# Synthesis of 3-Oxoalkylphosphonates via the Conjugate Addition of Acylcuprates to Diethyl Vinylphosphonate

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*Summary: Acylcuprate reagents generated by the reaction of dialkylcyanocuprates with carbon monoxide at low temperature (−110 °C) readily react with diethyl vinylphosphonate to give 3-oxoalkylphosphonates in good yields after hydrolysis. The reaction intermediates can also be trapped by allylic bromides to give 1-allyl-3-oxoalkylphosphonates in good yields.*



## Introduction

The conjugate addition of organocuprates to α,β-unsaturated carbonyl compounds has received a great deal of attention.[1] The direct 1,4-acylation of α,β-unsaturated carbonyl compounds using acylcuprate reagents has also been a subject of interest. For example, Seyferth reported the 1,4-acylation of α,β-unsaturated carbonyl compounds using acylcuprates prepared via the carbonylation of alkylcyanocuprates with carbon monoxide;[2] Lipshutz reported the 1,4-acylation of conjugated enones by allylic cuprates in the presence of carbon monoxide;[3] Saegusa reported the 1,4-acylation of enones with bis(*N*,*N*-diethylcarbamoyl)-cuprate prepared via the insertion reaction of carbon monoxide into bis(*N*,*N*-diethylamino)cuprate.[4] However, to the best of our knowledge, little is known about conjugate addition of organocuprate reagents to alkenylphosphonates.[5,6] In a continuation of our studies focused on acyl anion chemistry,[7] we wish to report the 1,4-acylation of diethyl vinylphosphonate. The reaction provides a new method for the preparation of 3-oxoalkylphosphonates and 1-allyl-3-oxoalkylphosphonates, which are useful as precursors to alkenes[8] and in the preparation of alkylidene-3-oxoalkylphosphonates.[9] Alkylphosphonates are also important due to their biological activity.[10]

## Results and Discussions

Acylcyanocuprate reagents, prepared in situ via the carbonylation of dialkylcyanocuprates with carbon monoxide at −110 °C in a mixed solvent system of THF, diethyl ether, and pentane,[2a] react with diethyl vinylphosphonate at −110 °C. Hydrolysis of the reaction mixture at 0 °C gives 3-oxoalkylphosphonates in 69−82% yields, as shown in Scheme 1.

Acylcyanocuprate reagents, generated by the carbonylation of monoalkylcyanocuprates such as *sec*-butylcyanocuprate or *tert*-butylcyanocuprate with carbon monoxide at −110 °C,[2b] also react with diethyl vinylphosphonate to give the corresponding 3-oxoalkylphosphonates. The reaction yields are lower than those obtained in the dialkylcyanocuprate reactions, Scheme 2. No product is formed when the *n*-butylcyanocuprate/CO-derived reagent is used; the diethyl vinylphosphonate is recovered in 91% yield after workup. This may be a consequence of the lower reactivity of monoalkylcyanocuprates compared to the dialkylcyanocuprates.[11]

The anionic reaction intermediate can be trapped by other electrophiles. After the conjugate addition of *n*-$Bu_2(CN)CuLi_2$/CO to diethyl vinylphosphonate, allyl bromide can be added to afford a mixture of α- and β-allyl-3-oxoalkylphosphonates. These results are consistent with an experiment involving the trapping of the reaction intermediate by $D_2O$, which gave a mixture of α-D- and β-D-3-oxoheptylphosphonates in 80% yield. The results suggest the migration of the β-proton to the α-position in the reaction intermediate, Scheme 3. Fortunately, this rearrangement can be avoided. We found that the α-anion intermediate can be trapped if the conjugate addition is carried out at low temperature (≤ −78 °C) prior to addition of the allyl bromide. The results of a study focused on the preparation of 1-allyl-3-oxoheptylphosphonate under various conditions are presented in Table 1. As shown in Table 1, the reaction time is generally greater than 3 h when carried out at temperatures that eliminate formation of the β-allylation product (Table 1 and Scheme 4).

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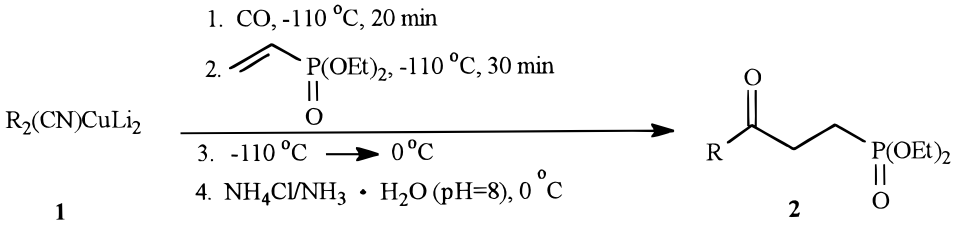
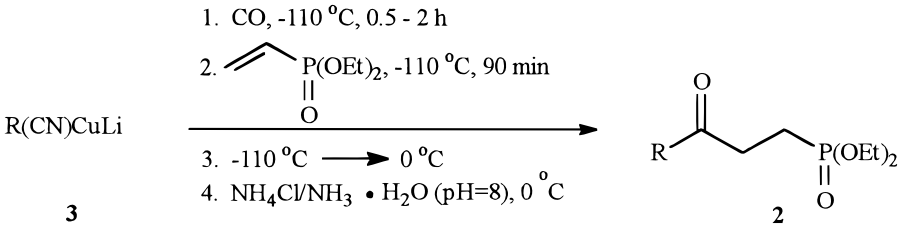
**Scheme 1**




| | Yield |
|---|---|
| **2a**, R = *n*-Bu | 76% |
| **2b**, R = *s*-Bu | 82% |
| **2c**, R = *t*-Bu | 69% |

**Scheme 2**




| | Yield |
|---|---|
| **2a**, R = *n*-Bu | 0% |
| **2b**, R = *s*-Bu | 62% |
| **2c**, R = *t*-Bu | 58% |

**Scheme 3**

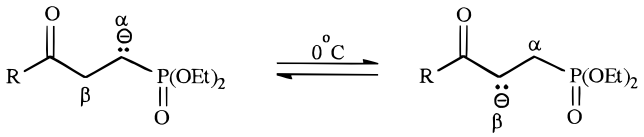



**Table 1. Preparation of 1-Allyl-3-oxoheptylphosphonate**

| entry[a] | reaction conditions | yield (%)[b] |
|---|---|---|
| 1[c] | −110 °C, 30 min | 28 |
| 2 | −110 °C, 3 h | 55 |
| 3 | −110 °C, 6 h | 60 |
| 4 | −78 °C, 4 h | 63 |
| 5 | −110 °C, 30 min, then −78 °C, 4 h | 65 |

[a] Acylcuprate reagent prepared from *n*-$Bu_2(CN)CuLi_2$ and CO at −110 °C for 20 min. [b] Isolated yield. [c] Reaction is incomplete, and diethyl vinylphosphonate is recovered.

The results of a study involving the sequential reaction of diethyl vinylphosphonate with various acylcuprate reagents and allylic bromides are summarized in Table 2. Trimethylsilyl chloride, methyl iodide, and benzyl iodide can also be utilized as trapping agents, but the yields are lower. Under similar conditions, benzaldehyde and benzyl bromide were found to be unreactive as electrophiles. Trapping with benzoyl chloride results, primarily, in the formation of a byproduct, 1-phenyl-1-pentanone.

## Experimental Section

All reagents and solvents were transferred using techniques designed to eliminate contact with air. All glassware and syringes were oven-dried for 24 h prior to use. THF and diethyl ether were distilled over sodium benzophenone ketyl. Pentane was dried and distilled over calcium hydride. *n*-Butyllithium (1.6 M in hexanes), *sec*-butyllithium (1.3 M in cyclohexane), *tert*-butyllithium (1.7 M in pentane), diethyl vinylphosphonate, allyl bromide, and substituted allyl bromide were purchased from Aldrich Chemical Co. and used as received. Copper(I) cyanide, obtained from Aldrich Chemical Co., was dried under vacuum at 150 °C. $^1$H NMR, $^{13}$C NMR, and $^{31}$P NMR spectra were recorded on a Bruker AMX-400 NMR spectrometer. Elemental analyses were performed by Atlantic Microlab, Inc., Norcross, GA. HRMS were performed by the mass spectrometry laboratory at The University of Tennessee, Knoxville, TN.

**Diethyl 3-Oxoheptylphosphonate (2a).** Typical procedure: di-*n*-butylcyanocuprate (2.5 mmol) was prepared under an argon atmosphere by addition of *n*-BuLi (5.0 mmol, 3.1 mL of a 1.6 M solution in hexane) to copper(I) cyanide (2.5 mmol, 0.23 g) in THF (5 mL) at −78 °C. The mixture was warmed briefly to obtain a clear solution and then maintained at −78 °C under argon.[2a] A 4:4:1 mixture of THF, diethyl ether, and pentane (75 mL) was placed in a separate three-necked, 100 mL, round-bottomed flask equipped with a magnetic stirrer, glass-enclosed thermocouple, and a fritted-glass gas dispersion tube. The mixture was cooled to −110 °C by using a low-temperature bath. Carbon monoxide was then bubbled through the mixture for 20 min at −110 °C. The cooled *n*-$Bu_2(CN)CuLi_2$ (2.5 mmol) solution was then added slowly to the solvent mixture (by cannula) while the CO stream was continued. The resulting solution was kept at −110 °C for 20 min under a CO atmosphere, and then diethyl vinylphosphonate (2.5 mmol, 0.41 g, 0.38 mL) was added by syringe. The deep orange solution was stirred at −110° C for 30 min as the addition of CO was continued, and the mixture was warmed to 0 °C by removing the cooling bath and treated with 20 mL of a 1:10, by volume, mixture of concentrated $NH_4OH$ and saturated

**Scheme 4**

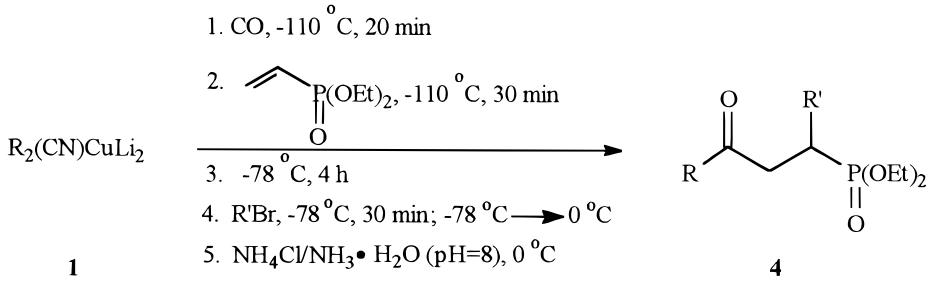



**Table 2. Preparation of 1-Allylic-3-oxoalkylphosphonates (4)**

| entry | product[a] | R | R′ | yield (%)[b] |
|---|---|---|---|---|
| 1 | **4a** | n-Bu | $CH_2$=$CHCH_2$ | 65 |
| 2 | **4b** | s-Bu | $CH_2$=$CHCH_2$ | 80 |
| 3 | **4c** | t-Bu | $CH_2$=$CHCH_2$ | 51 |
| 4 | **4d** | n-Bu | $CH_2$=$C(CH_3)CH_2$ | 75 |
| 5 | **4e** | n-Bu | $(CH_3)_2C$=$CHCH_2$ | 66 |
| 6 | **4f** | n-Bu | (*E*)−$(CH_3)_2C$=$CH(CH_2)_2C(CH_3)$=$CHCH_2$ | 60 |

[a] All products characterized by $^1$H NMR, $^{13}$C NMR, HRMS, and elemental analysis. [b] Isolated yields.



aqueous $NH_4Cl$. The product was extracted into ether (3 × 20 mL), and the combined organic layers were dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. Diethyl 3-oxoheptylphosphonate (0.48 g, 76% yield) was isolated by silica gel chromatography using hexane/ethyl acetate = 1/9 (v/v) as the eluant. $^1$H NMR ($CDCl_3$/TMS): $\delta$ 4.20−4.00 (m, 4H), 2.93−2.68 (m, 2H), 2.44 (t, 2H, $J$ = 7.4 Hz), 2.05−1.97 (m, 2H), 1.61−1.53 (m, 2H), 1.36−1.26 (m, 8H), 0.93 (t, 3H, $J$ = 7.2 Hz). $^{13}$C NMR ($CDCl_3$): $\delta$ 208.0 (d, $J$ $^{31}$P = 14.6 Hz), 61.4 (d, $J$ $^{31}$P = 6.0 Hz), 42.0, 35.1, 25.6, 22.0, 19.1 (d, $J$ $^{31}$P = 144.9 Hz), 16.1 (d, $J$ $^{31}$P = 5.0 Hz), 13.5. $^{31}$P NMR ($CDCl_3$/$H_3PO_4$): $\delta$ 32.42. Anal. Calcd for $C_{11}H_{23}O_4P$: C, 52.79; H, 9.26. Found: C, 52.87; H, 9.18.

**Diethyl 4-Methyl-3-oxohexylphosphonate (2b).** The product was prepared via the procedure outlined for **2a** in 82% yield (0.514 g). **2b** was also prepared in 62% yield (0.42 g) via the conjugate addition of *sec*-butylcyanocuprate/CO reagent[2b] to diethyl vinylphosphonate at −110 °C for 90 min. $^1$H NMR ($CDCl_3$/TMS): $\delta$ 4.21−4.00 (m, 4H), 2.85−2.65 (m, 2H), 2.60−2.40 (m, 1H), 2.05−1.97 (m, 2H), 1.70 (m, 1H), 1.50−1.30 (m, 7H), 1.09 (d, 3H, $J$ = 8.0 Hz), 0.88 (t, 3H, $J$ = 8.0 Hz). $^{13}$C NMR ($CDCl_3$): $\delta$ 211.5 (d, $J$ $^{31}$P =14.1 Hz), 61.4 (d, $J$ $^{31}$P = 5.7 Hz), 47.5, 33.7, 25.7, 19.0 (d, $J$ $^{31}$P = 144.4 Hz), 16.2 (d, $J$ $^{31}$P = 5.3 Hz), 15.0, 11.3. $^{31}$P NMR ($CDCl_3$/$H_3PO_4$): $\delta$ 32.55. Anal. Calcd for $C_{11}H_{23}O_4P$: C, 52.79; H, 9.26; Found: C, 52.70; H, 9.23.

**Diethyl 4,4-Dimethyl-3-oxopentylphosphonate (2c).** The product was prepared via the procedure outlined for **2a** in 69% yield (0.43 g). **2c** was also prepared in 58% yield (0.37 g) via the conjugate addition of *tert*-butylcyanocuprate/CO reagent[2b] to diethyl vinylphosphonate at −110 °C for 90 min. $^1$H NMR ($CDCl_3$/TMS): $\delta$ 4.20−4.00 (m, 4H), 2.83−2.77 (m, 2H), 2.04−1.95 (m, 2H), 1.35 (m, 6H), 1.17 (s, 9H). $^{13}$C NMR ($CDCl_3$): $\delta$ 213.0 (d, $J$ $^{31}$P = 14.1 Hz), 61.4 (d, $J$ $^{31}$P = 6.0 Hz), 43.8, 29.5, 26.3, 19.4 (d, $J$ $^{31}$P = 143.9 Hz), 16.2 (d, $J$ $^{31}$P = 5.0 Hz). $^{31}$P NMR ($CDCl_3$/$H_3PO_4$): $\delta$ 32.81. Anal. Calcd for $C_{11}H_{23}O_4P$: C, 52.79; H, 9.26. Found: C, 52.85; H, 9.28.

**Diethyl 1-Allyl-3-oxoheptylphosphonate (4a).** The acylcyanocuprate reagent was prepared in situ by the reaction of *n*-$Bu_2$(CN)CuLi with CO at −110 °C for 20 min via the procedure outlined for **2a**, and then diethyl vinylphosphonate (2.5 mmol, 0.41 g, 0.38 mL) was added via syringe. The reaction mixture was stirred at −110 °C for 30 min and then warmed to −78 °C and stirred for 4 h while maintaining a CO atmosphere. Allyl bromide (6.0 mmol, 0.73 g, 0.52 mL) was then added to the reaction mixture at −78 °C. After stirring at −78 °C for 30 min under a CO atmosphere, the mixture was warmed to 0 °C and treated with 20 mL of a 1:10, by volume, mixture of concentrated $NH_4OH$ and saturated aqueous $NH_4Cl$. The product was extracted into ether (3 × 20 mL) and isolated by silica gel chromatography using hexane/ethyl acetate = 2/8 (v/v) as the eluant to give **4a** (0.47 g, 65% yield). $^1$H NMR ($CDCl_3$/TMS): $\delta$ 5.80−5.60 (m, 1H), 5.10−4.95 (m, 2H), 4.15−4.00 (m, 4H), 2.80−2.05 (m, 7H), 1.57−1.50 (m, 2H), 1.35−1.20 (m, 8H), 0.90 (t, 3H, $J$ = 8.0 Hz). $^{13}$C NMR ($CDCl_3$): $\delta$ 207.8 (d, $J$ $^{31}$P = 10.4 Hz), 135.4 (d, $J$ $^{31}$P = 12.1 Hz), 117.2, 61.6 (d, $J$ $^{31}$P = 28.2 Hz), 42.8, 40.4, 33.1, 30.1 (d, $J$ $^{31}$P = 142.9 Hz), 25.7, 22.2, 16.3 (d, $J$ $^{31}$P = 5.0 Hz), 13.7. $^{31}$P NMR ($CDCl_3$/$H_3PO_4$): $\delta$ 33.49. Anal. Calcd for $C_{14}H_{27}O_4P$: C, 57.92; H, 9.37. Found: C, 57.75; H, 9.34.

**Diethyl 2-Allyl-4-methyl-3-oxohexylphosphonate (4b).** The product was prepared via the procedure outlined for **4a** in 80% yield (0.58 g). The ratio of diastereomers was approximately 50:50 based on the $^{13}$C NMR and $^{31}$P NMR data. $^1$H NMR ($CDCl_3$/TMS): $\delta$ 5.80−5.55 (m, 1H), 5.10−4.95 (m, 2H), 4.13−4.05 (m, 4H), 2.90−2.30 (m, 5H), 2.30−2.10 (m, 1H), 1.80−1.60 (m, 1H), 1.45−1.20 (m, 7H), 1.06 (m, 3H), 0.88 (m, 3H). $^{13}$C NMR ($CDCl_3$): $\delta$ 210.9 (d, $J$ $^{31}$P = 10.1 Hz), 135.2 (d, $J$ $^{31}$P = 11.1 Hz), 117.0 (d, $J$ $^{31}$P = 2.0 Hz), 61.42 (d, $J$ $^{31}$P = 29.3 Hz), 61.35 (d, $J$ $^{31}$P = 29.4 Hz), 47.7, 39.0, 38.9, 32.9, 29.5 (d, $J$ $^{31}$P = 142.4 Hz), 29.4 (d, $J$ $^{31}$P = 142.7 Hz), 25.5, 25.4, 16.09 (d, $J$ $^{31}$P = 5.3 Hz), 15.5, 15.4, 11.3. $^{31}$P NMR ($CDCl_3$/$H_3PO_4$): $\delta$ 33.76, 33.73. Anal. Calcd for $C_{11}H_{23}O_4P$: C, 57.92; H, 9.37. Found: C, 57.79; H, 9.37.

**Diethyl 2-Allyl-4,4-dimethyl-3-oxopentylphosphonate (4c).** The reagent was prepared via the procedure outlined for **4a** in 51% yield (0.37 g). $^1$H NMR ($CDCl_3$/TMS): $\delta$ 5.79−5.72 (m, 1H), 5.05−5.00 (m, 2H), 4.15−4.04 (m, 4H), 2.90−2.40 (m, 4H), 2.25−2.10 (m, 1H), 1.31 (m, 6H), 1.14 (s, 9H). $^{13}$C NMR ($CDCl_3$): $\delta$ 212.4 (d, $J$ $^{31}$P = 10.0 Hz), 135.3 (d, $J$ $^{31}$P = 12.1 Hz), 117.1, 61.5 (d, $J$ $^{31}$P = 32.2 Hz), 43.8, 34.7, 33.0, 29.5 (d, $J$ $^{31}$P = 141.9 Hz), 26.3, 16.2. $^{31}$P NMR ($CDCl_3$/$H_3PO_4$): $\delta$ 34.03. Anal. Calcd for $C_{14}H_{27}O_4P$: C, 57.92; H, 9.37. Found: C, 57.97; H, 9.34.

**Diethyl 1-(2-Methyl-2-propenyl)-3-oxoheptylphosphonate (4d).** The product was prepared via the procedure outlined for **4a** in 75% yield (0.57 g). $^1$H NMR ($CDCl_3$/TMS): $\delta$ 4.84 (s, 1H), 4.82 (s, 1H), 4.11−4.05 (m, 4H), 2.78−2.71 (m, 2H), 2.47−2.39 (m, 4H), 2.09 (m, 1H), 1.70 (s, 3H), 1.56−1.52 (m, 2H), 1.33−1.28 (m, 8H), 0.90 (t, 3H, $J$ = 7.4 Hz). $^{13}$C NMR ($CDCl_3$): $\delta$ 207.9 (d, $J$ $^{31}$P = 6.9 Hz), 142.4 (d, $J$ $^{31}$P = 15.8 Hz), 113.3, 61.7 (d, $J$ $^{31}$P = 31.6 Hz), 42.7, 40.7, 37.3, 28.4 (d, $J$ $^{31}$P = 142.6), 25.7, 22.2, 21.3, 16.3, 13.7. $^{31}$P NMR ($CDCl_3$/

$H_3PO_4$): $\delta$ 33.91. Anal. Calcd for $C_{15}H_{29}O_4P$: C, 59.19; H, 9.60. Found: C, 59.06; H, 9.60.

**Diethyl 1-(3-Methyl-2-butenyl)-3-oxoheptylphosphonate (4e).** The product was prepared via the procedure outlined for **4a** in 66% yield (0.53 g). $^1$H NMR ($CDCl_3$/TMS): $\delta$ 5.25 (t, 1H, $J$ = 8.7 Hz), 4.12−4.03 (m, 4H), 2.76−2.34 (m, 7H), 1.68 (s, 3H), 1.60 (s, 3H), 1.58−1.51 (m, 2H), 1.34−1.28 (m, 8H), 0.90 (t, 3H, $J$ $^{31}$P = 7.3 Hz). $^{13}$C NMR ($CDCl_3$): $\delta$ 208.2 (d, $J$ $^{31}$P = 9.9 Hz), 134.0, 121.3, 61.5 (d, $J$ = 22.1 Hz), 42.8, 40.6, 31.1 (d, $J$ $^{31}$P = 141.4 Hz), 27.1, 25.7, 25.6, 17.6, 16.3, 13.7. $^{31}$P NMR ($CDCl_3$/$H_3PO_4$): $\delta$ 33.98. Anal. Calcd for $C_{16}H_{31}O_4P$: C, 60.34, H, 9.82. Found: C, 60.43: H, 9.90.

**Diethyl *trans*-1-(2-Oxohexyl)-4,8-dimethyl-3,7-nonadienylphosphonate (4f).** The product was prepared via the procedure outlined for **4a** in 60% yield (0.58 g). $^1$H NMR ($CDCl_3$/TMS): $\delta$ 5.11−5.05 (m, 2H), 4.12−4.04 (m, 4H), 2.80−2.30 (m, 6H), 2.28−2.10 (m, 1H), 2.10−1.95 (m, 4H), 1.67 (s, 3H), 1.59−1.52 (m, 8 Hz), 1.33−1.28 (m, 8H), 0.90 (t, 3H, $J$ = 8.0 Hz). $^{13}$C NMR ($CDCl_3$): $\delta$ 208.2 (d, $J$ $^{31}$P = 9.6 Hz), 137.3, 131.3, 124.0 (d, $J$ $^{31}$P = 5.7 Hz), 121.1, 61.5 (d, $J$ $^{31}$P = 28.2 Hz), 42.8, 40.5, 39.6, 31.0 (d, $J$ $^{31}$P = 141.4 Hz), 26.9, 26.4, 25.7, 25.5, 22.2, 17.5, 16.3, 16.0, 13.7. $^{31}$P NMR ($CDCl_3$/$H_3PO_4$): $\delta$ 33.98. Anal. Calcd for $C_{21}H_{39}PO_4$: HRMS, 386.2586. Found: 386.2570. Calcd for $C_{21}H_{40}PO_4$ ($M + H^+$): HRMS, 387.2664. Found: 387.2670.

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