $^3J_{PH}$7.3); 3.63 ($POCH_3$, J_{PH} 11) and 3.29 (OCH_3); δ_C 129.77 (CH_2=, $^2J_{PC}$ 6.16); 134.7 (-C(P)=, $^1J_{PC}$ 174.97); 70.53 (CH_2, $^2J_{PC}$ 16.33); 51.68 ($POCH_3$, $^2J_{PC}$ 5.53) and 57.5 (OCH_3); δ_P 16.7 (determined relative to trimethyl phosphate from ^1H-{^{31}P} INDOR spectra).

Dimethyl 3-ethoxyprop-1-ene-2-ylphosphonate 4

To a stirred solution of the ester **4** (0.5 g) in ethanol (2.5 ml), a solution of sodium ethoxide, prepared from sodium (0.063 g) and ethanol (2.5 ml) was added dropwise. After stirring for 2 h at room temperature, dilution with ether (50 ml) gave a precipitate which was removed and the filtrate evaporated. To a stirred solution of the residue in ether (2 ml), triethylamine (1 ml) was added dropwise (to convert unreacted chloride **1** to its ammonium salt[13]). After stirring for 10 min at room temperature, the solution was chromatographed on a silica gel column (10 g), using ether as eluent. Evaporation of the appropriate fraction gave phosphonate **4** (0.32 g, 60 %); δ_H 6.07 (CH_AH_B=, $^3J_{AP}$ 47, J_{AH} 1.7); 6.07 (CH_AH_B=, $^3J_{BP}$ 24, J_{BH} 1.7); 4.03 (CH_2, $^3J_{PH}$ 8); 3.67 ($POCH_3$, J_{PH} 11); 3.47 (OCH_2, J_{HH} 7) and 1.13 (CH_3); δ_C 128.54 (CH_2=,$^2J_{PC}$ 6.54); 134.72 (-C(P)=, $^1J_{PC}$ 174.47); 67.81 (CH_2, $^2J_{PC}$ 16.72); 50.91 ($POCH_3$, $^2J_{PC}$ 5.41); 64.65 (OCH_2) and 13.6 (CH_3); δ_P 17.2 (determined relative to trimethyl phosphate from ^1H-{^{31}P} INDOR spectra).

Reaction of (1) with potassium tert-butoxide in tert-butanol

The reaction was carried out in the same manner as for dimethyl 3-methoxyprop-1-ene-2-ylphosphonate **3,** using the ester **1** (0.5 g), *tert*-butanol (5 ml) and potassium *tert*-butoxide (0.3 g). The phosphonate **3** (0.12 g) was isolated.

Dimethyl 3-thiocyanatoprop-1-ene-2-ylphosphonate 6

Sodium thiocyanate (0.9 g) was added to a stirred solution of the ester **1** (0.4 g) in methanol (10 ml). After stirring for 4 days at room temperature, dilution with ether (50 ml), gave a precipitate which was removed and the filtrate evaporated to gave the phosphonate **6** (0.38 g, 84 %), δ_H 6.18 (CH_AH_B=, $^3J_{AP}$ 45); 6.37 (CH_AH_B=, $^3J_{BP}$ 21); 3.7 (CH_2, $^3J_{PH}$ 7.5) and 3.7 ($POCH_3$, J_{PH} 11); δ_C 135.22 (CH_2=, $^2J_{PC}$ 8.42); 131.74 (-C(P)=, $^1J_{PC}$ 181.5); 45.72 (CH_2, $^2J_{PC}$ 19.36); 52.68 ($POCH_3$, $^2J_{PC}$ 5.28) and 111.16 (SCN); δ_P 15.4 (determined relative to trimethyl phosphate from ^1H-{^{31}P} INDOR spectra).

Dimethyl 3-(8-quinolylthio-S-yl)prop-1-ene-2-phosphonate 7

Ester **1** (0.86 g) was added to a stirred dispersion of sodium 8-quinolylthiolate (1.06 g) in methanol (80 ml) and water (40 ml). After stirring for 1.5 days at room temperature a precipitate was removed and a further quantity of sodium 8-quinolylthiolate (0.4 g) was added and stirring continued for 1 h. The precipitate was removed and the filtrate extracted by dichloromethane (3 × 50 ml). The combined organic extracts were evaporated, after which the residue was chromatographed on a silica gel column (20 g), using ether followed by dichloromethane: acetone : hexane (1: 1: 1) mixture as eluent. Evaporation of the appropriate fraction gave phosphonate **7** (1 g, 72 %), δ_H 6.16 (CH_AH_B=, $^3J_{AP}$ 48); 6.16 (CH_AH_B=, $^3J_{BP}$ 22); 3.84 (CH_2, $^3J_{PH}$ 9), 3.7 ($POCH_3$, J_{PH} 11) and 8.86, 8.02, 7.6 – 7.1 (CH); δ_C 132.58 (CH_2=, $^2J_{PC}$ 8.65); 132.9 (-C(P)=, $^1J_{PC}$ 174.82); 31.82 (CH_2, $^2J_{PC}$ 14.78); 52.72 ($POCH_3$, $^2J_{PC}$ 5.53) and 149.2 – 121.7 (C, CH); δ_P 17.3 (determined relative to trimethyl phosphate from ^1H-{^{31}P} INDOR spectra).

Dimethyl 3-cyanoprop-1-ene-2-ylphosphonate 8

Powdered potassium cyanide (0.07 g) was added to a stirred solution of the ester **1** (0.2 g) in acetonitrile (15 ml). After stirring for 1 h at room temperature dilution with ether (30 ml) gave a precipitate which was removed and the filtrate evaporated. The residue was chromatographed on a silica gel column (10 g), using ether as eluent. Evaporation of the appropriate fraction gave phosphonate **8** (0.08 g, 19 %); δ_H 6.2 (CH_AH_B=, $^3J_{AP}$ 45.5, J_{AB} 1.5, J_{AH} 1.5); 6.24 (CH_AH_B=, $^3J_{BP}$ 22); 3.26 (CH_2, $^3J_{PH}$ 8, J_{BH} 1.5)

and 3.72 ($POCH_3$, J_{PH} 11); δ_C 132.79 (CH_2=, $^2J_{PC}$ 8.17); 127.89 (-C(P)=, $^1J_{PC}$ 185.78); 20.52 (CH_2, $^2J_{PC}$ 16.47); 52.42 ($POCH_3$, $^2J_{PC}$ 5.78) and 115.29 (CN, $^3J_{PC}$ 13.32); δ_P 15.3 (determined relative to trimethyl phosphate from ^1H-{^{31}P} INDOR spectra).

Dimethyl 1-cyanoprop-1-ene-2-ylphosphonate 9

Powdered potassium cyanide (0.4 g) was added to a stirred solution of the ester **1** (1,2 g) in methanol (30 ml). After stirring for 1 h at room temperature dilution with ether (50 ml) gave a precipitate which was filtered off. The filtrate was evaporated and the residue vacuum distilled to gave the phosphonate **9** (0.91 g, 80 %), bp 70 °C (1 mm Hg); δ_H 6.1 (-CH=, $^3J_{HP}$ 20.5, J_{HH} 1.5); 2.08 (CH_3, $^3J_{HP}$ 14.3); and 3.68 ($POCH_3$, J_{PH} 12); δ_C 16.94 (CH_3, $^2J_{PC}$ 7.04); 149.48 (-C(P)=, $^1J_{PC}$ 176.36); 111.06 (-CH=, $^2J_{PC}$ 18.23); 52.68 ($POCH_3$, $^2J_{PC}$ 6.16) and 113.83 (CN, $^3J_{PC}$ 31.43); δ_P 14.2 (determined relative to trimethyl phosphate from ^1H-{^{31}P} INDOR spectra).

Dimethyl but-1-ene-2-ylphosphonate 10

The ester **1** (1 g) was added dropwise to a stirred solution (at 20 °C) of Grignard reagent, prepared from methyl iodide (0.77 g) and magnesium (0.15 g) in ether (50 ml). After stirring for 2 h at reflux, the solvent was evaporated. Water (5 ml) and chloroform (30 ml) was added to the residue and the pH brought to neutrality using dilute hydrochloric acid. The organic layer was separated and aqueous layer was extracted with trichloromethane (10 ml × 2). The combined extracts were dried with potassium chloride and evaporated. To a stirred solution of the residue in trichloromethane (3 ml), triethylamine (1 ml) was added dropwise (to convert unreacted chloride **1** to its ammonium salt[13]). After stirring for 10 min at room temperature, the solution was chromatographed on a silica gel column (20 g), using ether as eluent. Evaporation of the appropriate fraction gave phosphonate **10** (0.15 g, 17 %); δ_H 5.8 (CH_AH_B=, $^3J_{AP}$ 49.5; J_{AH} 1.5; J_{AB} 1.5) ; 6.03 (CH_AH_B=, $^3J_{BP}$ 23); 2.24 (CH_2, $^3J_{PH}$ 16, J_{HH} 7.5); 3.7 ($POCH_3$, J_{PH} 11); and 1.08 (CH_3); δ_C 128.46 (CH_2=, $^2J_{PC}$ 9.55); 139.37 (-C(P)=, $^1J_{PC}$ 170.95); 24.77 (CH_2, $^2J_{PC}$ 11.19); 52.02 ($POCH_3$, $^2J_{PC}$ 5.78); and 12.0 (CH_3 $^3J_{PC}$ 7.16); δ_P 19.6 (determined relative to trimethyl phosphate from ^1H-{^{31}P} INDOR spectra).

Dimethyl hexa-1,5-diene-2-ylphosphonate 11

The reaction was carried out in the same manner as for the phosphonate **10,** using the ester **1** (1 g), 3-bromopropene (0.82 g) and magnesium (0.16 g) to give phosphonate **11** (0.2 g, 19%); δ_H 5.78 (CH_AH_B=, $^3J_{AP}$ 49); 6.02 (CH_AH_B=, $^3J_{BP}$ 23); 2.24 (CH_2); 2.24 (CH_2); 5.02 (CH_CH_D=, J_{CH} 18); 4.96 (CH_CH_D=, J_{DH} 10); 3.66 ($POCH_3$, J_{PH} 11); and 5.68 (-CH=, J_{HH} 7); δ_C129.27 (CH_2=, $^2J_{PC}$ 9.18); 136.8 (-C(P)=, $^1J_{PC}$ 171.58); 30.75 (CH_2, $^2J_{PC}$ 11.44); 51.46 ($POCH_3$, $^2J_{PC}$ 5.28); 31.17 (CH_2, $^3J_{PC}$5.15); 136.4 (-CH=) and 114.58 (CH_2=); δ_P 17.7 (determined relative to trimethyl phosphate from ^1H-{^{31}P} INDOR spectra).

2-Propene-2(dimethoxyphosphonyl)-1-yl acetaminomalonic acid, diethyl ester 12

Acetaminomalonic ester (1.98 g) was added dropwise to a stirred solution of sodium ethoxide, prepared from sodium (0.21 g) and ethanol (50 ml), and the stirring was continued for 10 min at room temperature. To the resultant stirred mixture at –20 °C, the ester **1** (1.7 g) was added dropwise and the stirring was continued for 10 h at room temperature. The solvent was evaporated, the residue was dissolved in acetone, (50 ml), the precipitate was filtered off, the solvent was evaporated and the residue was chromatographed on a silica gel column (30 g), using ether and then acetone as eluents. Evaporation of the acetone fraction gave ester **12** (2.4 g, 64 %); δ_H 5.85 (CH_AH_B=, $^3J_{AP}$ 47.24, $^4J_{AH}$ 1.0, J_{AB}1); 6.17 (CH_AH_B=, $^3J_{BP}$ 20.46, $^4J_{AH}$ 1.34); 3.3 (CH_2, $^3J_{PH}$ 17); 3.7 ($POCH_3$, J_{PH} 11); 4.25 (OCH_2, J_{HH} 7.); 1.26 (CH_3); 2.0 ($C(O)CH_3$) and 7.01 (NH); δ_C 135.4 (CH_2=, $^2J_{PC}$ 7.69); 132.65 (-C(P)=, $^1J_{PC}$ 175.0); 65.7 (C, $^3J_{PC}$ 3.29); 34.53 (CH_2, $^2J_{PC}$ 12.09), 166.93 (-C(O)O-), 52.4 ($POCH_3$, $^2J_{PC}$ 6.59); 62.24 (OCH_2), 13.69 (CH_3), 169.36 (C(O)) and 22.41 ($C(O)CH_3$); δ_P 20.35.

2-Propene-2(dimethoxyphosphonyl)-1-yl malonic acid, diethyl ester 13

To a stirred solution of sodium ethoxide, prepared from sodium (0.36 g) and ethanol (20 ml), malonic ester (2.49 g) was added dropwise and the stirring was continued for 10 min at room temperature. To the resultant stirred mixture, the ester **1** (2.86 g) was added dropwise and the stirring continued for 10 h at room temperature. After dilution with ether (50 ml), the precipitate was filtered off, the solvent was evaporated and the residue was chromatographed on a silica gel column (10 g), using ether and then

acetone as eluents. Evaporation of the ether fraction gave ester **13** (1.7 g, 35 %); δ_H 5.88 (CH_AH_B=, $^3J_{AP}$ 47.68, $^4J_{AH}$ 1.1, J_{AB} 1.1); 6.13 (CH_AH_B=, $^3J_{BP}$ 22.08, $^4J_{BH}$ 0.66); 2.85 (CH_2, $^3J_{PH}$ 14.5, J_{HH} 7.91); 3.81 (CH); 3.74 ($POCH_3$, J_{PH} 11); 4.2 (OCH_2, J_{HH} 7.42) and 1.27 (CH_3); δ_C 132.97 (CH_2=, $^2J_{PC}$ 9.89); 134.77 (-C(P)=, $^1J_{PC}$ 174.69); 31.82 (CH_2, $^2J_{PC}$ 11.19); 50.74 (CH, $^3J_{PC}$ 4.39), 168.73 (-C(O)O-), 52.81 ($POCH_3$, $^2J_{PC}$ 5.5); 61.9 (OCH_2) and 14.37 (CH_3); δ_P 20.8.

2-Propene-2(dimethoxyphosphonyl)-1-yl acetoacetic acid, ethyl ester 14

To a stirred solution of sodium ethoxide, prepared from sodium (0.125 g) and ethanol (10 ml), ethyl acetoacetate (0.71 g) was added dropwise and the stirring was continued for 10 min at room temperature. To the resultant stirred mixture, the ester **1** (1 g) was added dropwise and the stirring was continued for 20 min at room temperature. After dilution with ether (50 ml), the precipitate was filtered off, the solvent was evaporated and the residue was chromatographed on a silica gel column (10 g), using ether and then acetone as eluents. Evaporation of the ether fraction gave ester **15** (0.8 g, 53 %); δ_H 5.78 (CH_AH_B=, $^3J_{AP}$ 48.0); 5.96 (CH_AH_B=, $^3J_{BP}$ 23); 2.66 (CH_2, $^3J_{PH}$ 15.0, J_{HH} 7.0); 3.86 (CH); 3.64 ($POCH_3$, J_{PH} 11); 4.1 (OCH_2, J_{HH} 7.0); 1.16 (CH_3) and 2.14 ($C(O)CH_3$); δ_C 131.33 (CH_2=, $^2J_{PC}$ 8.42); 134.01 (-C(P)=, $^1J_{PC}$ 174.22); 29.82 (CH_2, $^2J_{PC}$ 11.82); 56.73 (CH, $^3J_{PC}$ 3.02), 167.25 (-C(O)O-), 51.62 ($POCH_3$, $^2J_{PC}$ 6.03); 60.56 (OCH_2); 13.11 (CH_3); 200.47 (-C(O)-) and 28.35 ($C(O)CH_3$); δ_P 17.93 (determined relative to trimethyl phosphate from ^1H-{^{31}P} INDOR spectra).

Di(2-propene-2[dimethoxyphosphonyl]-1-yl) malonic acid, diethyl ester 15

The reaction was carried out in the same manner as for the diethyl ester **13,** but the acetone fraction was evaporated to give ester **15** (1g, 28%); δ_H 5.91 (CH_AH_B=, $^3J_{AP}$ 49.22); 5.72 (CH_AH_B=, $^3J_{BP}$ 24.39); 3.01 (CH_2, $^3J_{PH}$ 12.33); 3.71 ($POCH_3$, J_{PH} 10.8); 4.19 (OCH_2, J_{HH} 7.04) and 1.25 (CH_3); δ_C 133.45 (CH_2=, $^2J_{PC}$ 7.69); 133.99 (-C(P)=, $^1J_{PC}$ 174.69); 33.65 (CH_2, $^2J_{PC}$ 12.09); 56.88 (C, $^3J_{PC}$ 7.69, $^3J_{PC}$7.69), 170.39 (-C(O)O-), 52.91 ($POCH_3$, $^2J_{PC}$ 5.49); 62.15 (OCH_2) and 14.32 (CH_3); δ_P 21.2.

Di(2-propene-2[dimethoxyphosphonyl]-1-yl) acetoacetic acid, ethyl ester 16

The reaction was carried out in the same manner as for the diethyl ester **14,** but the acetone fraction was evaporated to give ester **16** (0.4g, 35%); δ_H 5.46 (CH_AH_B=, $^3J_{AP}$ 48.0); 6.06 (CH_AH_B=, $^3J_{BP}$ 24.0); 2.87 (CH_2, $^3J_{PH}$ 23.0); 3.63 ($POCH_3$, J_{PH} 11.0); 4.12 (OCH_2, J_{HH} 7.0); 1.14 (CH_3) and 2.1 ($C(O)CH_3$); δ_C 132.24 (CH_2=, $^2J_{PC}$ 6.91); 133.23 (-C(P)=, $^1J_{PC}$ 174.85); 32.17 (CH_2, $^2J_{PC}$ 12.32); 61.94 (C, $^3J_{PC}$ 6.54, $^3J_{PC}$ 6.54); 170.10 (-C(O)O-); 202.39 (-C(O)-); 51.81 ($POCH_3$, $^2J_{PC}$ 5.66); 61.32 (OCH_2); 13.19 (CH_3) and 26.10 ($C(O)CH_3$); δ_P 17.93 (determined relative to trimethyl phosphate from ^1H-{^{31}P} INDOR spectra).

Di(2-propene-2[dimethoxyphosphonyl]-1-yl) cyanoacetic acid, ethyl ester 17

To a stirred solution of sodium ethoxide, prepared from sodium (0.125 g) and ethanol (10 ml), ethyl cyanoacetate (0.61 g) was added dropwise and the stirring was continued for 1 min at room temperature. To the resulted stirred mixture, the ester **1** (1 g) was added dropwise and the stirring was continued for 20 min at room temperature. After dilution with ether (50 ml), the precipitate was filtered off, the solvent was evaporated and the residue was chromatographed on a silica gel column (10 g), using ether and then acetone as eluents. Evaporation of the acetone fraction gave ester **17** (0.45 g, 40 %); δ_H 6.09 (CH_AH_B=, $^3J_{AP}$ 48.0); 6.2 (CH_AH_B=, $^3J_{BP}$ 24); 2.78 (H_EH_D, $^3J_{PD}$ 13); 2.72 (H_EH_D, $^3J_{PE}$ 13); 3.6 ($POCH_3$, J_{PH} 11); 4.14 (OCH_2, J_{HH} 7.0) and 1.18 (CH_3); δ_C 134.04 (CH_2=); 131.63 (-C(P)=, $^1J_{PC}$ 177.87); 37.89 (CH_2, $^2J_{PC}$ 12.7); 47.96 (C, $^3J_{PC}$ 5.28), 166.52 (-C(O)O-), 52.02 ($POCH_3$, $^2J_{PC}$ 5.41); 62.49 (OCH_2); 13.16 (CH_3) and 117.08 CN); δ_P 15.78 (determined relative to trimethyl phosphate from ^1H-{^{31}P} INDOR spectra).

5-(Dimethoxyphosphonyl)-5-hexen-2-one 18

A mixture of the ester **1** (0.5 g), acetylacetone (0.27g), and potassium carbonate (0.29g) in absolute ethanol was refluxed for 48 h. After dilution with ether (50 ml), the precipitate was filtered off, the solvent was evaporated and the residue was chromatographed on a silica gel column (7 g),

using ether as eluent. Evaporation of the appropriate fraction gave ketone **18,** (0.39 g, 70 %); δ_H 5.54 (CH_AH_B=, $^3J_{AP}$ 48.0); 5.74 (CH_AH_B=, $^3J_{BP}$ 22.6); 2.23 (CH_2, $^3J_{PH}$ 6.9, J_{HH} 6.9); 2.43 (CH_2); 3.45 ($POCH_3$, J_{PH} 10.9) and 1.87 (CH_3); δ_C 129.86 (CH_2=, $^2J_{PC}$ 9.05); 136.44 (-C(P)=, $^1J_{PC}$ 173.09); 25.86 (CH_2, $^2J_{PC}$ 11.69); 41.05 (CH_2, $^3J_{PC}$ 4.15); 206.27 (C(O)) and 29.29 (CH_3). δ_P 19.3 (determined relative to trimethyl phosphate from ^1H-{^{31}P} INDOR spectra).

3,3-Di(2-propene-2[dimethoxyphosphonyl]-1-yl)-2,4-pentanedione 19

To a stirred solution of sodium ethoxide, prepared from sodium (0.125 g) and ethanol (10 ml), acetylacetone (0.53 g) was added by one portion and to the resulted stirred mixture, the ester **1** (1 g) was added dropwise. The stirring was continued for 20 min at room temperature. After dilution with ether (50 ml), the precipitate was filtered off, the solvent was evaporated and the residue was chromatographed on a silica gel column (10 g), using ether and then acetone as eluents. Evaporation of the acetone fraction gave diketone **19** (0.38 g, 31 %); δ_H 5.54 (CH_AH_B=, $^3J_{AP}$ 49.0); 6.04 (CH_AH_B=, $^3J_{BP}$ 24); 2.94 (CH_2, $^3J_{PH}$ 11); 3.61 ($POCH_3$, J_{PH} 11) and 2.03 (CH_3); δ_C 131.71 (CH_2=, $^2J_{PC}$ 7.54); 133.45 (-C(P)=, J_{PC} 174.47); 31.29 (CH_2, $^2J_{PC}$ 12.44); 51.96 ($POCH_3$, $^2J_{PC}$ 6.03); 69.28 (C); 25.92 (CH_3) and 204.33 (-C(O)-); δ_P 18.4 (determined relative to trimethyl phosphate from ^1H-{^{31}P} INDOR spectra).

Cyclohexylamine salt of 2-amino-4-phosphono-4-pentenoic acid 20

A solution of ester **12** (0.95 g) in 6 mol dm^{-3} HCl (20 ml) was refluxed for 5 h after which it was concentrated and the residue dried in vacuo. The residue was dissolved in methanol and cyclohexylamine added until pH 6. The solution was concentrated in vacuo and then poured into acetone (100 ml). The precipitate formed was separated and dried in vacuo to give hydroscopic salt **20** (0.35 g, 46%); bp 90 °C (dec); δ_H 5.84 (CH_AH_B=, $^3J_{AP}$ 20.02); 5.64 (CH_AH_B=, $^3J_{BP}$ 41.5); 2.89 (CH_CH_D, $^3J_{PC}$ 11.23, J_{DC} 15.13, $^3J_{CH}$ 3.9,); 2.62 (CH_CH_D, $^3J_{PD}$ 18.07, J_{DH} 9.27); 3.9 (CH); 3.07 (CH-N); 1.3 and 1.5 – 2 (CH_2); δ_C 130.34 (CH_2=, $^2J_{PC}$ 7.69); 141.02 (-C(P)=, $^1J_{PC}$ 165.9); 36.07 (CH_2, $^2J_{PC}$ 13.18); 56.11 (CH); 175.46 (C(O)OH); 52.11 (CH-N); 32.07 (CH_2); 26.02 (CH_2) and 25.54 (CH_2); δ_P 11.86.

Cyclohexylamine salt of 4-phosphono-4-pentenoic acid 21

A solution of ester **13** (0.4 g) in 6 mol dm^{-3} HCl (10 ml) was refluxed for 6 h after which it was concentrated and the residue dried in vacuo. The residue was dissolved in methanol to which solution cyclohexylamine was added until pH 5. The solution was concentrated in vacuo and then poured into acetone (100 cm^3). The precipitate formed was separated and dried in vacuo to give salt **21** (0.26 g, 62%); bp 182 °C (dec); δ_H 5.49 (CH_AH_B=, $^3J_{AP}$ 43.45, J_{AH} 1.46); 5.69 (CH_AH_B=, $^3J_{BP}$ 22); 2.51 (CH_2, $^3J_{PH}$ 18.56, J_{HH} 7.8); 2.6 (CH_2, $^4J_{PH}$ 2.44); 3.1 (CH-N); 1.25 and 1.5 – 2 (CH_2); δ_C 125.59 (CH_2=, $^2J_{PC}$ 8.79); 144.92 (-C(P)=, $^1J_{PC}$ 165.89); 29.26 (CH_2, $^2J_{PC}$ 12.09); 34.63 (CH_2, $^3J_{PC}$ 5.49); 179.85 (C(O)OH); 52.11 (CH-N); 32.07 (CH_2); 26.02 (CH_2) and 25.54 (CH_2); δ_P 13.48.

Dicyclohexylamine salt of 5-oxo-2-hexen-2-phosphonic acid 22

A solution of ester **16** (0.8 g) in 6 mol dm^{-3} HCl (20 ml) was refluxed for 4 hours after which it was concentrated and the residue dried in vacuo. The residue was dissolved in methanol and cyclohexylamine added until pH 7. The solution was concentrated in vacuo and then poured into acetone (100 ml). The precipitate formed was separated and dried in vacuo to give salt **22** (0.3 g, 43%); δ_H 5.37 (CH_AH_B=, $^3J_{AP}$ 44.5); 5.6 (CH_AH_B=, $^3J_{BP}$ 21.3); 2.38 (CH_2, $^3J_{PH}$ 8.2, J_{HH} 8.2); 2.72 (CH_2); 2.11 (CH_3); 3.03 (CH-N); 1.22 and 1.4 – 2 (CH_2).

Dicyclohexylamine salt of 4-phosphono-2-(2-phosphono-2-propenyl)-4-pentenoic acid 23

A solution of ester **15** (0.6 g) in 6 mol dm^{-3} HCl (10 ml) was refluxed for 6 h after which it was concentrated and the residue dried in vacuo. The residue was dissolved in methanol and cyclohexylamine added until pH 5. The solution was concentrated in vacuo and then poured into acetone (100 ml). The precipitate formed was separated and dried in vacuo to give salt **23** (0.51 g, 73%); bp 210 °C (dec); δ_H 5.57 (CH_AH_B=, $^3J_{AP}$ 42.41); 5.76 (CH_AH_B=, $^3J_{BP}$ 20.0); 2.51 (CH_2, $^3J_{PH}$ 12.53, J_{HH} 6.16); 3.15 (CH); 3.15 (CH-N); 1.31 and 1.4 – 2 (CH_2); δ_C 127.4 (CH_2=, $^2J_{PC}$ 8.79); 127.25 (CH_2=, $^2J_{PC}$ 8.79); 143.48 (-C(P)=, $^1J_{PC}$ 166.7); 143.36 (-C(P)=, $^1J_{PC}$ 165.89); 37.22 (CH_2, $^2J_{PC}$ 12.08); 36.97 (CH_2, $^2J_{PC}$ 12.09); 45.62 (CH, $^3J_{PC}$ 4.4); 180.01 (C(O)OH); 181.66 (C(O)OH); 52.06 (CH-N); 32.07 (CH_2); 26.02 (CH_2) and 25.54 (CH_2); δ_P 13.07.

Cyclohexylamine salt of 2-amino-4-phosphonopentanoic acid 25

To a stirred solution of sodium ethoxide, prepared from sodium (0.24 g) and ethanol (50 ml), acetaminomalonic ester (2.27 g) was added dropwise and the stirring was continued for 10 min at room temperature. To the resultant stirred mixture dimethyl propene-2-phosphonate[12] (1.57 g) was added dropwise and the solution was refluxed for 6 h. The solvent was evaporated, the residue was desolved in dichloromethane, (50 ml), washed with water and the organic layer was dried over magnesium sulphate. The solvent was evaporated and the residue was chromatographed on a silica gel column (30 g), using ether and then acetone as eluents. After evaporation of the appropriate fraction, the residue was desolved in 6 mol dm^{-3} HCl (20 ml) and the solution was refluxed for 5 h after which it was concentrated and the residue dried in vacuo. The residue was dissolved in methanol to which solution ammonium hydroxide was added until it reached pH 6. The solution was concentrated in vacuo and then poured into acetone (100 ml). The precipitate was separated and dried in vacuo to give salt **25** (0.56 g, 23%); bp 82 °C (dec); δ_H 1.1 (CH_3, $^3J_{HP}$ 16.6, J_{HH} 6.35); 3.93 (CH-N, J_{HA} 6.35, J_{HB} 6.35); 3.88 (CH-N, J_{HA} 3.2, J_{HB} 8.3); 2.3 – 1.6 (CH_AH_B, CH); δ_P 26.8.

Tetraethyl methylene diphosphonate 30

Diphosphonate **30** was prepared by the literature procedure[16] from triethyl phosphite and methylene bromide.

Diethyl 3-hydroxypropen-2-phosphonate 26

Phosphonate **26** was prepared by the Wittig-Horner reaction of tetraethyl methylene diphosphonate with formaldehyde in boiling water and potassium carbonate as base, using the method of Rambaud et al.[15]

Diethyl 3-fluoropropene-2-phosphonate 27

Diethyl 3-hydroxypropen-2-phosphonate **26** (0.56 g) was added to a stirred solution of tetrabutylammonium fluoride (0.69 g) in dry THF (4 ml) at room temperature. After stirring for 10 h the solvent was evaporated in vacuo. The residue was extracted with ether, the solvent was evaporated

and the residue was distilled in vacuo to give phosphonate **27** (0.48 g, 95%), bp 46 °C (1 mm Hg); δ_H 6.24 (CH_AH_B=, $^3J_{AP}$ 22.19; J_{AB} 1.3; $^4J_{AH}$ 1.3; $^4J_{AF}$ 1.3); 6.13 (CH_AH_B=, $^3J_{BP}$ 46.14; $^4J_{BH}$ 1.75; $^4J_{\hat{A}F}$ 1.54); 5.02 (CH_2, $^3J_{PH}$ 7.91, J_{FH} 46.8); 4.12 (OCH_2, J_{PH} 7.25; J_{HH} 7.25); 1.34 (CH_3); δ_C 130.69 (CH_2=); 135.61 (-C(P)=, $^1J_{PC}$ 179.49, $^2J_{FC}$ 17.12); 81.52 (CH_2, $^2J_{PC}$ 20.05, $^1J_{FC}$ 175.08); 62.27 (OCH_2, $^2J_{PC}$ 5.5); 16.34 (CH_3, $^3J_{PC}$ 6.36) ; δ_P 17.11 ($^3J_{PF}$ 19.53); m/z 148 (100%), 141 (74.8), 57 (71.5), 121 (60.3), 123 (53.0), 81 (42.4), 65 (36.3), 169 (34.3), 142 (31.2), 140 (30.4), $[C_7H_{14}O_3PF - 1H]^+$ 195 (3.1).

Diethyl 3-chloropropene-2-phosphonate 28

To a stirred solution of diethyl 3–hydroxypropen-2-phosphonate **26** (1 g) in dry chloroform (5 ml) was added thionyl chloride (0.6 g) The resulted mixture was refluxed for 5 min. The solvent was evaporated and the residue distilled in vacuo to give phosphonate **28** (0.86g, 79%) bp 72 °C (1 mm Hg); δ_H 6.29 (CH_AH_B=, $^3J_{AP}$ 21.54; $^4J_{AH}$ 1.07; J_{AB} 1.1); 6.22 (CH_AH_B=, $^3J_{BF}$ 44.83; $^4J_{BH}$ 1.53); 4.24 (CH_2, $^3J_{PH}$ 9.66); 4.13 (OCH_2, J_{PH} 7.69; J_{HH} 7.69); 1.35 (CH_3); δ_C 132.66 (CH_2=, $^2J_{PC}$ 7.72); 135.72 (-C(P)=, $^1J_{PC}$ 177.98); 42.99 (CH_2, $^2J_{PC}$ 15.57); 62.32 (OCH_2, $^2J_{PC}$ 5.49); 16.32 (CH_3, $^3J_{PC}$ 6.9) ; δ_P 15.24; m/z 149 (100%), 177 (42.5), 121 (41.4), 65 (27.2), 81 (25.7), 139 (22.8), 156 (20.9), 57 (19.7), 157 (15.8), 109 (11.6), $[C_7H_{14}O_3PCl + 1H]^+$ 213 (0.6), 215 (0.2).

Diethyl 3-bromopropene-2-phosphonate 29

Phosphorus (III) bromide (1 g) was added to a stirred solution of diethyl 3-hydroxypropen-2-phosphonate **26** (1.1 g) in dry ether (20 ml) at -10 °C. The temperature was allowed to rise to 20 °C and stirring was continued for 30 min. Water (10 ml) was added at –10 °C, the organic phase was separated and dried with magnesium sulphate. The solvent was evaporated and the residue was distilled in vacuo to give phosphonate **29** (0.75g, 51%) bp 86 °C (1 mm Hg); δ_H 6.29 (CH_AH_B=, $^3J_{AP}$ 21.1; $^4J_{AH}$ 0.44; J_{AB} 1.3); 6.22 (CH_AH_B=, $^3J_{BP}$ 44.38; $^4J_{BH}$ 1.3); 4.14 (CH_2, $^3J_{PH}$ 10); 4.14 (OCH_2, J_{PH} 7.; J_{HH} 7.); 1.36 (CH_3); δ_C 134.7 (CH_2=, $^2J_{PC}$ 8.79); 136.06 (-C(P)=, $^1J_{PC}$ 177.98); 29.90 (CH_2, $^2J_{PC}$ 16.48); 63.56 (OCH_2, $^2J_{PC}$ 5.49); 16.52 (CH_3, $^3J_{PC}$ 5.69) ; δ_P 15.1; m/z 82 (100%), 149 (94.8), 80 (90.9), 81

(70.1), 177 (55.1), 121 (47.4), 65 (42.8), 79 (42.8), 57 (25.4), 109 (16.5), $[C_7H_{14}O_3PBr + 1H]^+$ 257 (2.3), 259 (1.6)

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