Conjugate Addition of Organocuprates to Diethyl Vinylphosphonate

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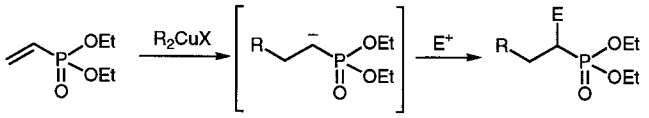
The reaction of organocuprate reagents with diethyl vinylphosphonate affords the conjugate addition product. The intermediate α-metalloalkylphosphonate can be quenched with electrophiles to afford α-substituted alkylphosphonates.

Alkylphosphonates are useful as Wadsworth–Emmons precursors to alkenes,[1] and also due to their various biological properties.[2,3]

We envisioned a flexible synthetic route to substituted phosphonates involving conjugate addition of an organocuprate to an alkenylphosphonate followed by an electrophilic quench. Herein we report the success of this approach.



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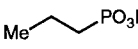
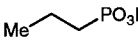
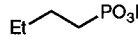
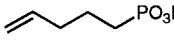
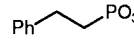
Whilst the conjugate addition of organocuprates to α,β-unsaturated carbonyl compounds has received a great deal of attention,[4] little is known about conjugate addition to alkenylphosphonates.[5]

We have found that under suitable conditions, standard cuprates will function as suitable nucleophiles, and that the intermediate phosphorus-stabilised anion can be trapped with reactive electrophiles.

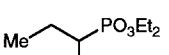
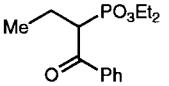
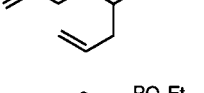
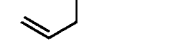
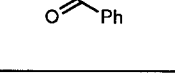
Preliminary experiments involved the treatment of diethyl vinylphosphonate (**1**)[6] with an organocuprate, followed by a quench with saturated ammonium chloride/ammonia solution (E = H). As indicated in Table 1, the reaction proceeds well for cuprates derived from copper bromide–dimethyl sulfide complex and either an alkyllithium or Grignard reagent. Copper iodide was also employed as a precursor to the cuprate reagents, but afforded slightly lower yields in the subsequent conjugate addition reactions (64% yield when using Me_2CuLi).

Table 1. Addition of cuprates to diethylvinylphosphonate **1**

Cuprate	Product		Yield (%)
$Me_2CuLi.Me_2S$		(4)	89
$Me_2CuLi.LiI$		(4)	64
$Et_2CuMgI.Me_2S$		(5)	89
$(allyl)_2CuMgBr.Me_2S$		(6)	72
$Ph_2CuMgBr.Me_2S$		(7)	83

Using the same protocol for the conjugate addition reactions, the assumed intermediate phosphorus-stabilised anionic intermediate **2** could be trapped with other electrophiles, as indicated in Table 2. Fairly reactive electrophiles such as allyl bromide and benzoyl chloride were found to most suitable. Whilst the trapping could be achieved with methyl iodide, the yields were not reproducible. Under similar conditions, benzaldehyde, benzyl bromide, *N*-bromosuccinimide, ethyl chloroformate and 2,4,6-triisopropylbenzenesulfonyl azide were found to be unreactive as electrophiles.

Table 2. Addition to diethylvinylphosphonate **1** and electrophilic quench

Cuprate	Electrophile	Product		Yield (%)
$Me_2CuLi.Me_2S$	AllylBr		(8)	84
$Me_2CuLi.Me_2S$	PhCOCl		(9)	92
$(Allyl)_2CuMgBr.Me_2S$	AllylBr		(10)	93
$Ph_2CuMgBr.Me_2S$	AllylBr		(11)	64
$Ph_2CuMgBr.Me_2S$	PhCOCl		(12)	47

α-Methyl- and β-methyl-substituted diethyl vinylphosphonate did not undergo conjugate addition reactions under similar conditions, possibly for steric reasons.

In summary, this methodology affords a rapid entry into a variety of functionalised phosphonates in a one-pot process from commercially available diethyl vinylphosphonate.

All NMR spectra recorded on a Bruker WH 400 spectrometer at 400 MHz for ^1H, 100.6 MHz for ^{13}C and 161.98 MHz for ^{31}P NMR. All samples run in $CDCl_3$ with TMS as internal standard for ^1H and ^{13}C and H_3PO_4 for ^{31}P. Mass spectra determined with a Kratos MS 80 spectrometer at 70 eV. IR spectra recorded on a Nicolet 205 FT-IR spectrometer. Et_2O was freshly distilled from sodium benzophenone ketal. Commercially available reagents and compounds were purchased from the Aldrich chemical company. All the reactions were carried out under an inert atmosphere of N_2 and in oven dried glassware.

Preparation of $Me_2CuLi \cdot LiI$ (Cuprate A):
$Me_2CuLi \cdot LiI$ was prepared by the method of Piers and Keziere.[7] Thus CuI (1.16 g, 6 mmol) in Et_2O (30 mL) was cooled to −78 °C and 1.5 M MeLi in Et_2O (12 mmol) was added dropwise, maintaining the temperature at −78 °C (reaction underwent a colour change from yellow to clear indicating the cuprate formation). The cuprate solution was used immediately.

Preparation of $R_2CuBr \cdot Me_2S$ (Cuprate B):
Me_2SCuBr[8] (500 mg, 2.43 mmol) in Et_2O (30 mL was cooled to −5 °C and the alkyllithium (5.6 mmol) was added dropwise, maintaining the temperature below 0 °C (reaction underwent a colour change from yellow to clear indicating the cuprate formation). The cuprate solution was used immediately.

Preparation of $R_2CuMgBr \cdot Me_2S$ (Cuprate C):
Me_2SCuBr (532 mg, 2.6 mmol) in Et_2O (30 mL) was cooled to −78 °C and the Grignard reagent (2.4 mmol) (either preformed or purchased from Aldrich) was added dropwise, maintaining the temperature at −78 °C. The cuprate solution was used immediately.

Diethyl Propylphosphonate (4); Typical Procedure:
Diethyl vinylphosphonate (**1**, 200 mg, 1.2 mmol) in Et_2O (5 mL) was added to cuprate B [formed at −5 °C with 1.5 M MeLi in Et_2O (3.25 mL, 4.87 mmol)] at −5 °C. The reaction mixture was allowed to warm to r.t. (20 min). The reaction was quenched with NH_4Cl/NH_3 solution (pH 8, 10 mL) and the Et_2O layer separated and washed with water (20 mL), brine (20 mL), dried ($MgSO_4$) and evaporated to yield **4** as a colourless oil; yield: 213 mg, (89 %).

Diethyl Butylphosphonate (5); Typical Procedure:
Diethyl vinylphosphonate (**1**, 200 mg, 1.2 mmol) in Et_2O (5 mL) was added to cuprate C (formed from EtMgI) at −5 °C. The reaction mixture was allowed to warm to r.t. (20 min). The reaction was quenched with NH_4Cl/NH_3 solution (pH 8, 10 mL) and the Et_2O layer separated and washed with water (20 mL), brine (20 mL), dried ($MgSO_4$) and evaporated to yield **5** as a colourless oil; yield: 211 mg, (89 %).

Diethyl (1-Benzoylpropyl)phosphonate (9); Typical Procedure:
Diethyl vinylphosphonate (**1**, 200 mg, 1.2 mmol) in Et_2O (5 mL) was added to cuprate B [formed at −5 °C with 1.5 MeLi in Et_2O (3.25 mL, 4.87 mmol)] at −5 °C. The reaction mixture was allowed to warm to r.t. and was stirred for 120 min before being cooled to −50 °C. Benzoyl chloride (210 mg, 1.5 mmol) was added dropwise and the reaction allowed to warm to r.t. before quenching with NH_4Cl/NH_3 solution (pH 8, 10 mL). The Et_2O layer was separated and washed with water (20 mL), brine (20 mL), dried ($MgSO_4$) and evaporated to yield **9** as a colourless oil; yield: 318 mg, (92 %).

Diethyl (1-Allylpent-4-enyl)phosphonate (10); Typical Procedure:
Diethyl vinylphosphonate (**1**, 200 mg, 1.2 mmol) in Et_2O (5 mL) was added to cuprate C (formed from allyl MgBr) at −78 °C. The reaction mixture was stirred at −78 °C for 20 min and then allowed to warm to r.t. The reaction mixture was then cooled to −78 °C and allyl bromide (360 mg, 2.97 mmol) was added dropwise. The reaction mixture was allowed to warm to r.t. and was stirred for 90 min before quenching with NH_4Cl/NH_3 solution (pH 8, 10 mL). The Et_2O layer was separated and washed with water (20 mL), brine (20 mL), dried ($MgSO_4$) and evaporated to yield **10** as a colourless oil; yield: 279 mg, (93 %).

Diethyl Propylphosphonate **(4)**:
IR (thin film): $\nu = 1024, 1254\ cm^{-1}$.
MS: *m/z* (%) = 180 (M^+, 20), 165 (25), 152 (40), 138 (70), 125 (100), 111 (45), 97 (35).
^1H NMR: $\delta = 0.98$ (dt, 3H, $J = 1.7, 7.2$ Hz, CH_3), 1.28 (t, 6H, $J = 7.1$ Hz, $2 \times CH_3$), 1.58–1.70 (m, 4H, CH_2CH_2), 4.00–4.09 (m, 4H, $2 \times OCH_2$).
^{13}C NMR: $\delta = 15.1$ (d, $J^{31P} = 16.9$ Hz, CH_3), 16.0 (d, $J^{31P} = 4.7$ Hz, CH_2CH_3), 16.3 (d, $J^{31P} = 6.0$ Hz, $2 \times CH_3$), 27.6 (d, $J^{31P} = 140.3$, $CH_2P{=}O$), 61.2 (d, $J^{31P} = 6.9$, $2 \times OCH_2$).
^{31}P NMR: $\delta = 32.98$.
HRMS: *m/z* calc. for $C_7H_{17}O_3P$: 180.0915; found: 180.0920.

Diethyl Butylphosphonate **(5)**:
IR (thin film): $\nu = 1027, 1247\ cm^{-1}$.
MS: *m/z* (%) = 194 (M^+, 10), 165 (40), 152 (90), 138 (50), 125 (80), 111 (70), 97 (70).
^1H NMR: $\delta = 0.89$ (t, 3H, $J = 7.3$ Hz, CH_3), 1.30 (t, 6H, $J = 7.1$ Hz, $2 \times CH_3$), 1.38 (pentet, 2H, $J = 7.4$ Hz, $CH_2CH_2CH_2$), 1.51–1.59 (m, 2H, CH_3CH_2), 1.61–1.77 (m, 2H, $CH_2P{=}O$), 4.02–4.11 (m, 4H, $2 \times OCH_2$).
^{13}C NMR: $\delta = 13.4$ (CH_3), 16.4 (d, $J^{31P} = 6.0$ Hz, $2 \times CH_3$), 23.6 (d, $J^{31P} = 4.7$ Hz, CH_2), 24.3 (d, $J^{31P} = 4.7$ Hz, CH_2), 25.0 (d, $J^{31P} = 140.4$ Hz, $CH_2P{=}O$), 61.2 (d, $J^{31P} = 7.0$ Hz, $2 \times OCH_2$).
^{31}P NMR: $\delta = 33.42$.
HRMS: *m/z* calc. for $C_8H_{19}O_3P$: 194.1072; found: 194.1072.

Diethyl Pent-4-enylphosphonate **(6)**:
IR (thin film): $\nu = 1030, 1242\ cm^{-1}$.
MS: *m/z* (%) = 206 (M^+, 30), 165 (20), 152 (80), 125 (100), 109 (50).
^1H NMR: $\delta = 1.30$ (t, 6H, $J = 7.1$ Hz, $2 \times CH_3$), 1.64–1.76 (m, 4H, CH_2CH_2), 2.11–2.14 (m, 2H, $CH_2P{=}O$), 4.01–4.15 (m, 4H, $2 \times OCH_2$), 4.96–5.04 (m, 2H, $CH_2{=}$), 5.69–5.79 (m, 1H, $CH_2{=}CH{-}$).
^{13}C NMR: $\delta = 16.3$ (d, $J^{31P} = 6.1$ Hz, $2 \times CH_3$), 21.5 (d, $J^{31P} = 4.6$ Hz, CH_2), 24.5 (d, $J^{31P} = 141.0$ Hz, $CH_2P{=}O$), 34.2 (d, $J^{31P} = 16.9$ Hz, CH_2), 61.3 (d, $J^{31P} = 7.0$ Hz, $2 \times OCH_2$), 115.5 ($CH_2{=}CH{-}$), 137.3 ($CH_2{=}CH{-}$).
^{31}P NMR: $\delta = 33.06$.
HRMS: *m/z* calc. for $C_9H_{19}O_3P$: 206.1072; found: 206.1081.

Diethyl (2-Phenylethyl)phosphonate **(7)**:
IR (thin film): $\nu = 1030, 1245\ cm^{-1}$.
MS: *m/z* (%) = 242 (M^+, 50), 180 (40), 154 (50), 138 (100), 111 (90).
^1H NMR: $\delta = 1.31$ (t, 6H, $J = 7.1$ Hz, $2 \times CH_3$), 2.00–2.15 (m, 2H, CH_2), 2.87–2.94 (m, 2H, CH_2CH_2Ph), 4.04–4.12 (m, 4H, $2 \times OCH_2$), 7.1–7.31 (m, 5H, Ar*H*).
^{13}C NMR: $\delta = 16.3$ (d, $J^{31P} = 6.0$ Hz, $2 \times CH_3$), 27.5 (d, $J^{31P} = 139.0$ Hz, $CH_2P{=}O$), 28.4 (d, $J^{31P} = 4.1$ Hz, CH_2), 61.4 (d, $J^{31P} = 7.0$ Hz, $2 \times OCH_2$), 126.2 (ArC). 127.9 (ArC), 128.4 (ArC), 129.3 (ArC), 140.8 (ArC), 140.9 (ArC).
^{31}P NMR: $\delta = 31.52$.
HRMS: *m/z* calc. for $C_{12}H_{19}O_3P$: 242.1072; found: 242.1089.

Diethyl (1-Ethylbut-3-enyl)phosphanate **(8)**:
IR (thin film): $\nu = 1029, 1245\ cm^{-1}$.
MS: *m/z* (%) = 220 (M^+, 40), 205 (35), 191 (40), 179 (60), 138 (90), 123 (30), 111 (100).
^1H NMR: $\delta = 0.97$ (t, 3H, $J = 7.3$ Hz, CH_3), 1.29 (t, 6H, $J = 7.1$ Hz, $2 \times CH_3$), 1.44–1.77 (m, 3H, CH_2CH), 2.17–2.51 (m, 2H, CH_2), 4.02–4.11 (m, 4H, $2 \times OCH_2$), 4.99–5.08 (m, 2H, $CH_2{=}$), 5.73–5.84 (m, 1H, $-CH{=}$).
^{13}C NMR: $\delta = 11.9$ (d, $J^{31P} = 8.8$ Hz, CH_3), 16.3 (d, $J^{31P} = 5.8$ Hz, $2 \times CH_3$), 20.6 (d, $J^{31P} = 3.1$ Hz, CH_2), 32.0 (d, $J^{31P} = 3.0$ Hz, CH_2, 37.0 (d, $J^{31P} = 138.7$ Hz, CH), 61.2 (d, $J^{31P} = 4.5$ Hz, OCH_2), 61.3 (d, $J^{31P} = 4.6$ Hz, OCH_2), 116.5 ($CH_2{=}$), 135.9 (d, $J^{31P} = 12.1$ Hz, $CH_2{=}CH{-}$).
^{31}P NMR: $\delta = 22.84$.
HRMS: *m/z* calc. for $C_{10}H_{21}O_3P$: 220.1228; found: 220.1236.

Diethyl (1-Benzoylpropyl)phosphonate **(9)**:
IR (thin film): $\nu = 1025, 1251, 1681\ cm^{-1}$.
MS: *m/z* (%) = 284 (M^+, 10), 179 (10), 152 (10), 125 (15), 105 (100).
^1H NMR: $\delta = 0.92$ (t, 3H, $J = 6.8$ Hz, CH_3), 1.14 (t, 3H, $J = 7.1$ Hz, CH_3), 1.25 (t, 3H, $J = 7.1$ Hz, CH_3), 1.69–1.95 (m, 1H, $CHP{=}O$), 1.98–2.05 (m, 1H, HC*H*), 2.18–2.28 (m, 1H, *H*CH), 4.00–4.15 (m, 4H, $2 \times OCH_2$), 7.43–7.98 (m, 5H, Ar*H*).
^{13}C NMR: $\delta = 13.0$ (d, $J^{31P} = 15.4$ Hz, CH_3), 16.0 (d, $J^{31P} = 6.2$ Hz, CH_3), 16.2 (d, $J^{31P} = 5.8$ Hz, CH_3), 21.1 (d, $J^{31P} = 5.1$ Hz, CH_2), 48.9 (d, $J^{31P} = 128.2$ Hz, $CHP{=}O$), 62.3 (d, $J^{31P} = 6.6$ Hz, OCH_2), 62.6 (d, $J^{31P} = 6.6$ Hz, OCH_2), 128.4 (ArC), 128.5

(2 × ArC), 133.1 (2 × ArC), 137.8 (ArC), 196.3 (d, J^{31P} = 4.8 Hz, *C*=O).

^{31}P NMR: δ = 23.12.

HRMS: *m/z* calc. for $C_{14}H_{21}O_4P$: 284.1177; found: 284.1179.

Diethyl (1-Allylpent-4-enyl)phosphonate **(10)**:

IR (thin film): ν = 1027, 1248 cm^{-1}.

MS: *m/z* (%) = 246 (M^+, 15), 245 (30), 205 (50), 192 (45), 138 (100), 111 (70).

^{1}H NMR: δ = 1.31 (t, 6H, *J* = 7.1 Hz, 2 × C*H*$_3$), 1.53–1.88 (m, 4H, C*H*$_2$C*H*$_2$), 2.15–2.19 (m, 2H, C*H*$_2$), 2.41–2.74 (m, 1H, C*H*), 4.06–4.13 (m, 4H, 2 × OC*H*$_2$), 4.94–5.10 (m, 4H, 2 × C*H*$_2$=), 5.72–5.85 (m, 2H, 2 × –C*H*=).

^{13}C NMR: δ = 16.4 (d, J^{31P} = 6.0 Hz, 2 × *C*H$_3$), 26.7 (d, J^{31P} = 3.1 Hz, *C*H$_2$), 31.3 (d, J^{31P} = 8.9 Hz, *C*H$_2$), 32.5 (d, J^{31P} = 3.1 Hz, *C*H$_2$), 35.0 (d, J^{31P} = 140.0 Hz, *C*HP=O), 61.3 (d, J^{31P} = 7.5 Hz, OCH$_2$), 61.4 (d, J^{31P} = 8.9 Hz, OCH$_2$), 115.1 (*C*H$_2$=), 116.7 (*C*H$_2$=), 135.7 (d, J^{31P} = 11.8 Hz, –*C*H=), 137.8 (–*C*H=).

^{31}P NMR: δ = 34.35.

HRMS: *m/z* calc. for $C_{12}H_{23}O_3P$: 246.1385; found: 246.1398.

Diethyl (1-Benzylbut-3-enyl)phosphonate **(11)**:

IR (thin film): ν = 1025, 1239 cm^{-1}.

MS: *m/z* (%) = 282 (M^+, 15), 241 (100), 185 (30), 154 (40), 91 (70).

^{1}H NMR: δ = 1.26 (ap. q, 6H, *J* = 7.0 Hz, 2 × C*H*$_3$), 2.11–2.45 (m 3H, C*H*$_2$C*H*), 2.72 (ddd, 1H, *J* = 9.0, 14.0, 21.0 Hz, PhC*H*), 3.05 (ddd, 1H, *J* = 5.3, 14.0, 20.9 Hz, PhC*H*), 3.97–4.10 (m, 4H, 2 × OC*H*$_2$), 4.97–5.02 (m, 2H, =C*H*$_2$), 5.75–5.85 (m, 1H, –C*H*=), 7.16–7.31 (m, (5H, Ar*H*).

^{13}C NMR: δ = 16.2 (d, J^{31P} = 3.4 Hz, *C*H$_3$), 16.3 (d, J^{31P} = 3.2 Hz, *C*H$_3$), 32.1 (d, J^{31P} = 3.2 Hz, *C*H$_2$), 33.8 (d, J^{31P} = 3.0 Hz, *C*H$_2$), 38.0 (d, J^{31P} = 139.5 Hz, *C*H), 61.4 (d, J^{31P} = 5.4 Hz, OCH$_2$), 61.5 (d, J^{31P} = 6.1 Hz, OCH$_2$), 116.9 (*C*H$_2$=), 126.1 (–*C*H=), 128.2 (ArC), 129.0 (ArC), 135.6 (d, J^{31P} = 8.1 Hz, ArC), 139.4 (d, J^{31P} = 12.8, ArC).

^{31}P NMR: δ = 33.27.

HRMS: *m/z* calc. for $C_{15}H_{23}O_3P$: 282.1385; found: 282.1385.

Diethyl (1-Benzoyl-2-phenylethyl)phosphonate **(12)**:

IR (thin film): ν = 1022, 1251, 1681 cm^{-1}.

MS: *m/z* (%) = 346 (M^+, 5), 241 (100), 209 (15), 185 (20), 105 (70).

^{1}H NMR: δ = 1.16 (t, 3H, *J* = 7.1 Hz, C*H*$_3$), 1.27 (t, 3H, *J* = 7.1 Hz, C*H*$_3$), 3.31 (ddd, 1H, *J* = 3.3, 7.7, 17.0 Hz, C*H*), 3.54 (ddd, 1H, *J* = 7.7, 10.9, 21.8 Hz, C*H*), 4.04 (pentet, 2H, *J* = 7.2 Hz, OC*H*$_2$), 4.13 (pentet, 2H, *J* = 7.4 Hz, OC*H*$_2$), 4.40 (ddd, 1H, *J* = 3.3, 10.9, 23.2 Hz, C*H*), 7.10–7.81 (m, 10H, Ar*H*).

^{13}C NMR: δ = 16.0 (d, J^{31P} = 6.2 Hz, *C*H$_3$), 16.2 (d, J^{31P} = 6.1 Hz, *C*H$_3$), 33.1 (d, J^{31P} = 4.6 Hz, *C*H$_2$), 49.4 (d, J^{31P} = 125.2 Hz, *C*H), 62.7 (d, J^{31P} = 7.4 Hz, OCH$_2$), 62.8 (d, J^{31P} = 7.4 Hz, OCH$_2$), 126.4 (ArC), 128.3 (ArC), 128.4 (d, J^{31P} = 4.1 Hz, ArC), 128.5 (ArC), 133.0 (ArC), 138.9 (ArC), 195.5 (d, J^{31P} = 5.2 Hz, *C*=O).

^{31}P NMR: δ = 22.16.

HRMS: *m/z* calc. for $C_{19}H_{23}O_4P$: 346.1333; found: 346.1317.

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