

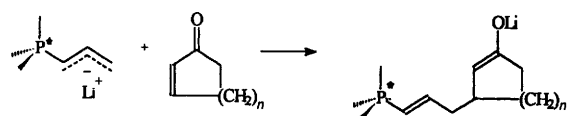
# Reaction of carbanions generated from allylic phosphonates with $\beta$ -substituted cyclic enones

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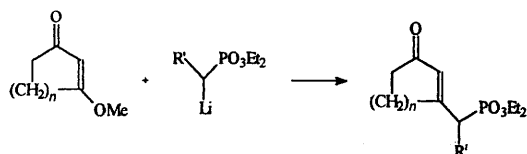
Lithiated allylic phosphonates react with 3-methoxy- or 3-chloro-substituted cyclohexanones and cyclopentanones at the  $\beta$ -carbon according to the addition–elimination mechanism. The initial adducts undergo spontaneous isomerisation to the fully conjugated products, which upon treatment with  $I_2$  in MeOH aromatise to the corresponding 3-substituted anisole derivatives.

The reaction of phosphorus-stabilised carbanions with  $\alpha,\beta$ -unsaturated carbonyl substrates attracts increasing attention because of the synthetic potential of the reaction products. It was demonstrated that chirally modified (at phosphorus) *P*-allyl anions derived from tertiary phosphine oxides,<sup>1</sup> phosphonic amidoesters<sup>2</sup> or phosphonodiamidates<sup>3</sup> add to cyclic enones exclusively or predominantly *via* the  $\gamma$ -1,4 mechanism with a high degree of diastereoselectivity (Scheme 1). We have recently shown<sup>4</sup> that the reaction between  $\alpha$ -



Scheme 1

lithiated dialkyl alkylphosphonic esters and cyclic enones bearing a potential leaving group in the  $\beta$ -position follows chemoselectively one of the two available reaction pathways. For 3-chloro substituted substrates, addition to the carbonyl group occurs as for the unsubstituted enones,<sup>5</sup> while the 3-methoxycycloalkenones react according to the addition–elimination mechanism yielding the 3-(phosphonoalkyl)substituted products (Scheme 2). The reaction represents a valuable

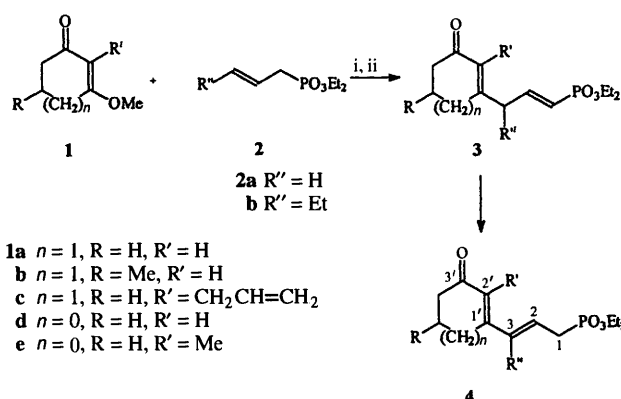


Scheme 2

variation of the addition shown in Scheme 1, since it allows preparation of phosphonates with retention of the enone functionality. In this work we report an extension of the reaction shown in Scheme 2 on the 'delocalised' carbanions, that is, carbon nucleophiles derived from allylic phosphonates.

## Results and discussion

Three 3-methoxycyclohexenones and two 3-methoxycyclopentenones **1** were treated with lithiated diethyl prop-2-enyl- or pent-2-enyl-phosphonate **2** under standard conditions.<sup>4</sup> Without exception, the reaction followed the addition–elimination mechanism involving the  $\gamma$ -carbon of the nucleophile; the final products **4** resulted from the *in situ* isomerisation of the initial substitution products **3** to the fully conjugated systems (Scheme 3). In one case (reaction of **1a** with **2a**) the corresponding intermediate **3** could be isolated and characterised, thus



Scheme 3 Reagents and conditions: i, BuLi, THF,  $-78\text{ }^\circ\text{C}$ ; ii,  $\text{H}_3\text{O}^+$

confirming the reaction mechanism. In contrast to all phosphonates **4**, intermediate **3** showed in the  $^{31}\text{P}$  NMR spectrum a high-field signal at  $\delta_{\text{p}}$  18.2, characteristic for the vinylphosphonic system. Product **3** changed gradually to **4a**, which was independently isolated and characterised. Facile isomerisation **3**  $\rightarrow$  **4** gives evidence for the weak effect of the phosphoryl group on the adjacent alkenic bond relative to the effect of the enone function. Similar prototropic shift of the alk-1-enyl to the alk-2-enylphosphonate system was reported for the 3-chloro substituted alkenylphosphonates<sup>6</sup> and was utilised for the preparation of allylic phosphonates from the corresponding vinylic precursors.<sup>7</sup> Spontaneous formation of **4** is advantageous since those products represent vinylogues of 2-ketophosphonates, and hence can serve as substrates for further condensations *via* the phosphorus-stabilised carbanions.<sup>8</sup> Only the *E*-isomer of **4** with respect to the exocyclic alkenic bond were obtained (single signal in the  $^{31}\text{P}$  NMR spectrum). For the products derived from **2a** the *E*-geometry was easily established from the vicinal coupling constants in the  $^1\text{H}$  NMR spectrum of the alkenic hydrogens. When **2b** was used as a substrate, no NOE experiments were carried out to determine the geometry of the double bond, but the similarity of the NMR spectroscopic parameters ( $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{31}\text{P}$ ) for all products **4** strongly indicated common configuration. Table 1 includes compounds **4** prepared according to Scheme 3, together with the characterisation of the products. Product **4a** was also prepared from 3-chlorocyclohexenone. When 3-chlorocyclohexenones were previously treated with 'localised' carbanions derived from diethyl alkylphosphonates ( $\text{R}'\text{CH}_2\text{PO}_3\text{Et}_2$ ,  $\text{R}' = \text{H}, \text{Me}$ ), the reaction occurred exclusively at the carbonyl group (1,2 addition).<sup>4</sup> Our present result indicates that in the case of a 'delocalised' carbanion (derived from an allylic phosphonate), the exclusive chemoselectivity with respect to the  $\beta$ -carbon

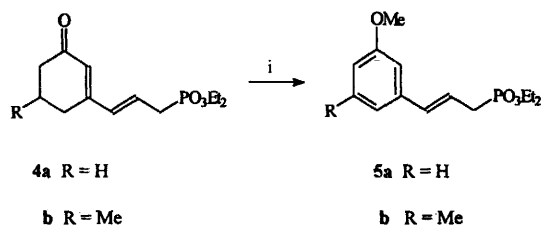
Table 1 Phosphonic esters 4<sup>a</sup>

4	<i>n</i> , R', R''	Yield (%)	<sup>1</sup> H NMR	<sup>13</sup> C NMR	<sup>31</sup> P NMR	IR/cm <sup>-1</sup>	MS	Elemental analysis (%)	
								Calc.	Found
a	1, H, H, H	68 <sup>b,c</sup>	2.02 (2 H, t, <sup>3</sup> J <sub>HH</sub> 6.2, 9.3, 5'-H <sub>2</sub> ), 2.39 (2 H, dd, <sup>3</sup> J <sub>HH</sub> 6.3, 9.3, 4'-H <sub>2</sub> ), 2.43 (2 H, dd, <sup>3</sup> J <sub>HH</sub> 6.2, 9.2, 6'-H <sub>2</sub> ), 2.72 (2 H, dd, <sup>2</sup> J <sub>HP</sub> 22.9, <sup>3</sup> J <sub>HH</sub> 7.4, 1-H <sub>2</sub> ), 5.89 (1 H, s, 2'-H), 6.11 (1 H, dq, <sup>3</sup> J <sub>HH trans</sub> 15.1, <sup>3</sup> J <sub>HP</sub> = <sup>3</sup> J <sub>HP</sub> = 7.4, 2-H), 6.30 (1 H, dd, <sup>3</sup> J <sub>HH trans</sub> 15.1, <sup>4</sup> J <sub>HP</sub> 4.1, 3-H)	16.4 (d, <i>J</i> 5.4), 22.2 (s), 24.9 (s), 31.4 (d, <i>J</i> 139.0), 37.6 (s), 62.1 (d, <i>J</i> 6.9), 126.5 (d, <i>J</i> 12.5), 127.6 (d, <i>J</i> 2.9), 135.8 (d, <i>J</i> 14.8), 156.1 (s), 200.1 (s)	26.1	1257 1548 1667	272 (M <sup>+</sup> , 19%), 152 (96), 134 (100), 125 (59), 97 (22), 81 (38)	C <sub>13</sub> H <sub>21</sub> O <sub>4</sub> P C, 57.35 C, 57.33 H, 7.77 H, 7.92	
b	1, Me, H, H	50 <sup>d</sup>	1.07 (3 H, d, <sup>3</sup> J <sub>HH</sub> 6.2, 5'-Me), 2.11-2.19 (2 H, m, 4'-H <sub>2</sub> ), 2.13-2.21 (1 H, m, 5'-H), 2.44 (1 H, dd, <sup>3</sup> J <sub>HH trans</sub> 15.7, <sup>3</sup> J <sub>HH cis</sub> 3.0, 6'-H), 2.57 (1 H, dd, <sup>3</sup> J <sub>HH trans</sub> 16.0, <sup>3</sup> J <sub>HH cis</sub> 3.5), 2.71 (2 H, dd, <sup>2</sup> J <sub>HP</sub> 23.0, <sup>3</sup> J <sub>HH</sub> 7.5, 1-H <sub>2</sub> ), 5.86 (1 H, br s, 2'-H), 6.11 (1 H, dq, <sup>3</sup> J <sub>HH trans</sub> 15.2, <sup>3</sup> J <sub>HP</sub> = <sup>3</sup> J <sub>HP</sub> = 7.5, 2'-H), 6.29 (1 H, dd, <sup>3</sup> J <sub>HH trans</sub> 15.8, <sup>4</sup> J <sub>HP</sub> 4.5, 3-H)	16.3 (d, <i>J</i> 6.0), 21.8 (s), 26.0 (s), 28.3 (s), 31.6 (d, <i>J</i> 139.4), 37.7 (s), 61.9 (d, <i>J</i> 6.9), 114.6 (s), 126.2 (d, <i>J</i> 11.9), 132.7 (d, <i>J</i> 14.9), 133.3 (s), 135.8 (s), 149.8 (s), 198.6 (s)	26.2	1252 1547 1667	312 (M <sup>+</sup> , 5%), 175 (32), 174 (100), 152 (54), 125 (81), 97 (41)	C <sub>14</sub> H <sub>23</sub> O <sub>4</sub> P C, 58.73 C, 58.30 H, 8.10 H, 8.13	
c	1, H, C <sub>3</sub> H <sub>5</sub> , H	45 <sup>d</sup>	1.90 (2 H, t, <sup>3</sup> J <sub>HH</sub> 6.4, 9.5, 5'-H <sub>2</sub> ), 2.44 (2 H, dd, <sup>3</sup> J <sub>HH</sub> 6.0, 9.2, 6'-H <sub>2</sub> ), 2.68 (2 H, dd, <sup>2</sup> J <sub>HP</sub> 22.8, <sup>3</sup> J <sub>HH</sub> 7.4, 1-H <sub>2</sub> ), 3.10 (2 H, d, <sup>3</sup> J <sub>HH</sub> 5.7, 1'-H <sub>2</sub> ), 4.81-4.87 (2 H, m, 3'-H <sub>2</sub> ), 5.74 (1 H, ddt, <sup>3</sup> J <sub>HH trans</sub> 12.7, <sup>3</sup> J <sub>HH cis</sub> 2.4, <sup>3</sup> J <sub>HH</sub> 7.4, 2'-H), 6.03 (1 H, dq, <sup>3</sup> J <sub>HH trans</sub> 15.3, <sup>3</sup> J <sub>HP</sub> = <sup>3</sup> J <sub>HP</sub> = 7.6, 2'-H), 6.59 (1 H, dd, <sup>3</sup> J <sub>HH trans</sub> 15.6, <sup>4</sup> J <sub>HP</sub> 4.7, 3-H)	13.1 (d, <i>J</i> 2.3), 16.1 (d, <i>J</i> 6.1), 20.4 (s), 22.3 (s), 26.4 (s), 27.1 (d, <i>J</i> 140.0), 37.1 (s), 61.8 (d, <i>J</i> 6.9), 121.0 (d, <i>J</i> 11.2), 124.3 (d, <i>J</i> 2.6), 144.3 (d, <i>J</i> 14.5), 158.5 (d, <i>J</i> 4.0), 200.1 (s)	26.8	1255 1548 1670	300 (M <sup>+</sup> , 28%), 163 (100), 152 (98), 125 (98), 97 (29), 81 (23), 65 (18)	C <sub>15</sub> H <sub>25</sub> O <sub>4</sub> P C, 59.99 C, 60.13 H, 8.39 H, 8.18	
d	1, H, H, Et	58 <sup>d</sup>	0.86 (3 H, t, <sup>3</sup> J <sub>HH</sub> 7.5, 5'-H <sub>3</sub> ), 1.87 (2 H, t, <sup>3</sup> J <sub>HH</sub> 6.3, 9.5, 5'-H <sub>2</sub> ), 2.15-2.26 (4 H, m, 4'-H <sub>2</sub> , 4-H <sub>2</sub> ), 2.34 (2 H, dd, <sup>3</sup> J <sub>HH</sub> 6.0, 9.4, 6'-H <sub>2</sub> ), 2.60 (2 H, dd, <sup>2</sup> J <sub>HP</sub> 23.2, <sup>3</sup> J <sub>HH</sub> 8.1, 1-H <sub>2</sub> ), 2.76 (1 H, q, <sup>3</sup> J <sub>HH</sub> = <sup>3</sup> J <sub>HP</sub> = 7.9, 2'-H), 5.93 (1 H, s, 2'-H)	16.2 (d, <i>J</i> 5.5), 26.8 (s), 31.2 (d, <i>J</i> 139.4), 34.5 (s), 62.0 (d, <i>J</i> 6.5), 128.4 (d, <i>J</i> 12.0), 130.0 (d, <i>J</i> 2.8), 130.6 (d, <i>J</i> 14.4), 171.0 (d, <i>J</i> 4.3), 209.1 (s)	25.7	1252 1582 1713	258 (M <sup>+</sup> , 63%), 202 (18), 125 (23), 121 (74), 109 (64), 91 (75), 81 (76), 65 (50), 29 (100)	C <sub>17</sub> H <sub>19</sub> O <sub>4</sub> P C, 55.81 C, 55.20 H, 7.42 H, 7.39	
e	0, H, H, H	45 <sup>d</sup>	2.42 (2 H, dd, <sup>3</sup> J <sub>HH</sub> 2.8, 3.7, 4'-H <sub>2</sub> ), 2.70 (2 H, m, 5'-H <sub>2</sub> ), 2.74 (2 H, ddd, <sup>2</sup> J <sub>HP</sub> 23.0, <sup>3</sup> J <sub>HH</sub> 7.7, <sup>4</sup> J <sub>HP</sub> 1.2, 1'-H <sub>2</sub> ), 5.98 (1 H, s, 2'-H), 6.20 (1 H, dq, <sup>3</sup> J <sub>HH trans</sub> 15.5, <sup>3</sup> J <sub>HP</sub> = <sup>3</sup> J <sub>HP</sub> = 7.9, 2'-H), 6.63 (1 H, dd, <sup>3</sup> J <sub>HH trans</sub> 15.5, <sup>4</sup> J <sub>HP</sub> 4.9, 3-H)	8.0 (s), 16.4 (d, <i>J</i> 5.6), 25.2 (s), 31.6 (d, <i>J</i> 139.3), 33.5 (s), 62.1 (d, <i>J</i> 6.9), 126.7 (d, <i>J</i> 12.5), 127.8 (d, <i>J</i> 14.6), 150.1 (s), 162.5 (s), 199.0 (s)	26.0	1253 1642 1707	272 (M <sup>+</sup> , 100%), 135 (98), 134 (99), 125 (91), 91 (78), 81 (85), 29 (91)	C <sub>15</sub> H <sub>25</sub> O <sub>4</sub> P C, 57.35 C, 56.65 H, 7.77 H, 8.06	
f	0, H, Me, H	60 <sup>c</sup>	1.77 (3 H, s, 2'-Me), 2.41 (2 H, dd, <sup>3</sup> J <sub>HH</sub> 2.2, 4.2, 4'-H <sub>2</sub> ), 2.62 (2 H, m, 5'-H <sub>2</sub> ), 2.78 (2 H, dd, <sup>2</sup> J <sub>HP</sub> 23.1, <sup>3</sup> J <sub>HH</sub> 7.7, 1-H <sub>2</sub> ), 6.17 (1 H, dq, <sup>3</sup> J <sub>HH trans</sub> 15.4, <sup>3</sup> J <sub>HP</sub> = <sup>3</sup> J <sub>HP</sub> = 7.8, 2'-H), 6.72 (1 H, dd, <sup>3</sup> J <sub>HH trans</sub> 15.6, <sup>4</sup> J <sub>HP</sub> 4.8, 3-H)	13.3 (s), 16.3 (d, <i>J</i> 4.9), 21.7 (s), 27.2 (d, <i>J</i> 140.2), 27.6 (s), 34.7 (s), 62.0 (d, <i>J</i> 6.1), 123.3 (d, <i>J</i> 11.6), 127.7 (s), 141.5 (s), 150.1 (s), 209.5 (s)	26.4	1253 1578 1695	286 (M <sup>+</sup> , 36%), 149 (100), 148 (60), 91 (37), 29 (39)	C <sub>14</sub> H <sub>23</sub> O <sub>4</sub> P C, 58.73 C, 57.73 H, 8.10 H, 8.77	
g	0, H, H, Et	45 <sup>d</sup>	1.04 (3 H, t, <sup>3</sup> J <sub>HH</sub> 7.6, 5'-Me), 2.34-2.46 (4 H, m, 4'-H <sub>2</sub> , 4-H <sub>2</sub> ), 2.72-2.82 (2 H, m, 5'-H <sub>2</sub> ), 2.77 (2 H, dd, <sup>2</sup> J <sub>HP</sub> = 23.5, <sup>3</sup> J <sub>HH</sub> 8.1, 1-H <sub>2</sub> ), 6.05 (1 H, q, <sup>3</sup> J <sub>HH</sub> = <sup>3</sup> J <sub>HP</sub> = 8.0, 2-H), 6.11 (1 H, s, 2'-H)						

<sup>a</sup> For the sake of clarity, the <sup>1</sup>H NMR signals of the POEt ester groups are not included. In all cases those groups gave rise to the following signals: 1.16-1.31 (6 H, t, <sup>3</sup>J<sub>HH</sub> 7.0-7.1, 2 × Me of POEt), 3.96-4.13 (4 H, dq, <sup>3</sup>J<sub>HP</sub> *ca.* 11, <sup>3</sup>J<sub>HH</sub> *ca.* 7, 2 × CH<sub>2</sub> of POEt). <sup>b</sup> Purified by column chromatography (benzene-acetone, 1:1, v/v). <sup>c</sup> The same product was also obtained from 3-chlorocyclohex-2-enone (65%). <sup>d</sup> Purified by column chromatography (CHCl<sub>3</sub>-acetone, 4:1). <sup>e</sup> Purified by column chromatography (AcOEt-CHCl<sub>3</sub>, 2:1).

atom (addition–elimination) operates also for the 3-chloro substituted enones.

In addition to their potential as precursors for cyclic enones substituted at position 3 with an unsaturated chain,<sup>8</sup> phosphonates **4** ( $n = 1$ ) could be easily converted into the corresponding aromatic derivatives. As reported before for similar systems,<sup>9</sup> treatment of the ketophosphonates **4a–4d** with iodine in methanol<sup>10</sup> led to the formation of new 3-substituted anisole derivatives **5** in moderate yields (Scheme 4).



Scheme 4 Reagents:  $I_2$ , MeOH

As with compounds **4**, products **5** can be lithiated at the allylic carbon and used in the olefination reactions that should lead to aromatic derivatives substituted with an unsaturated chain and functionalised additionally in the *meta* position. Application of products **4** and **5** in further syntheses is currently being studied in our laboratory.

## Experimental

Solvents and commercially available substrates were purified by conventional methods. Reactions with lithiated reagents were performed under dry nitrogen. Merck Kieselgel 60 (0.063–0.200) was used for column chromatography. Mass spectra were recorded on a Varian MAT-212 double-focusing direct-inlet spectrometer at an ionisation potential of 70 eV. IR spectra were recorded on a Bomen Inc. Michelson 100 spectrometer in  $CCl_4$ . NMR spectra were recorded on a Bruker AC300 spectrometer in  $CDCl_3$ , and the chemical shift values ( $\delta$ ) are given in ppm relative to the solvent ( $^1H$ ,  $\delta$  7.24;  $^{13}C$ ,  $\delta$  77.0).  $^{31}P$  NMR chemical shifts are given relative to 85%  $H_3PO_4$  as external standard. For structural assignments, both  $^1H$ -decoupled and  $^1H$ -coupled  $^{13}C$  NMR spectra were recorded.  $J$  Values are given in Hz. Elemental analyses (C/H) were performed at the Chemistry Department, University of Cape Town.

3-Methoxycycloalkenones **1a**, **1c**, **1d** and **1e**, and 3-chlorocyclohex-2-en-1-one were prepared as described before.<sup>4</sup> 3-Methoxy-5-methylcyclohex-2-en-1-one **1b**,<sup>11</sup> diethyl prop-2-enylphosphonate **2a**<sup>12</sup> and diethyl pent-2-enylphosphonate **2b**<sup>13</sup> were prepared according to the literature procedures.

### General procedure for the reaction of 3-methoxycycloalk-2-en-1-ones **1** with lithiated diethyl alkenylphosphonates **2**

To a stirred solution of butyllithium (1.6 mol  $dm^{-3}$  solution in hexane, 1.5 equiv.) in diethyl ether (2  $cm^3$  per mmol of BuLi) was added a solution of a phosphonate **2** (1 mol equiv.) in diethyl ether (0.2  $cm^3$  per mmol of **2**) dropwise at  $-78^\circ C$ . The mixture was stirred at  $-78^\circ C$  for 1 h, and a solution of cycloalkenone **1** (1 equiv.) in diethyl ether (0.2  $cm^3$  per mmol of **1**) was added dropwise at the same temperature. After stirring at  $-78^\circ C$  for 1 h, the mixture was allowed to warm to room temperature and stirred for another 2 h. Aqueous 10% HCl was added, the mixture was extracted with  $CHCl_3$ , the chloroform extract was washed with brine and with water, dried ( $Na_2SO_4$ ) and the solvent evaporated under reduced pressure.  $^{31}P$  NMR spectra of the crude product showed the disappearance of **2** and the formation of a single phosphorus-containing product which was purified by column chromatography.

### Diethyl 3-(3'-oxocyclohexenyl)prop-1-enylphosphonate **3**

During the preparation of **4a**, column chromatography yielded

a separate vinylic phosphonate **3** in pure form (5.3%); the product was identified by NMR spectroscopy:  $\delta_H$  1.27 (6 H, t,  $J_{HH}$  7.0, 2  $\times$  Me of POEt), 1.50 (1 H, m, 4'-CH), 1.68 (2 H, m, 5'-CH<sub>2</sub>), 1.85 (1 H, m, 4'-CH), 2.24 (2 H, m, 6'-CH<sub>2</sub>), 2.44 (2 H, d,  $J_{HH}$  7.2, 3-CH<sub>2</sub>), 4.02 (4 H, m, 2  $\times$  CH<sub>2</sub> of POEt), 5.67 (1 H, dd,  $J_{HP}$  21.1,  $J_{HH}$  17.0, 1-CH), 5.73 (1 H, s, 2'-CH), 5.76 (1 H, ddt,  $J_{HH}$  12.1, 17.0,  $J_{HP}$ , 2.7, 2-CH);  $\delta_C$  16.3 (d,  $J_{CP}$  6.3, 2  $\times$  Me of POEt), 19.7 (s, 5'-C), 32.8, 34.5 (two s, 4'-C, 6'-C), 46.7 (d,  $J_{CP}$  21.5, 3-C), 61.7 (d,  $J_{CP}$  5.8, 2  $\times$  CH<sub>2</sub> of POEt), 120.6 (d,  $J_{CP}$  186.5, 1-C), 129.0 (s, 2'-C), 136.7 (s, 3'-C), 148.4 (d,  $J_{CP}$  5.4, 2-C), 200.0 (s, CO);  $\delta_P$  18.2. When left at room temperature for a few days, the product changed gradually into **4a** (see Table 1).

### General procedure for the reaction of phosphonates **4** with iodine in methanol

A solution of phosphonate **4** (1 equiv.) and iodine (2 equiv.) in methanol (8  $cm^3$  per mmol of **4**) was heated under reflux for 90 min. The solvent was evaporated under reduced pressure, chloroform (30  $cm^3$  per mmol of **4**) was added, and the chloroform solution was washed with saturated aqueous  $NaHCO_3$  (2  $\times$  10  $cm^3$ ), saturated aqueous  $Na_2S_2O_3$  (2  $\times$  10  $cm^3$ ), 5% aqueous NaOH (2  $\times$  10  $cm^3$ ) and water (2  $\times$  10  $cm^3$  per mmol of **4**). After drying ( $Na_2SO_4$ ) and evaporation of the solvent under reduced pressure, crude products were purified by column chromatography using  $CHCl_3$ –AcOEt (3:1, v/v) as eluting solvent.

### Diethyl 3-(3'-methoxyphenyl)prop-2-enylphosphonate **5a**

Yield 55%;  $m/z$  284 ( $M^+$ , 72%), 256 (11), 147 (100), 146 (64);  $\delta_H$  1.30 (6 H, t,  $J_{HH}$  7.1, 2  $\times$  Me of POEt), 2.74 (2 H, dd,  $J_{HP}$  22.2,  $J_{HH}$  7.6, 1-CH<sub>2</sub>), 3.79 (3 H, s, OMe), 4.10 (4 H, dq,  $J_{HP}$  11.1,  $J_{HH}$  7.1, 2  $\times$  CH<sub>2</sub> of POEt), 6.14 (1 H, dt,  $J_{HH}$  15.3, 7.3, 2-H), 6.48 (1 H, dd,  $J_{HH}$  15.8, 5.1, 3-H), 6.77 (1 H, d,  $J_{HH}$  7.2, 6'-H), 6.87 (1 H, s, 2'-H), 6.90 (1 H, d,  $J_{HH}$  7.6, 4'-H), 7.20 (1 H, t,  $J_{HH}$  7.9, 5'-H);  $\delta_C$  16.5 (d,  $J_{CP}$  6.0, 2  $\times$  Me of POEt), 31.1 (d,  $J_{CP}$  139.8, 1-C), 55.2 (s, OMe), 62.1 (d,  $J_{CP}$  6.8, 2  $\times$  CH<sub>2</sub> of POEt), 111.6 (s, 6'-C), 113.2 (s, 2'-C), 118.9 (s, 4'-C), 119.1 (d,  $J_{CP}$  11.9, 3-C), 129.5 (s, 5'-C), 134.6 (d,  $J_{CP}$  14.8, 2-C), 135.7 (s, 1'-C), 139.5 (s, 3'-C);  $\delta_P$  27.4 (Calc. for  $C_{14}H_{21}O_4P$ : C, 59.15; H, 7.45. Found: C, 58.60; H, 7.40%).

### Diethyl 3-(3'-methoxy-5'-methylphenyl)prop-2-enylphosphonate **5b**

Yield 60%;  $m/z$  298 ( $M^+$ , 94%), 161 (100), 160 (73);  $\delta_H$  1.30 (6 H, t,  $J_{HH}$  7.1, 2  $\times$  Me of POEt), 2.29 (3 H, s, 5'-Me), 2.73 (2 H, dd,  $J_{HP}$  22.1,  $J_{HH}$  7.4, 1-CH<sub>2</sub>), 3.77 (3 H, s, OMe), 4.09 (4 H, dq,  $J_{HP}$  11.0,  $J_{HH}$  7.3, 2  $\times$  CH<sub>2</sub> of POEt), 6.12 (1 H, dt,  $J_{HP}$  15.2,  $J_{HH}$  7.4, 2-H), 6.44 (1 H, dd,  $J_{HH}$  15.6, 5.0, 3-H), 6.59 (1 H, s, 6'-H), 6.68 (1 H, s, 4'-H), 6.76 (1 H, s, 2'-H);  $\delta_C$  16.4 (d,  $J_{CP}$  6.0, 2  $\times$  Me of POEt), 31.0 (d,  $J_{CP}$  139.9, 1-C), 43.3 (s, 5'-Me), 55.2 (s, OMe), 62.0 (d,  $J_{CP}$  6.6, 2  $\times$  CH<sub>2</sub> of POEt), 108.6 (s, 6'-C), 114.1 (s, 4'-C), 118.9 (d,  $J_{CP}$  11.6, 3-C), 119.8 (s, 2'-C), 134.7 (d,  $J_{CP}$  14.8, 2-C), 135.7 (s, 5'-C), 137.9 (s, 1'-C), 139.5 (s, 3'-C);  $\delta_P$  27.5 (Calc. for  $C_{15}H_{23}O_4P$ : C, 60.39; H, 7.77. Found: C, 59.90; H, 7.80%).

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