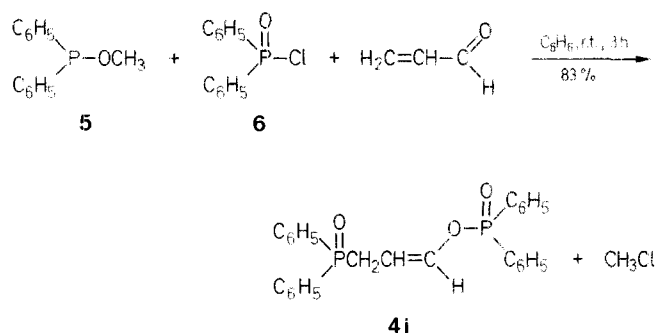
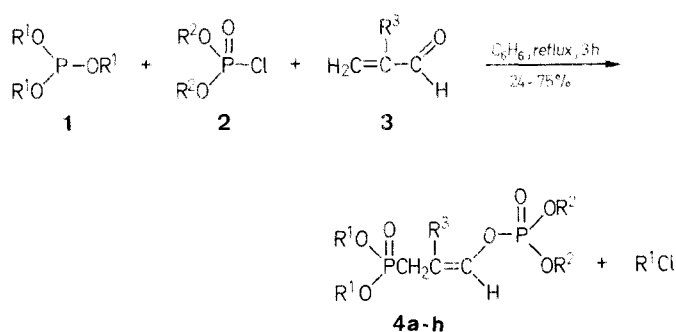


phosphine oxide (**4i**) can be expected to be interesting bifunctional intermediates for organic synthesis. Enol phosphates have been widely used as an intermediates for the synthesis of alkyl or alkenyl-substituted olefins<sup>1</sup>, vinylsilanes<sup>2</sup>, allylsilanes<sup>3</sup>, allenes<sup>4</sup>, and optically active secondary alcohols<sup>5</sup>. Dialkyl 2-propenephosphonate has been also utilized successfully in olefination<sup>6</sup> and olefin synthesis by reductive C—P bond cleavage followed by  $\alpha$ -alkylation<sup>7</sup>.

Recently, we described the synthesis of dialkyl 2-(alkoxyphosphinyloxy)alkanephosphonates by the reaction of a mixed reagent of trialkyl phosphite and dialkyl phosphorochloridate with several epoxides in the presence of zinc iodide as a catalyst<sup>8</sup>.

In this paper, we reported the synthesis of **4** by the mixed reagent of trivalent phosphorus oxo acid ester (soft nucleophile) (**1**) and pentavalent phosphorus oxo acid chloride (hard electrophile) (**2**) with several  $\alpha,\beta$ -unsaturated aldehydes (**3**). No product could be obtained from 3-substituted  $\alpha,\beta$ -unsaturated aldehydes or  $\alpha,\beta$ -unsaturated ketones.



### Synthesis of Dialkyl 3-(Dialkylphosphinyloxy)-2-alkenephosphonate and Diphenyl-[3-(diphenylphosphinyloxy)-2-propenyl]phosphine Oxide

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Dialkyl 3-(dialkoxyposphinyloxy)-2-alkenephosphonates and diphenyl-[3-(diphenylphosphinyloxy)-2-propenyl]phosphine oxide were prepared by the reaction of the mixed reagent of trivalent phosphorus oxo acid ester and pentavalent phosphorus oxo acid chloride with several  $\alpha,\beta$ -unsaturated aldehyde.

Dialkyl 3-(dialkoxyposphinyloxy)-2-alkenephosphonates (**4a-h**) and diphenyl-[3-(diphenylphosphinyloxy)alkenyl]

### Dialkyl 3-(dialkoxyposphinyloxy)-2-alkenephosphonate (**4a-h**); General Procedure:

To an equimolar mixture of dialkyl phosphorochloridate (**2**; 20 mmol) and trialkyl phosphite (**1**; 20 mmol) in benzene (20 ml),  $\alpha,\beta$ -unsaturated aldehyde (**3**; 20 mmol) is added with protection from atmospheric moisture during 20 min at ambient temperature. The reaction mixture is heated to reflux and stirred for 3 h. The solvent is then removed and the residue distilled under reduced pressure (Table).

### Diphenyl-[3-(diphenylphosphinyloxy)-2-propenyl]phosphine Oxide (**4i**):

To an equimolar mixture of methyl diphenylphosphinite (**5**; 4.25 g, 20 mmol) and diphenylphosphinyl chloride (**6**; 4.32 g, 20 mmol) in benzene (20 ml), 2-propenal (1.12 g, 20 mmol) is added dropwise during 20 min under nitrogen at ambient temperature. The product begins to precipitate. After stirring for 3 h, the precipitate is filtered and recrystallization from benzene gives pure **4i**; yield: 7.6 g (83%); m.p. 216–217°C.

$\text{C}_{27}\text{H}_{24}\text{P}_2\text{O}_3$  calc. C 70.74 H 5.28 P 13.51  
(458.4) found 70.51 5.02 13.28

**Table.** Dialkyl 3-(Dialkoxyphosphinyloxy)-2-propenephosphonates **4a–h**

Prod- uct	R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	Yield [%]	b. p. [°C]/torr	Molecular Formula <sup>a</sup>	<sup>1</sup> H-NMR (CDCl <sub>3</sub> /TMS) <sup>b</sup> δ [ppm]
<b>a</b>	CH <sub>3</sub>	C <sub>2</sub> H <sub>5</sub>	H	75	155–158°/0.1	C <sub>9</sub> H <sub>20</sub> P <sub>2</sub> O <sub>7</sub> (302.2)	1.36 (t, 6H, <i>J</i> = 7.1 Hz); 2.71 (ddd, 2H, <i>J</i> = 21.7 Hz, 7.8 Hz, 0.7 Hz); 3.75 (d, 6H, <i>J</i> = 11.0 Hz); 4.18 (quint, 4H, <i>J</i> = 7.1 Hz); 4.96 (tdd, 1H, <i>J</i> = 11.0 Hz, 7.8 Hz, 2.2 Hz); 6.60 (tdd, 1H, <i>J</i> = 12.0 Hz, 11.0 Hz, 0.7 Hz)
<b>b</b>	CH <sub>3</sub>	C <sub>6</sub> H <sub>5</sub>	H	61	156–165°/0.01	C <sub>17</sub> H <sub>20</sub> P <sub>2</sub> O <sub>7</sub> (398.3)	2.70 (ddd, 2H, <i>J</i> = 22.0 Hz, 7.7 Hz, 1.0 Hz); 3.88 (d, 6H, <i>J</i> = 11.6 Hz); 5.10–5.20 (m, 1H); 6.81–6.83 (m, 1H); 7.19–7.32 (m, 10H)
<b>c</b>	C <sub>2</sub> H <sub>5</sub>	CH <sub>3</sub>	H	72	153–155°/0.1	C <sub>9</sub> H <sub>20</sub> P <sub>2</sub> O <sub>7</sub> (302.2)	1.33 (t, 6H, <i>J</i> = 7.0 Hz); 2.71 (ddd, 2H, <i>J</i> = 22.0 Hz, 7.8 Hz, 0.7 Hz); 3.83 (d, 6H, <i>J</i> = 11.4 Hz); 4.11 (td, 4H, <i>J</i> = 7.0 Hz, 8.1 Hz); 4.98 (tdd, 1H, <i>J</i> = 12.0 Hz, 7.8 Hz, 2.2 Hz); 6.58 (tdd, 1H, <i>J</i> = 12.0 Hz, 11.0 Hz, 0.7 Hz)
<b>d</b>	C <sub>2</sub> H <sub>5</sub>	C <sub>2</sub> H <sub>5</sub>	H	61	120–122°/0.01	C <sub>11</sub> H <sub>24</sub> P <sub>2</sub> O <sub>7</sub> (330.3)	1.33 (t, 6H, <i>J</i> = 7.0 Hz); 1.37 (t, 6H, <i>J</i> = 7.0 Hz); 2.70 (ddd, 2H, <i>J</i> = 21.8 Hz, 7.8 Hz, 0.7 Hz); 4.11 (td, 8H, <i>J</i> = 7.0 Hz, 8.1 Hz); 4.95 (tdd, 1H, <i>J</i> = 12.0 Hz, 7.8 Hz, 2.2 Hz); 6.58 (tdd, 1H, <i>J</i> = 12.0 Hz, 11.0 Hz, 0.7 Hz)
<b>e</b>	C <sub>2</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>	H	42	160–167°/0.01	C <sub>19</sub> H <sub>24</sub> P <sub>2</sub> O <sub>7</sub> (426.35)	1.27 (t, 6H, <i>J</i> = 7.5 Hz); 2.64 (ddd, 2H, <i>J</i> = 22.0 Hz, 7.8 Hz, 1.0 Hz); 4.07 (quint, 4H, <i>J</i> = 7.5 Hz); 4.92–5.22 (m, 1H); 6.55–6.75 (m, 1H); 7.19–7.40 (m, 10H)
<b>f</b>	C <sub>2</sub> H <sub>5</sub>	CH <sub>3</sub>	CH <sub>3</sub>	54	142–145°/0.5	C <sub>10</sub> H <sub>22</sub> P <sub>2</sub> O <sub>7</sub> (316.2)	1.33 (t, 6H, <i>J</i> = 7.4 Hz); 1.78 (d, 3H, <i>J</i> = 1.3 Hz); 2.71 (d, 2H, <i>J</i> = 22.7 Hz); 3.82 (d, 6H, <i>J</i> = 11.3 Hz); 4.12 (quint, 4H, <i>J</i> = 7.4 Hz); 6.42 (m, 1H)
<b>g</b>	C <sub>2</sub> H <sub>5</sub>	C <sub>2</sub> H <sub>5</sub>	CH <sub>3</sub>	68	157–160°/0.1	C <sub>12</sub> H <sub>26</sub> P <sub>2</sub> O <sub>7</sub> (344.3)	1.33 (t, 12H, <i>J</i> = 7.2 Hz); 1.77 (d, 3H, <i>J</i> = 1.2 Hz); 2.70 (d, 2H, <i>J</i> = 22.5 Hz); 4.17 (quint, 8H, <i>J</i> = 7.2 Hz); 6.42 (m, 1H)
<b>h</b>	(CH <sub>3</sub> ) <sub>2</sub> CH	C <sub>2</sub> H <sub>5</sub>	H	24	123–126°/0.01	C <sub>13</sub> H <sub>28</sub> P <sub>2</sub> O <sub>7</sub> (358.3)	1.32 (d, 12H, <i>J</i> = 6.2 Hz); 1.36 (t, 6H, <i>J</i> = 7.1 Hz); 2.66 (ddd, 2H, <i>J</i> = 21.6 Hz, 7.7 Hz, 0.7 Hz); 4.18 (quint, 4H, <i>J</i> = 7.1 Hz); 4.70 (dd, 1H, <i>J</i> = 7.9 Hz, 6.2 Hz); 4.94 (tdd, 1H, <i>J</i> = 12.9 Hz, 7.7 Hz, 2.5 Hz); 6.58 (tdd, 1H, <i>J</i> = 12.9 Hz, 11.0 Hz, 0.7 Hz)

<sup>a</sup> Satisfactory microanalysis obtained: C ± 0.29, H ± 0.27, P ± 0.29.<sup>b</sup> Recorded on a Bruker WM 360 NMR spectrometer.<sup>1</sup>H-NMR (CDCl<sub>3</sub>/TMS): δ = 2.98 (dd, 2H, *J* = 13.8 Hz, 8 Hz); 5.53–5.59 (m, 1H); 6.45–6.55 (m, 1H); 7.29–7.75 ppm (m, 20H).Received: October 10, 1985  
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