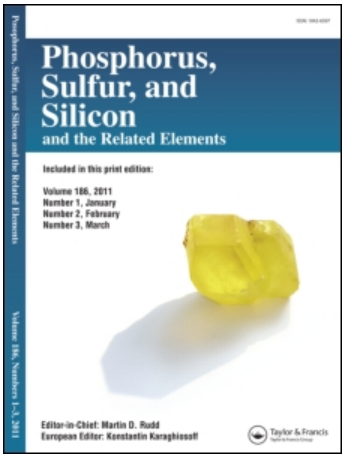

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PHOSPHONIC SYSTEMS. 2. FUNCTIONAL GROUP AND SKELETON MODIFICATIONS IN DIETHYL ESTERS OF 2-PROPENYL (AND 2-PENTENYL) PHOSPHONIC ACIDS

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Diethyl 2-propenylphosphonate (**1a**) undergoes complete prototropic isomerisation to the 1-propenyl derivative; in the presence of alkoxide ions the reaction is followed by β-addition and transesterification. Alkylation of allylic anions derived from **1a** and its 2-pentenyl analogue (**1b**) occurs, with one exception, exclusively at α-C.

Key words: Alkenyl phosphonates; prototropic isomerization; nucleophilic addition; allylic anions, alkylation.

Although phosphorus-stabilized anions derived from phosphonate esters found wide application in organic synthesis,[1] the most common systems involve additional stabilization of the carbanionic centre by another, in most cases carbonyl, group. Carbanions generated from 2-alkenylphosphonates (allylphosphonates) have been used for the preparation of dienes[2] and polyenes,[3] *via* the olefination with carbonyl electrophiles. When allylphosphonates were applied as precursors for alkenes *via* alkylation, followed by reduction,[4] substitution exclusively at the α-position was observed. It was however pointed out[1] that in reactions with carbonyl compounds γ-addition commonly occurs, and only the reversibility of the reaction allows the system to arrive at the alkene product. The regioselectivity in the reactions of the phosphonate-derived allylic anions with electrophiles is related to the prototropic equilibria of these systems, which was shown[5] to depend critically on substrate's structure. In this paper we report the prototropic and nucleophilic properties determined for two substrates: diethyl 2-propenylphosphonate, (**1a**) (no substitution at position γ), and (E)-diethyl 2-pentenylphosphonate, (**1b**) (γ-substitution by the ethyl group).

$CH_2{=}CH{-}CH_2{-}P(O)(OEt)_2$ **1a**

(E) $Et{-}CH{=}CH{-}CH_2{-}P(O)(OEt)_2$ **1b**

RESULTS AND DISCUSSION

Prototropic equilibria in simple alkenylphosphonic esters depend on the alkyl substitution at carbon atom 3 of the alkenyl chain. It was reported[5] that for diethyl butenylphosphonate the equilibrium mixture consisted of both, α, β, and β, γ isomers (ratio 1:3), as determined by I.R. spectroscopy. This result seems doubtful in view of our earlier[6] and present observations on **1b** which represents the exclusive

product (as determined by high resolution ^{31}P and ^{1}H n.m.r. spectroscopy) of the dehydrohalogenation of diethyl 2-chloropentylphosphonate under conditions of thermodynamic control.

$$CH_3CH_2CH_2CHClCH_2P(O)(OEt)_2 \xrightarrow[\text{r.t., 3 days}]{\text{excess base}} \mathbf{1b} \qquad (1)$$

It seems therefore that a single alkyl group at position 3 is a sufficient structural condition to shift the equilibrium completely towards the β,γ-unsaturated system. For the unsubstituted (propenyl) substrate, the situation is different; according to earlier reports, treatment of **1a** with catalytic amounts of sodium ethoxide[5] or potassium tert-butoxide,[7] resulted in complete isomerisation to the 1-propenyl derivative. We have now found that when **1a** is treated with one mole-equivalent of sodium ethoxide in ethanol, the reaction does not involve simple prototropic isomerisation, but gives 2-ethoxy substituted phosphonic ester (**2**) in high yields.

$$\mathbf{1a} \xrightarrow{\text{EtONa/EtOH}} CH_3CH(OEt)CH_2P(O)(OEt)_2 \qquad (2)$$

2

Product **2** obviously results from the complete isomerisation to the 1-propenyl derivative, followed by the Michael-type addition of EtO^-/H^+ to the α,β-unsaturated system. Similar addition of alcohols to the C=C—P=O functionality has been reported[8] for vinylic phosphine oxides. Treatment of **1a** with the MeONa/MeOH system introduces, independently of isomerisation followed by the addition, another reaction, that is, transesterification. When ten mole-equivalents of sodium methoxide were used, the only product obtained was dimethyl 2-methoxypropylphosphonate (**3**). With lower amounts of the methoxide ion the non- and partially-transesterified 2-methoxy derivatives were observed, indicating the relative sequence of the reactions as shown in Equation (3).

$$\mathbf{1a} \xrightarrow{MeO^-/MeOH} CH_3CH{=}CHP(O)(OEt)_2 \xrightarrow{MeO^-/MeOH}$$

$$CH_3\underset{\displaystyle OMe}{\underset{|}{C}}HCH_2P(O)(OEt)_2 \xrightarrow{MeO^-/MeOH} CH_3\underset{\displaystyle OMe}{\underset{|}{C}}HCH_2P(O)(OEt)(OMe) \qquad (3)$$

$$\xrightarrow{MeO^-/MeOH} CH_3\underset{\displaystyle OMe}{\underset{|}{C}}HCH_2P(O)(OMe)_2$$

3

Figure 1 illustrates the situation, in which in addition to the final product **3**, the intermediate 2-methoxy diethyl ester (A) and 2-methoxy methylethyl ester (B) (as a pair of diastereomers) are still present in the reaction mixture. Reaction of **1a** with the tBuOK/tBuOH system proved to be even more complex. Treatment of **1a** with one mole-equivalent of the base in tBuOH, followed by the usual aqueous work-up, resulted in the isolation, with low yield, of the same 2-*ethoxy*propylphosphonate, **2**, as the sole organic phase soluble product. This, rather unexpected,

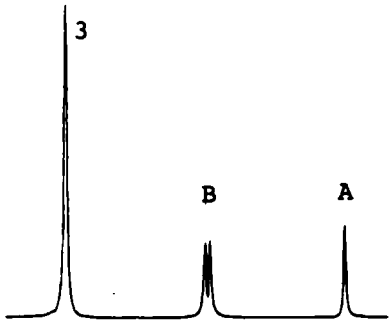

FIGURE 1 ^{31}P n.m.r. spectrum ($CDCl_3$) of the product obtained after incubating **1a** in MeOH containing one mole-equivalent of MeONa at 25°C for 20 h.

result indicates that in that case the transesterification (exchange of EtO^- by $tBuO^-$) is faster than the addition of $tBuO^-$ to the β-carbon, and that it is *only* the released EtO^- ion that adds to the α,β-unsaturated bond of the isomerised **1a**. It seems therefore that with respect to substrates of the type **1**, alkoxide ions, RO^- behave as bases (isomerisation) and nucleophiles (transesterification and addition), the relative nucleophilicity being a function of group R.

Nucleophilicity of allylic anions derived from substrates **1a** and **1b** was studied by treating them with butyllithium or LDA, and quenching the lithium derivatives formed with alkyl halides. For **1b** the regioselectivity of the condensation was clear; in agreement with earlier reports,[4] exclusive substitution at the α position was observed.

$$\mathbf{1b} \xrightarrow[\text{(ii) RX}]{\text{(i) BuLi or LDA}} CH_3CH_2CH{=}CHCHP(O)(OEt)_2 \quad (4)$$

			R
4 a,	R	=	Me
b,	R	=	Pr
c,	R	=	iPr
d,	R	=	CH_2Ph
e,	R	=	$SiMe_3$

The α-selectivity of the reaction is so high that when **1b** was treated with the excess of base and bromopropane, the product of α,α-dialkylation, diethyl 1,1-dipropyl-2-pentenylphosphonate was formed as a sole product. This regioselectivity offers a general route for structural modifications of the position 1 of a terminal alkene, from which the corresponding 2-alkenylphosphonic ester had been prepared.

The unsubstituted phosphonate **1a** showed less rigorous selectivity in the reactions of its allylic anion with electrophiles. Although alkylations occurred again at position α, reaction with trimethylchlorosilane gave exclusively the product of γ-substitution.

$$\mathbf{1a} \xrightarrow[\text{(ii) RX}]{\text{(i) BuLi (LDA)}} CH_2{=}CH\,CHP(O)(OEt)_2 \text{ or } CH_2CH{=}CHP(O)(OEt)_2 \quad (5)$$

		R			R	
5	**a,**	R	= Me	**6,**	R	= Me_3Si
	b,	R	= iPr			
	c,	R	= $PhCH_2$			

The exclusive formation of **6** represents the first instance of the rigorous γ-substitution in reactions of phosphonate stabilised allylic anions with simple electrophiles and indicates that steric effects play important role in the regioselectivity of the substitution.

EXPERIMENTAL

Solvents and commercially available substrates were purified by conventional methods immediately before use. All reactions involving organometallic reagents were carried out in an atmosphere of dry nitrogen. N.m.r. spectra were recorded on a Bruker AC 300 MHz spectrometer in $CDCl_3$, and the chemical shift values are given relative to TMS (^1H, ^{13}C) and trimethyl phosphate (^{31}P). Both, ^1H-decoupled, and ^1H-coupled ^{13}C n.m.r. spectra were obtained in order to support the structural assignments. Diastereomeric nuclei (^1H, ^{13}C) are denoted by superscripts a & b. Mass spectra were recorded on a Varian MAT-212 double focusing direct inlet spectrometer at an ionization potential of 70 eV. Only the values for M^+ and selected ions, most relevant to structural determinations, are given. "Bulb to bulb" distillations were performed on a Büchi GKR-50 apparatus. For column chromatography Merck Kieselgel 60 (0.063–0.200 mm) was used as a stationary phase. The products were collected as homogeneous (according to T.L.C.) fractions.

Diethyl 2-propenylphosphonate (**1a**) was prepared from triethyl phosphite and 3-bromopropene.[9] 93%; bp 55°C/0.75 mm (lit.:[9] bp 99–102°C/18 mm). ^1H n.m.r.: δ 1.27 (6H, *t*, J_{HH} 7.1 Hz, 2 × Me of OEt); 2.57 (2H, *d* of *d*, J_{HP} 22.0 Hz, J_{HH} 7.3 Hz, α—CH_2); 4.06 (4H, quint, $J_{HP} = J_{HH}$ 7.1 Hz, 2 × CH_2 of OEt); 5.17 (2H, m, $J_{HH\text{-}trans}$ 17.0 Hz, $J_{HH\text{-}cis}$ 6.9 Hz, $J_{HH\text{-}gem}$ 1.3 Hz, γ—CH_2); 5.76 (1H, m, $J_{HH\text{-}trans}$ 17.0 Hz, $J_{HH\text{-}cis}$ 6.9 Hz, $J_{HH\text{-}vic}$ 7.3 Hz, J_{HP} 3.2 Hz, β—CH). ^{13}C n.m.r.: δ 16.33 (*d*, J_{CP} 4.2 Hz, 2 × Me of OEt), (J_{CH} 128 Hz); 31.75 (*d*, J_{CP} 139 Hz, α—CH_2), (J_{CH} 130 Hz); 61.83 (*d*, J_{CP} 7.0 Hz, 2 × CH_2 of OEt), (J_{CH} 149 Hz); 119.7 (*d*, J_{CP} 15.2 Hz, γ—CH), (J_{CH} 160 Hz); 127.5 (*d*, J_{CP} 11.8 Hz, β—CH), (J_{CH} 159 Hz). ^{31}P n.m.r.: δ 24.7. M.S.: m/z 178 (M^+, 25%); 109 ($EtOPO_2H^+$, 100).

Diethyl 2-pentenylphosphonate (**1b**) was prepared as described before.[6]

Reactions of **1a** *with sodium alkoxides in alcohols. Diethyl 2-ethoxypropylphosphonate* (**2**). **1a** (0.2 g, 1.12 mmol) was dissolved in 5.1 mL of a 2.2 M solution of sodium ethoxide in ethanol and the solution was incubated at 25°C for 20 h. 10% aq. ammonium chloride solution was added until the pH was approximately 7, and the product was extracted with chloroform (3 × 10 mL). The combined chloroform extracts were filtered through anh. $MgSO_4$, and the solvent was removed under reduced pressure, yielding (**2**) as a colorless oil; 66%. ^1H n.m.r.: δ 1.41 (3H, *t*, J_{HH} 7.1 Hz, Me of COEt); 1.24 (3H, *d*, J_{HH} 6.2 Hz, γ—Me); 1.28 (6H, *t*, J_{HH} 7.0 Hz, 2 × Me of POEt); 1.81 (1H, *d* of *d* of *d*, J_{HH} 6.6, 15.4 Hz, J_{HP} 18.0 Hz, α—CH^a); 2.10 (1H, *d* of *d* of *d*, J_{HH} 5.9, 15.2 Hz, J_{HP} 19.2 Hz, α—CH^b); 3.46 (2H, *m*, CH_2 of COEt); 3.75 (1H, *m*, β—CH); 4.05 (4H, *m*, 2 × CH_2 of POEt). ^{13}C n.m.r.: δ 15.41 (*s*, Me of COEt), (J_{CH} 126 Hz); 16.34 (two *d*, J_{CP} 2.4 Hz, 2 × Me of POEt), (J_{CH} 134 Hz); 21.12 (*d*, J_{CP} 8.4 Hz, γ—Me), (J_{CH} 129 Hz); 33.66 (*d*, J_{CP} 139 Hz, α—CH_2), (J_{CH} 133 Hz); 61.28 (*d*, J_{CP} 7.0 Hz, CH_2^a of POEt), (J_{CH} 156 Hz); 61.55 (*d*, J_{CP} 7.0 Hz, CH_2^b of POEt), (J_{CH} 156 Hz); 63.73 (*s*, CH_2 of COEt), (J_{CH} 138 Hz); 70.47 (*s*, β—CH), (J_{CH} 146 Hz). ^{31}P n.m.r.: δ 26.6. M.S.: m/z 224 (M^+, 0.9%); 125 (M^+-$3C_2H_4$—CH_3, 100).

Dimethyl 2-methoxypropylphosphonate (**3**). **1a** (0.45 g, 2.53 mmol) was dissolved in 11.6 mL of a 2.2 M solution of sodium methoxide in methanol and the solution was treated in the same way as for (**2**). The crude product was purified by column chromatography (chloroform/acetone, 4:1), yielding (**3**) as a colorless oil, 65%. ^1H n.m.r.: δ 1.22 (3H, *d*, J_{HH} 6.1 Hz, γ—Me); 1.82 (1H, *d* of *d* of *d*, J_{HH} 6.3, 15.3 Hz, J_{HP} 18.2 Hz, α—CH^a); 2.08 (1H, *d* of *d* of *d*, J_{HH} 6.3, 15.3 Hz, J_{HP} 18.8 Hz, α—CH^b); 3.29 (3H, *s*, Me of COMe); 3.66 (1H, *m*, β—CH); 3.67 (3H, *d*, J_{HP} 4.2 Hz, Me of $POMe^a$); 3.70 (3H, *d*, J_{HP} 4.4 Hz, Me of $POMe^b$). ^{13}C n.m.r.: δ 20.34 (*d*, J_{CP} 9.8 Hz, γ—Me), (J_{CH} 129 Hz); 32.61 (*d*, J_{CP} 139 Hz, α—CH_2), (J_{CH} 129 Hz); 51.99 (*d*, J_{CP} 7.0 Hz, Me of $POMe^a$), (J_{CH} 147 Hz); 52.39 (*d*, J_{CP} 5.9 Hz, Me of $POMe^b$), (J_{CH} 147 Hz); 56.01 (*s*, Me of COMe), (J_{CH} 147 Hz); 72.09 (*d*, J_{CP} 2.5 Hz, β—CH), (J_{CH} 148 Hz). ^{31}P n.m.r.: δ 29.1. M.S.: m/z 181 (M^+—1, 10%); 167 (M^+—CH_3, 58); 109 ($Me_2PO_3^+$, 100).

Reaction of **1a** *with potassium tert-butoxide*. **1a** (2.0 g, 0.011 mol) was dissolved in a solution of tBuOK (1.26 g, 0.011 mol) in tBuOH (5.1 mL) and the solution was kept under nitrogen for 20 h at 25°C. Aq. NH_4Cl (10%) was added until pH was 7 and the product was extracted with chloroform. After filtration

through anh. $MgSO_4$ and evaporation of the solvent, a pale yellow oil (0.79 g, 32%) was obtained. Column chromatography (chloroform/acetone, 4:1) afforded pure product as a colorless oil. ^1H and ^{31}P n.m.r. spectra of this product were identical to those of 2 described above.

Reactions of allylic anions with electrophiles. General procedures. A. *n*-Butyllithium (1.6 M solution in hexane, 1.2 mol equiv.) was added to a solution of the phosphonate in THF at −78°C, and stirred at this temperature for 1 h. The electrophile (1 mol equiv.) was then added dropwise to the solution. After stirring for an additional 30 min at −78°C, the reaction mixture was allowed to warm up to room temperature. The mixture was quenched by the addition of 10% aq. ammonium chloride and the product was extracted with ether. The ether solution was dried ($MgSO_4$) and evaporated under reduced pressure, yielding the crude product.

B. The solution of *n*-butyllithium (1.2 mol equiv.) was added dropwise to a stirred solution of diisopropylamine (1.2 mol equiv.) in THF at −78°C. The temperature was raised to 0°C and 15 min later cooled again to −78°C, at which temperature the phosphonate was added dropwise. The temperature was raised to −30°C and after 15 min the mixture was cooled to −78°C and left at that temperature for 1 h. The electrophile (1 mol equiv.) was added dropwise and after 30 min the reaction mixture was allowed to warm up to room temperature. The product was then isolated as in A.

Diethyl 1-methyl-2-pentenylphosphonate (**4a**) (electrophile = MeI). Purified by column chromatography (chloroform/acetone, 4:1). 79%. ^1H n.m.r.: δ 0.96 (3H, *t*, J_{HH} 7.5 Hz, C(5)H_3); 1.20 (3H, *d*, J_{HH} 5.3 Hz, C(2)CH_3); 1.26 (3H, *t*, J_{HH} 7.0 Hz, Me of POEt[a]); 1.27 (3H, *t*, J_{HH} 7.0 Hz, Me of POEt[b]); 2.02 (2H, *d* of *q*, J_{HH} 6.3, 7.5 Hz, δ—CH_2); 2.51 (1H, *m*, α—CH); 4.06 (4H, *d* of *q*, J_{HH} 7.0 Hz, J_{HP} 7.2 Hz, 2 × CH_2 of POEt); 5.42 (2H, *m*, CH=CH). ^{13}C n.m.r.: δ 13.53 (*d*, J_{CP} 3.8 Hz, C(5)H_3), (J_{CH} 132 Hz); 14.09 (*d*, J_{CP} 6.2 Hz, C(2)CH_3), (J_{CH} 132 Hz); 16.43 (*d*, J_{CP} 4.0 Hz, 2 × Me of POEt), (J_{CH} 132 Hz); 25.61 (*d*, J_{CP} 2.3 Hz, δ—CH_2), (J_{CH} 134 Hz); 35.43 (*d*, J_{CP} 140 Hz, α—CH), (J_{CH} 125 Hz); 61.72 (*d*, J_{CP} 7.2 Hz, CH_2 of POEt[a]), (J_{CH} 156 Hz); 61.95 (*d*, J_{CP} 7.4 Hz, CH_2 of POEt[b]), (J_{CH} 156 Hz); 124.9 (*d*, J_{CP} 9.3 Hz, γ—CH), (J_{CH} 144 Hz); 135.0 (*d*, J_{CP} 13.8 Hz, β—CH), (J_{CH} 157 Hz). ^{31}P n.m.r.: δ 28.5. M.S.: m/z 220 (M^+, 2.3%).

Diethyl 1-propyl-2-pentenylphosphonate (**4b**) (electrophile = PrBr). Purified as (**4a**). 83%. ^1H n.m.r.: δ 0.86 (3H, *t*, J_{HH} 7.2 Hz, Me of Pr); 0.97 (3H, *t*, J_{HH} 7.5 Hz, C(5)H_3); 1.27 (3H, *t*, J_{HH} 7.0 Hz, Me of POEt[a]); 1.28 (3H, *t*, J_{HH} 6.7 Hz, Me of POEt[b]); 1.45 (2H, *m*, P—C—C—CH_2); 1.70 (2H, *m*, P—C—CH_2) 2.07 (2H, *m*, δ—CH_2); 2.39 (1H, *d* of *d* of *t*, J_{HH} 10.4, 3.1 Hz, J_{HP} 21.4 Hz, α—CH_2); 4.05 (4H, quint, J_{HH} = J_{HP} 7.2 Hz, 2 × CH_2 of POEt); 5.21 (1H, *m*, γ—CH); 5.57 (1H, *m*, β—CH). ^{13}C n.m.r.: δ 13.62 (*d*, J_{CP} 5.6 Hz, Me of C(5)H_3 and of Pr), (J_{CH} 129 Hz); 16.42 (*d*, J_{CP} 5.6 Hz, Me of POEt[a]), (J_{CH} 122 Hz); 16.45 (*d*, J_{CP} 6.1 Hz, Me of POEt[b]), (J_{CH} 122 Hz); 20.52 (*d*, J_{CP} 15.6 Hz, P—C—C—$\underline{C}H_2$), (J_{CH} 133 Hz); 25.67 (*s*, δ—CH_2), (J_{CH} 129 Hz); 30.47 (*d*, J_{CP} 4.2 Hz, P—C—$\underline{C}H_2$), (J_{CH} 133 Hz); 41.49 (*d*, J_{CP} 138 Hz, α—CH), (J_{CH} 133 Hz); 61.50 (*d*, J_{CP} 7.3 Hz, CH_2 of POEt[a]), (J_{CH} 155 Hz); 62.03 (*d*, J_{CP} 7.3 Hz, CH_2 of POEt[b]), (J_{CH} 155 Hz); 123.6 (*d*, J_{CP} 10.7 Hz, γ—CH), (J_{CH} 155 Hz); 137.0 (*d*, J_{CP} 14.0 Hz, β—CH), (J_{CH} 155 Hz). ^{31}P n.m.r.: δ 28.1. M.S.: m/z 248 (M^+, 46%).

Diethyl 1-isopropyl-2-pentenylphosphonate (**4c**) (electrophile = iPrBr). Purified as (**4a**). 53%. ^1H n.m.r.: δ 0.96 (9H, *m*, C(5)H_3, 2 × Me of iPr); 1.26 (3H, *t*, J_{HH} 7.3 Hz, Me of POEt[a]); 1.27 (3H, *t*, J_{HH} 7.3 Hz, Me of POEt[b]); 1.27 (1H, *m*, CH of iPr); 2.05 (2H, *m*, δ—CH_2); 2.30 (1H, *d* of *d* of *d*, J_{HH} 4.3, 10.2 Hz, J_{HP} 21.8 Hz, α—CH); 4.05 (4H, *m*, J_{HH} 7.3 Hz, J_{HP} 7.4 Hz, 2 × CH_2 of POEt); 5.35 (1H, *m*, γ—CH); 5.56 (1H, *m*, β—CH). ^{13}C n.m.r.: δ 13.72 (*d*, J_{CP} 2.9 Hz, C(5)H_3), (J_{CH} 130 Hz); 16.45 (*d*, J_{CP} 5.4 Hz, 2 × Me of POEt), (J_{CH} 113 Hz); 19.04 (*d*, J_{CP} 4.3 Hz, Me[a] of iPr); 22.08 (*d*, J_{CP} 14.0 Hz, Me[b] of iPr), (J_{CH} 63 Hz); 25.79 (*d*, J_{CP} 2.4 Hz, δ—CH_2), (J_{CH} 115 Hz); 27.78 (*d*, J_{CP} 3.0 Hz, CH of iPr), (J_{CH} 126 Hz); 48.27 (*d*, J_{CP} 136 Hz, α—CH), (J_{CH} 144 Hz); 61.32 (*d*, J_{CP} 7.9 Hz, CH_2 of POEt[a]), (J_{CH} 132 Hz); 61.76 (*d*, J_{CP} 7.9 Hz, CH_2 of POEt[b]), (J_{CH} 132 Hz); 120.7 (*d*, J_{CP} 8.5 Hz, γ—CH), (J_{CH} 151 Hz); 138.2 (*d*, J_{CP} 15.2 Hz, β—CH), (J_{CH} 151 Hz). ^{31}P n.m.r.: δ 27.6. M.S.: m/z 248 (M^+, 8%); 205 (M—C_3H_7, 52); 41 ($C_3H_5^+$, 100).

Diethyl 1-benzyl-2-pentenylphosphonate, **4d** (electrophile = $PhCH_2Br$. Purified by column chromatography (benzene/ethyl acetate, 7:3). 65%. ^1H n.m.r.: δ 0.84 (3H, *t*, J_{HH} 7.6 Hz, C(5)H_3); 1.28 (3H, *t*, J_{HH} 7.1 Hz, Me of POEt[a]); 1.29 (3H, *t*, J_{HH} 7.1 Hz, Me of POEt[b]); 1.93 (2H, *d* of *q*, J_{HH} 2.3, 7.6 Hz, δ—CH_2); 2.73 (2H, *m*, Ch_2 of benzyl); 3.17 (1H, *m*, α—CH); 4.08 (4H, *d* of *q*, J_{HH} 7.1 Hz, J_{HP} 7.2 Hz, 2 × CH_2 of POEt); 5.31 (2H, *m*, β—, and γ—CH); 7.17 (5H, *m*, Ph). ^{13}C n.m.r.: δ 13.44 (*d*, J_{CP} 2.5 Hz, C(5)H_3), (J_{CH} 131 Hz); 16.44 (*d*, J_{CP} 4.8 Hz, 2 × Me of POEt), (J_{CH} 133 Hz); 25.61 (*s*, δ—CH_2), (J_{CH} 127 Hz); 35.11 (*s*, CH_2 of benzyl), (J_{CH} 133 Hz); 43.56 (*d*, J_{CP} 138 Hz, α—CH_2), (J_{CH} 133 Hz); 61.77 (*d*, J_{CP} 6.8 Hz, CH_2 of POEt[a]), (J_{CH} 145 Hz); 62.28 (*d*, J_{CP} 7.3 Hz, CH_2 of POEt[b]), (J_{CH} 149 Hz); 122.65 (*d*, J_{CP} 9.7 Hz, γ—CH), (J_{CH} 154 Hz); 126.1 (*s*, *p*-C of Ph), (J_{CH} 143 Hz); 128.1 (*d*, J_{CP}

4.2 Hz, *o*-C of Ph), (J_{CH} 153 Hz); 129.0 (*s*, *m*-C of Ph), (J_{CH} 145 Hz); 145.0 (*s*, 1-C of Ph); 138.0 (*d*, J_{CP} 14 Hz, β—CH), (J_{CH} 153 Hz). ^{31}P n.m.r.: δ 26.9. M.S.: m/z 296 (M^+, 3%).

Diethyl 1-trimethylsilyl-2-pentenylphosphonate, **4e** (electrophile = Me_2SiCl). Purified as (**4a**). 77%. ^{1}H n.m.r.: δ 0.06 (9H, *s*, Me_3Si); 0.91 (3H, *t*, J_{HH} 7.5 Hz, C(5)H_3); 1.22 (6H, *t*, J_{HH} 7.1 Hz, 2 × Me of POEt); 1.98 (2H, *m*, δ—CH_2); 2.45 (1H, *m*, α—CH); 3.98 (4H, *m*, 2 × CH_2 of POEt); 5.30 (2H, *m*, β— and γ—CH). ^{13}C n.m.r.: δ −1.82 (*s*, Me_3Si), (J_{CH} 122 Hz); 13.89 (*d*, J_{CP} 4.2 Hz, C(5)H_3), (J_{CH} 124 Hz); 16.28 (*d*, J_{CP} 6.0 Hz, 2 × Me of POEt), (J_{CH} 127 Hz); 25.73 (*s*, δ—CH_2), (J_{CH} 125 Hz); 33.36 (*d*, J_{CP} 128 Hz, α—CH), (J_{CH} 122 Hz); 60.87 (*d*, J_{CP} 7.0 Hz, CH_2 of POEt[a]), (J_{CH} 147 Hz); 61.45 (*d*, J_{CP} 7.0 Hz, CH_2 of POEt[b]), (J_{CH} 144 Hz); 120.4 (*d*, J_{CP} 11.0 Hz, γ—CH), (J_{CH} 158 Hz); 134.7 (*d*, J_{CP} 15.3 Hz, β—CH). (J_{CH} 159 Hz). ^{31}P n.m.r.: δ 28.1. M.S.: m/z 278 (M^+, 21%); 191 (M^+—CH_3—C_2H_4—CH_3CHO, 100).

Diethyl 1,1-dipropyl-2-pentenylphosphonate. Prepared using one mole-equivalent of **1b**, two mole-equivalents of BuLi, and two mole-equivalents of PrBr. Purified by column chromatography (chloroform/acetone, 9:1). 73%. ^{1}H n.m.r.: δ 0.87 (6H, *t*, J_{HH} 7.0 Hz, 2 × Me of Pr); 0.96 (3H, *t*, J_{HH} 7.2 Hz, C(5)H_3); 1.26 (6H, *t*, J_{HH} 7.1 Hz, 2 × Me of POEt); 1.45 (6H, *m*, 3 × CH_2 of Pr); 1.70 (2H, *m*, CH_2 of Pr); 2.05 (2H, *m*, δ—CH_2); 4.03 (4H, quint, J_{HH} = J_{HP} 7.2 Hz, 2 × CH_2 of POEt); 5.45 (2H, *m*, β and γ—CH). ^{13}C n.m.r.: δ 13.6 (*d*, J_{CP} 1.66 Hz, C(5)H_3), (J_{CH} 126 Hz); 14.7 (*w*, 2 × Me of Pr), (J_{CH} 125 Hz); 16.6 (*d*, J_{CP} 6.41 Hz, 2 × Me of POEt), (J_{CH} 127 Hz); 16.9 (*d*, J_{CP} 6.4 Hz, 2 × CH_2 of C(2) of Pr), (J_{CH} 126 Hz); 26.2 (*d*, J_{CP} 2.9 Hz, δ—CH_2), (J_{CH} 123 Hz); 34.2 (*d*, J_{CP} 3.6 Hz, 2 × CH_2 of C(1) of Pr), (J_{CH} 126 Hz); 44.4 (*d*, J_{CP} 135 Hz, α—C); 62.0 (*d*, J_{CP} 7.9 Hz, 2 × CH_2 of POEt), (J_{CH} 144 Hz); 130.0 (*d*, J_{CP} 9.6 Hz, γ—CH), (J_{CH} 161 Hz); 133.7 (*d*, J_{CP} 11.2 Hz, β—CH), (J_{CH} 148 Hz). ^{31}P n.m.r.: δ 29.7. M.S.: m/z 290 (M^+, 10%).

Diethyl 1-methyl-2-propenylphosphonate, **5a** (electrophile = MeI). Purified by column chromatography (chloroform/acetone, 7:3). 73%. ^{1}H n.m.r.: δ 1.27 (6H, *t*, J_{HH} 7.6 Hz, 2 × Me of POEt); 1.30 (3H, *d*, J_{PH} 6.8 Hz, Me of C(1)Me); 2.61 (1H, *m*, α—CH); 4.03 (4H, quint, J_{HH} = J_{HP} 7.5 Hz, 2 × CH_2 of POEt); 5.12 (2H, *m*, γ—CH_2); 5.87 (1H, *m*, β—CH). ^{13}C n.m.r.: δ 13.21 (*d*, J_{CP} 7.7 Hz, Me of C(1)CH_3), (J_{CH} 126 Hz); 16.41 (*d*, J_{CP} 6.3 Hz, 2 × Me of POEt), (J_{CH} 131 Hz); 36.46 (*d*, J_{CP} 139 Hz, α—CH), (J_{CH} 135 Hz); 61.97 (*d*, J_{CP} 7.1 Hz, 2 × CH_2 of POEt), (J_{CH} 148 Hz); 117.0 (*d*, J_{CP} 13.7 Hz, γ—CH_2), (J_{CH} 166 Hz); 134.4 (*d*, J_{CP} 11.8 Hz, β—CH), (J_{CH} 160 Hz). ^{31}P n.m.r.: δ 27.6. M.S.: m/z 192 (M^+, 50%); 164 (M^+-C_2H_4, 12); 136 (M^+—C_2H_4—C_2H_4, 31); 55 ($C_4H_7^+$, 84).
The same product (86%) was obtained using CF_3SO_3Me as an electrophile.

Diethyl 1-isopropyl-2-propenylphosphonate, **5b** (electrophile = iPrI). Purified as **4a.** 51%. ^{1}H n.m.r.: δ 0.91 (6H, two *d*, J_{HH} 6.9 Hz, 2 × Me of iPr); 1.20 (3H, *t*, J_{HH} 7.1 Hz, Me of POEt[a]); 1.22 (3H, *t*, J_{HH} 7.1 Hz, Me of POEt[b]); 2.12 (1H, *m*, CH of iPr); 2.30 (1H, *d* of *d* of *d*, J_{HH} 4.1, 9.5 Hz, J_{HP} 14.5 Hz, α—CH); 4.00 (4H, quint, J_{HH} = J_{HP} 7.2 Hz, 2 × CH_2 of POEt); 5.11 (2H, *m*, γ—CH_2); 5.65 (1H, *m*, β—CH). ^{13}C n.m.r.: δ 16.19 (*d*, J_{CP} 6.0 Hz, Me[a] of iPr), (J_{CH} 133 Hz); 18.92 (*d*, J_{CP} 5.6 Hz, Me[b] of iPr), (J_{CH} 128 Hz); 21.64 (*d*, J_{CP} 5.7 Hz, Me of POEt[a]), (J_{CH} 129 Hz); 22.02 (*d*, J_{CP} 5.7 Hz, Me of POEt[b]), (J_{CH} 129 Hz); 27.49 (*d*, J_{CP} 4.1 Hz, CH of iPr), (J_{CH} 136 Hz); 49.56 (*d*, J_{CP} 136 Hz, α—CH), (J_{CH} 133 Hz); 61.36 (*d*, J_{CP} 7.8 Hz, CH_2 of POEt[a]), (J_{CH} 144 Hz); 61.72 (*d*, J_{CP} 7.5 Hz, CH_2 of POEt[b]), (J_{CH} 149 Hz); 120.0 (*d*, J_{CP} 15.1 Hz, γ—CH_2), (J_{CH} 156 Hz); 130.6 (*d*, J_{CP} 9.6 Hz, β—CH), (J_{CH} 156 Hz). ^{31}P n.m.r.: δ 26.6 M.S.: m/z 220 (M^+, 3%); 177 (M^+—C_3H_7, 43); 149 (M^+—C_3H_7—C_2H_4, 30).

Diethyl 1-benzyl-2-propenylphosphonate, **5c** (electrophile = $PhCH_2Br$). 64%. ^{1}H n.m.r.: δ 1.26 (3H, *t*, J_{HH} 7.1 Hz, Me of POEt[a]); 1.27 (3H, *t*, J_{HH} 7.1 Hz, Me of POEt[b]); 2.79 (2H, m, CH_2 of benzyl); 3.20 (1H, *t* of *t*, J_{HH} = J_{HP} 10.4 Hz, J_{HH} ca. 4 Hz, α—CH); 4.04 (4H, *d* of *q*, J_{HH} 7.1 Hz, J_{HP} 6.2 Hz, 2 × CH_2 of POEt); 5.01 (2H, *d* of *d* of *d*, J_{HH} 13.8, 3.6 Hz, J_{HP} 10.2 Hz. γ—CH_2); 5.64 (1H, *m*, β—CH); 7.17 (5H, *m*, Ph). ^{13}C n.m.r.: δ 16.39 (*d*, J_{CP} 6.7 Hz, 2 × Me of POEt), (J_{CH} 131 Hz); 34.57 (*d*, J_{CP} 4.8 Hz, CH_2 of benzyl), (J_{CH} 130 Hz); 44.63 (*d*, J_{CP} 137 Hz, α—CH), (J_{CH} 136 Hz); 61.81 (*d*, J_{CP} 5.0 Hz, CH_2 of POEt[a]), (J_{CH} 155 Hz); 62.28 (*d*, J_{CP} 4.4 Hz, CH_2 of POEt[b]), (J_{CH} 148 Hz); 119.66 (*d*, J_{CP} 13.9 Hz, γ—CH_2), (J_{CH} 149 Hz); 126.24 (*s*, p—C of Ph), (J_{CH} 165 Hz); 128.19 (s), (J_{CH} 169 Hz); 128.99 (s), (J_{CH} 176 Hz) (o— and m—C of Ph); 132.40 (*d*, J_{CP} 9.8 Hz, β—CH), (J_{CH} 159 Hz); 139.0 (*s*, 1—C of Ph). ^{31}P n.m.r.: δ 26.0. M.S.: m/z 268 (M^+, 22%); 240 (M^+—C_2H_4, 2); 212 (M^+—$2C_2H_4$, 2); 177 (M^+—C_7H_7, 6); 131 (M^+—PO_3Et_2, 100); 91 ($C_7H_7^+$, 91).

Diethyl 3-trimethylsilyl-1-propenylphosphonate, **6** (electrophile = Me_3SiCl). Purified by "bulb to bulb" distillation (oven temp 160–180°C/0.3 mm). 85%. ^{1}H n.m.r.: δ 0.02 (9H, s, Me_3Si); 1.28 (6H, *t*, J_{HH} 7.3 Hz, 2 × Me of POEt); 1.74 (2H, *d*, J_{HH} 8.0 Hz, γ—CH_2); 4.01 (4H, quint, J_{HH} = J_{HP} 7.3 Hz, 2 × CH_2 of POEt); 5.39 (1H, *m*, β—CH); 6.76 (1H, *m*, α—CH). ^{13}C n.m.r.: δ −1.93 (s, Me_3Si), (J_{CH}

119 Hz); 16.3 (*d*, J_{CP} 6.9 Hz, 2 × Me of POEt), (J_{CH} 123 Hz); 26.99 (*d*, J_{CP} 21.2 Hz, γ—CH_2), (J_{CH} 103 Hz); 61.3 (*d*, J_{CP} 5.8 Hz, 2 × CH_2 of POEt), (J_{CH} 147 Hz); 114.1 (*d*, J_{CP} 190 Hz, α—CH), (J_{CH} 155 Hz); 152.1 (*d*, J_{CP} 5.9 Hz, β—CH), (J_{CH} 155 Hz). ^{31}P n.m.r.: δ 17.2. M.S.: m/z 250 (M^+, 0.3%); 235 (M^+—CH_3, 1).

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