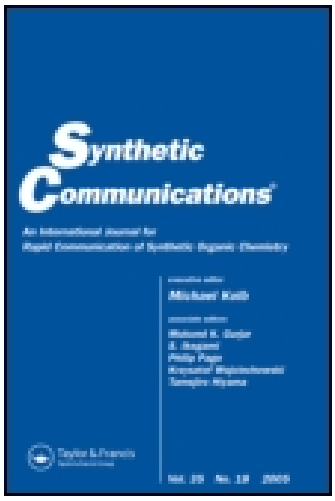

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# Preparation of α-Ketophosphonates by Oxidation of α-Hydroxyphosphonates with Chromium-Based Oxidants

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## ABSTRACT

Various types of diethyl α-hydroxyphosphonates were efficiently converted to diethyl α-ketophosphonates by nicotinium dichromate (NDC), nicotinium chlorochromate (NCC), and isonicotinium dichromate (INDC) in high yields.

*Key Words:* α-Ketophosphonates; α-Hydroxyphosphonates; Chlorochromates; Dichromates; Oxidation.

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## INTRODUCTION

Organophosphorus compounds have found wide applications in synthetic chemistry, medicinal chemistry, and biology. Phosphonates, as a class of organophosphorus compounds, are important complement to phosphates in terms of biological activity and these aspects as well as syntheses of phosphonates have been well documented in the literature.[1] $\alpha$-Ketophosphonates constitute an important subclass of phosphonates. The adjacent phosphoryl and carbonyl functional groups make $\alpha$-ketophosphonates interesting compounds as potential precursors in organic synthesis.[2] For instance, it is possible to convert them to $\alpha,\alpha$-difluorophosphonates[3] and oximes,[4] to reduce enantioselectively to the corresponding $\alpha$-hydroxyphosphonates,[5] and to use them in the hetero Diels–Alder[6] and the Wittig reactions.[7] It is also a very well known fact that the carbon–phosphorus bond in $\alpha$-ketophosphonates is readily cleaved as a result of nucleophilic attack.[8] This property makes $\alpha$-ketophosphonates potentially useful acylating agents, but also susceptible to hydrolysis and difficult to handle.[8]

The Michael–Arbuzov reaction is a general method for the preparation of these compounds from acyl chlorides and trialkylphosphites.[9] This method works well for simple acyl chlorides but it is less successful for preparation of $\alpha$-keto-$\beta,\gamma$-unsaturated phosphonates, where multiple addition products were often observed.[9] Another method which has rarely been used for the preparation of these compounds is the oxidation of $\alpha$-hydroxyphosphonates.[10] A literature survey shows that in contrast to the large number of existing methods for conversion of alcohols to carbonyl compounds, few methods are known for the preparation of diethyl $\alpha$-ketophosphonates from the corresponding diethyl $\alpha$-hydroxyphosphonates. Oxidation by known reagents such as $CrO_3$, $MnO_2$, $CrO_3/Al_2O_3$, and Pfitzner–Moffatt oxidation condition require long reaction times, high molar ratio of an oxidant/substrate, or special treatment for activation of the reagents.[3,11]

In recent years, we have reported new and efficient methods for the preparation of diethyl $\alpha$-functionalized phosphonates from diethyl $\alpha$-hydroxyphosphonates.[12]

In continuation of our interests for preparation of diethyl $\alpha$-ketophosphonates **2**, now we report successful and highly efficient oxidation of various types of diethyl $\alpha$-hydroxyphosphonates **1** by nicotinium dichromate (NDC),[13] nicotinium chlorochromate (NCC),[14] and isonicotinium dichromate (INDC)[15] in dry and refluxing $CH_3CN$ (Sch. 1 and Table 1). Fortunately, the cleavage of the C(O)–P bond in the presence of these oxidants has not been observed which constitutes a strong merit of the presented protocol.

As shown in Table 1, diethyl $\alpha$-hydroxy-(phenylmethyl)phosphonates with different substituents on the phenyl group (**1a**–**k**), diethyl $\alpha$-hydroxy-2-naphthyl,





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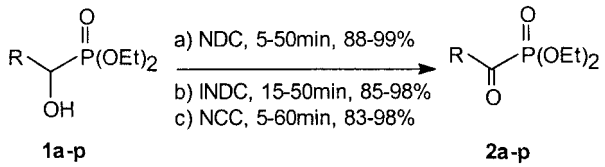


*Scheme 1.*

3-pyridyl, and also β,γ-unsaturated phosphonates (**1l–o**) were easily converted to the corresponding diethyl α-ketophosphonates (**2a–o**) in the presence of NDC, INDC, or NCC in 88–99%, 85–98%, and 87–98% yields, respectively.

We have observed that the oxidants such as PCC[16] and PDC[17] also worked efficiently but suffered from a troublesome workup such as vacuum distillation for isolation of α-ketophosphonates from pyridine, which is present in the reaction medium. We have also observed that the acidic work-up in those cases was always accompanied by the extensive cleavage

***Table 1.*** Oxidation of α-hydroxyphosphonates **1** to α-ketophosphonates **2** by NDC, INDC, and NCC in refluxing $CH_3CN$.

| | | NDC | | INDC | | NCC | |
|---|---|---|---|---|---|---|---|
| Product **2** | R- | Time (min) | Yield[a] (%) | Time (min) | Yield[a] (%) | Time (min) | Yield[a] (%) |
| **a** | $C_6H_5-$ | 5 | 99 | 30 | 97 | 5 | 98 |
| **b** | 4-$CH_3C_6H_4-$ | 15 | 90 | 30 | 96 | 10 | 93 |
| **c** | 4-$CH_3OC_6H_4-$ | 5 | 94 | 25 | 94 | 15 | 90 |
| **d** | 2,4,6-$(CH_3)_3C_6H_2-$ | 5 | 95 | 40 | 90 | 30 | 88 |
| **e** | 2-$ClC_6H_4-$ | 20 | 97 | 20 | 95 | 50 | 87 |
| **f** | 3-$ClC_6H_4-$ | 20 | 98 | 25 | 94 | 60 | 89 |
| **g** | 4-$ClC_6H_4-$ | 25 | 95 | 15 | 95 | 45 | 93 |
| **h** | 2,6-$Cl_2C_6H_3-$ | 5 | 99 | 20 | 98 | 40 | 92 |
| **i** | 2-$O_2NC_6H_4-$ | 40 | 90 | 45 | 89 | 35 | 91 |
| **j** | 3-$O_2NC_6H_4-$ | 50 | 91 | 50 | 90 | 45 | 88 |
| **k** | 4-$O_2NC_6H_4-$ | 40 | 90 | 40 | 87 | 30 | 90 |
| **l** | 2-Naphthyl | 30 | 91 | 35 | 87 | 40 | 87 |
| **m** | 3-Pyridyl | 15 | 97 | 25 | 96 | 15 | 96 |
| **n** | PhCH=CH- | 10 | 95 | 15 | 95 | 20 | 90 |
| **o** | $CH_3CH=CH-$ | 25 | 88 | 45 | 85 | 50 | 87 |

[a]Oxidant/substrate = 1/1, isolated yields. All of the products gave satisfactory spectral data compared with authentic samples.





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of the C(O)–P bond. Similar oxidations conducted in the presence of NDC, INDC, or NCC produced solid mixtures of chromium(III) residues (green) accompanied by nicotinic or isonicotinic acids which were simply isolated by filtration. Evaporation of the solvent produced the desired $\alpha$-ketophosphonates **2** in high yields and purities.

In conclusion, in this report we applied NDC, NCC, INDC as efficient oxidizing agents for the facile preparation of diethyl $\alpha$-ketophosphonates by direct oxidation of diethyl $\alpha$-hydroxyphosphonates. The absence of by-products due to the cleavage of the C(O)–P bond, the use of equimolar amounts of the oxidants and the simple work-up of reaction mixtures are the advantages of the presented protocol.

## EXPERIMENTAL

Chemicals were either prepared in our laboratories or were purchased from Fluka and Merck Chemical Companies. NDC, NCC, INDC were prepared according to the reported procedures.[14,15] Products were purified by plate chromatography. The purity determination of the products was accomplished by TLC on silica gel polygram SIL G/UV 254 plates. Mass spectra were run on a Shimadzu GC-Mass-QP 1000 EX at 70 eV. The IR spectra were recorded on a Shimadzu Fourier Transform Infrared Spectrophotometer (FT-IR-8300). The NMR spectra were recorded on a Bruker advance DPX 250 MHz spectrometer.

### Preparation of Diethyl α-Ketophosphonates by the Oxidation of Diethyl α-Hydroxyphosphonates (General Procedure)

To a solution of diethyl $\alpha$-hydroxyphosphonate (5 mmol) in dry $CH_3CN$ (50 mL), the oxidant (5 mmol) was added and the resulting mixture was stirred under reflux for the time given in Table 1. The resulting heterogeneous reaction mixture was then filtered and the filter cake was washed with $CCl_4$ ($4 \times 25$ mL). Evaporation of the solvent afforded an oily material containing a crude **2**, contaminated with the tiny amounts of white solid residues of nicotinic or isonicotinic acids. Further purification was proceeded by dissolution of the crude product in $CCl_4$ (25 mL), filtration, and distillation. All compounds gave satisfactory spectral data compared with authentic samples.

The following compounds were obtained:

**Diethyl benzoyl phosphonate (2a).** B.p. 125–126°C/0.05 mmHg (lit.[2a] b.p. 106–109°C/0.01 mmHg); $^1$H NMR ($CDCl_3$, TMS): $\delta$ 1.37–1.68 (t, 6H, $^2J_{HH} = 7.1$ Hz, 2-$OCH_2C\underline{H_3}$), 4.08–4.28 (dq, 4H, $^2J_{PH} = 7.1$ Hz,





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$^{2}J_{HH} = 7.1$ Hz, 2-OC$\underline{H_2}$CH$_3$), 7.28–7.6 (m, 3H), 8.03–8.25 (m, 2H) ppm; $^{13}$C NMR ($CDCl_3$, TMS): 16.64 (d, $^{3}J_{CP} = 5.7$ Hz, 2-OCH$_2$C$\underline{H_3}$), 64.31 (d, $^{2}J_{CP} = 7.5$ Hz, 2-O$\underline{C}$H$_2$CH$_3$), 129.15, 130.06, 135.03, 136.29 (–C$_6$H$_5$), 199.12 (d, $^{1}J_{CP} = 177.5$ Hz, C═O) ppm; IR (neat): $\nu$ 1650 (C═O), 1267 (P═O) cm$^{-1}$; MS: M$^+$ (242), M–P(O)(OEt)$_2$ (105); Elemental analysis for $C_{11}H_{15}O_4P$ requires C 54.5%, H 6.2%; found: C 54.2%, H 6.0%.

**Diethyl 4-methyl-benzoyl phosphonate (2b).** B.p. 130–131°C/0.05 mmHg (lit.[2a] b.p. 116–117°C/0.03 mmHg); $^{1}$H NMR ($CDCl_3$, TMS): $\delta$ 1.29–1.42 (t, 6H, $^{2}J_{HH} = 7.1$ Hz, 2-OCH$_2$C$\underline{H_3}$), 2.35 (s, 3H, –CH$_3$), 4.11–4.16 (dq, 4H, $^{2}J_{PH} = 7.1$ Hz, $^{2}J_{HH} = 7.1$ Hz, 2-OC$\underline{H_2}$CH$_3$), 7.12–7.21 (m, 2H), 8.04–8.07 (m, 2H) ppm; $^{13}$C NMR ($CDCl_3$, TMS): 16.67 (d, $^{3}J_{CP} = 5.7$ Hz, 2-OCH$_2$C$\underline{H_3}$), 22.18 (–CH$_3$), 64.24 (d, $^{2}J_{CP} = 7.5$ Hz, 2-O$\underline{C}$H$_2$CH$_3$), 127.35, 129.89, 130.31, 146.41 (–C$_6$H$_4$), 198.46 (d, $^{1}J_{CP} = 176.6$ Hz, C═O) ppm; IR (neat): $\nu$ 1650 (C═O), 1261 (P═O) cm$^{-1}$; MS: M$^+$ (256), M–P(O)(OEt)$_2$ (119); Elemental analysis for $C_{12}H_{17}O_4P$ requires C 56.2%, H 6.6%; found: C 56.0%, H 6.1%.

**Diethyl 4-methoxy-benzoyl phosphonate (2c).** B.p. 166–167°C/0.05 mmHg (lit.[2a] b.p. 175–179°C/1.5 mmHg); $^{1}$H NMR ($CDCl_3$, TMS): $\delta$ 1.11–1.29 (t, 6H, $^{2}J_{HH} = 7.1$ Hz, 2-OCH$_2$C$\underline{H_3}$), 3.80 (s, 3H, –CH$_3$), 3.90–4.10 (dq, 4H, $^{2}J_{PH} = 7.1$ Hz, $^{2}J_{HH} = 7.1$ Hz, 2-OC$\underline{H_2}$CH$_3$), 6.84–6.90 (m, 2H), 7.42–7.50 (m, 2H) ppm; $^{13}$C NMR ($CDCl_3$, TMS): 16.75 (d, $^{3}J_{CP} = 5.7$ Hz, 2-OCH$_2$C$\underline{H_3}$), 55.59 (–CH$_3$), 63.46 (d, $^{2}J_{CP} = 7.5$ Hz, 2-O$\underline{C}$H$_2$CH$_3$), 114.03, 128.82, 129.21, 159.78 (–C$_6$H$_4$), 198.01 (d, $^{1}J_{CP} = 176.2$ Hz, C═O) ppm; IR (neat): $\nu$ 1655 (C═O), 1265 (P═O) cm$^{-1}$; MS: M$^+$ (272), M–P(O)(OEt)$_2$ (135); Elemental analysis for $C_{12}H_{17}O_5P$ requires C 52.9%, H 6.2%; found: C 52.2%, H 5.9%.

**Diethyl 2,4,6-trimethyl-benzoyl phosphonate (2d).** B.p. 108–109°C/0.07 mmHg (lit.[2a] b.p. 131–132°C/0.3 mmHg);$^{1}$H NMR ($CDCl_3$, TMS): $\delta$ 1.25–1.32 (t, 6H, $^{2}J_{HH} = 7.1$ Hz, 2-OCH$_2$C$\underline{H_3}$), 2.23 (s, 6H, 2,6-diCH$_3$), 2.27 (s, 3H, 4-CH$_3$), 4.06–4.17 (dq, 4H, $^{2}J_{PH} = 7.1$ Hz, $^{2}J_{HH} = 7.1$ Hz, 2-OC$\underline{H_2}$CH$_3$), 6.83 (s, 2H) ppm; $^{13}$C NMR ($CDCl_3$, TMS): 16.81 (d, $^{3}J_{CP} = 5.7$ Hz, 2-OCH$_2$C$\underline{H_3}$), 21.17 (2,6-diCH$_3$), 21.38 (4-CH$_3$), 63.12 (d, $^{2}J_{CP} = 7.5$ Hz, 2-O$\underline{C}$H$_2$CH$_3$), 129.74, 130.3, 137.69, 137.75 (–C$_6$H$_2$), 199.01 (d, $^{1}J_{CP} = 177.0$ Hz, C═O) ppm; IR (neat): $\nu$ 1665 (C═O), 1250 (P═O) cm$^{-1}$; MS: M$^+$ (284), M–P(O)(OEt)$_2$ (142); Elemental analysis for $C_{14}H_{21}O_4P$ requires C 59.1%, H 7.4%; found: C 59.3%, H 7.6%.

**Diethyl 2-chloro-benzoyl phosphonate (2e).** B.p. 105–106°C/0.05 mmHg (lit.[18] b.p. 158–160°C, 2.3 mmHg); $^{1}$H NMR ($CDCl_3$, TMS): $\delta$ 1.58 (t, 6H, $^{2}J_{HH} = 7.1$ Hz, 2-OCH$_2$C$\underline{H_3}$), 4.17–4.30 (m, 4H, 2-OC$\underline{H_2}$CH$_3$), 7.24–7.44 (m, 3H), 8.14–8.20 (m, 1H) ppm; $^{13}$C NMR ($CDCl_3$, TMS): 16.65 (d, $^{3}J_{CP} = 5.7$ Hz, 2-OCH$_2$C$\underline{H_3}$), 64.82 (d, $^{2}J_{CP} = 7.4$ Hz, 2-O$\underline{C}$H$_2$CH$_3$), 126.84, 127.10, 130.64–132.07, 132.68–133.85,

134.16–135.98 ($-C_6H_4$), 200.53 (d, $^1J_{CP} = 182.0$ Hz, C═O) ppm; IR (neat): $\nu$ 1650 (C═O), 1245 (P═O) $cm^{-1}$; MS: $M^+$ (276), M + 2 (279), M–P(O)$(OEt)_2$ (139); Elemental analysis for $C_{11}H_{14}ClO_4P$ requires C 47.8%, H 5.1%; found: C 47.5%, H 4.9%.

**Diethyl 3-chloro-benzoyl phosphonate (2f).** B.p. = 101–102°C/0.06 mmHg (lit.[19] b.p. 127°C/0.4 mmHg); $^1$H NMR ($CDCl_3$, TMS): $\delta$ 1.28–1.34 (m, 6H, 2-OCH$_2$CH$_3$), 4.16–4.27 (m, 4H, 2-OCH$_2$CH$_3$), 7.22–7.53 (m, 3H), 7.96 (s, 1H) ppm; $^{13}$C NMR ($CDCl_3$, TMS): 18.44 (d, $^3J_{CP} = 5.7$ Hz, 2-OCH$_2$CH$_3$), 66.45 (d, $^2J_{CP} = 7.4$ Hz, 2-OCH$_2$CH$_3$), 130.15–139.50 ($-C_6H_4$), 201.46 (d, $^1J_{CP} = 182.0$ Hz, C═O) ppm; IR (neat): $\nu$ 1650 (C═O), 1267 (P═O) $cm^{-1}$; MS: $M^+$ (276), M + 2 (279), M–P(O)$(OEt)_2$ (139); Elemental analysis for $C_{11}H_{14}ClO_4P$ requires C 47.8%, H 5.1%; found: C 47.4%, H 4.7%.

**Diethyl 4-chloro-benzoyl phosphonate (2g).** B.p. 142–143°C/0.06 mmHg (lit.[2a] b.p. 112–113°C/0.01 mmHg); $^1$H NMR ($CDCl_3$, TMS): $\delta$ 1.13–1.42 (t, 6H, $^2J_{HH} = 7.1$ Hz, 2-OCH$_2$CH$_3$), 4.15–4.33 (dq, 4H, $^2J_{PH} = 7.1$ Hz, $^2J_{HH} = 7.1$ Hz, 2-OCH$_2$CH$_3$), 7.47–7.50 (m, 2H), 8.21–8.24 (m, 2H) ppm; $^{13}$C NMR ($CDCl_3$, TMS): 16.75 (d, $^3J_{CP} = 5.7$ Hz, 2-OCH$_2$CH$_3$), 64.49 (d, $^2J_{CP} = 7.5$ Hz, 2-OCH$_2$CH$_3$), 129.62, 131.58, 133.72, 141.85 ($-C_6H_4$), 198.09 (d, $^1J_{CP} = 180.0$ Hz, C═O) ppm; IR (neat): $\nu$ 1650 (C═O), 1260 (P═O) $cm^{-1}$; MS: $M^+$ (277), M + 2 (279), M–P(O)$(OEt)_2$ (139); Elemental analysis for $C_{11}H_{14}ClO_4P$ requires C 47.8%, H 5.1%; found: C 47.9%, H 5.3%.

**Diethyl 2,6-dichloro-benzoyl phosphonate (2h).** B.p. 150–151°C/0.05 mmHg; $^1$H NMR ($CDCl_3$, TMS): $\delta$ 1.04–1.24 (t, 6H, $^2J_{HH} = 7.1$ Hz, 2-OCH$_2$CH$_3$), 3.95–4.23 (dq, 4H, $^2J_{PH} = 7.1$ Hz, $^2J_{HH} = 7.1$ Hz, 2-OCH$_2$CH$_3$), 6.90–7.09 (m, 3H) ppm; $^{13}$C NMR ($CDCl_3$, TMS): 16.61 (d, $^3J_{CP} = 5.7$ Hz, 2-OCH$_2$CH$_3$), 64.85 (d, $^2J_{CP} = 7.5$ Hz, 2-OCH$_2$CH$_3$), 128.06, 128.56, 131.51, 132.07 ($-C_6H_3$), 204.36 (d, $^1J_{CP} = 195.5$ Hz, C═O) ppm; IR (neat): $\nu$ 1691 (C═O), 1264 (P═O) $cm^{-1}$; MS: $M^+$ (311), M + 2 (313), M + 4 (315), M–P(O)$(OEt)_2$ (174); Elemental analysis for $C_{11}H_{13}Cl_2O_4P$ requires C 42.4%, H, 4.2%; found: C 42.0%, H 4.0%.

**Diethyl 2-nitro-benzoyl phosphonate (2i).**[a] B.p. 146–147°C/0.05 mmHg; $^1$H NMR ($CDCl_3$, TMS): $\delta$ 1.34 (t, 6H, $^2J_{HH} = 7.0$ Hz, 2-OCH$_2$CH$_3$), 4.20–4.32 (dq, 4H, $^2J_{PH} = 7.2$ Hz, $^2J_{HH} = 7.3$ Hz, 2-OCH$_2$CH$_3$), 7.4 (d, 1H, $^2J_{HH} = 7.4$ Hz), 7.70–7.85 (m, 2H), 8.44 (d, 1H, $^2J_{HH} = 7.7$ Hz,) ppm; $^{13}$C NMR ($CDCl_3$, TMS): 16.64 (d, $^3J_{CP} = 5.7$ Hz,

[a]Compounds **2i**, **2j**, and **2n** are known compounds and they are reported in the literature.[11b] Physical and analytical data are not reported for any of them.





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2-OCH$_2$CH$_3$), 64.92 (d, $^2J_{CP} = 7.2$ Hz, 2-OCH$_2$CH$_3$), 123.92, 124.48, 128.56–130.44, 131.93–132.88, 136.24, 147.08 (–C$_6$H$_4$), 203.86 (d, $^1J_{CP} = 180.0$ Hz, C═O) ppm; IR (neat): $\nu$ 1655 (C═O), 1260 (P═O) cm$^{-1}$; MS: M$^+$ (287), M–P(O)(OEt)$_2$ (150); Elemental analysis for C$_{11}$H$_{14}$NO$_6$P requires C 46.0%, H 4.9%; found: C 46.3%, H 5.3%.

**Diethyl 3-nitro-benzoyl phosphonate (2j).** B.p. 149–150°C/0.05 mmHg; $^1$H NMR (CDCl$_3$, TMS): $\delta$ 1.15–1.43 (m, 6H, 2-OCH$_2$CH$_3$), 4.10–4.20 (q, 2H, $^2J_{HH} = 7.1$ Hz, 2-OCH$_2$CH$_3$), 4.30–4.39 (q, 2H, $^2J_{HH} = 7.1$ Hz, 2-OCH$_2$CH$_3$), 8.44–8.48 (m, 2H), 8.59–8.62 (m, 1H), 8.84 (s, 1H) ppm; $^{13}$C NMR (CDCl$_3$, TMS): 16.63 (d, $^3J_{CP} = 5.5$ Hz, 2-OCH$_2$CH$_3$), 65.12 (d, $^2J_{CP} = 7.5$ Hz, 2-OCH$_2$CH$_3$), 129.04, 129.94, 130.64, 132.74, 135.71–137.33, 167.0 (–C$_6$H$_4$), 197.75 (d, $^1J_{CP} = 183.4$ Hz, C═O) ppm; IR (neat): $\nu$ 1650 (C═O), 1260 (P═O) cm$^{-1}$; MS: M$^+$ (287), M–P(O)(OEt)$_2$ (150); Elemental analysis for C$_{11}$H$_{14}$NO$_6$P requires C 46.0%; H 4.9%; found: C 45.8%, H 4.6%.

**Diethyl 4-nitro-benzoyl phosphonate (2k).** M.p. 140–141°C (lit.[20] M.p. 142–143°C); $^1$H NMR (CDCl$_3$, TMS): $\delta$ 1.23–1.321 (m, 6H, 2-OCH$_2$CH$_3$), 4.00–4.18 (m, 2H, 2-OCH$_2$CH$_3$), 7.66 (d, 2H, $^2J_{HH} = 7.5$ Hz), 8.7 (d, 2H, $^2J_{HH} = 8.7$ Hz) ppm; IR (KBr): $\nu$ 1650 (C═O), 1260 (P═O) cm$^{-1}$; MS: M$^+$ (287), M–P(O)(OEt)$_2$ (150); Elemental analysis for C$_{11}$H$_{14}$NO$_6$P requires C 46.0%, H 4.9%; found: C 46.4%, H 5.2%.

**Diethyl 2-naphthoyl phosphonate (2l).** B.p. 152–153°C/0.07 mmHg (lit.[18] b.p. 188–191°C/1.2 mmHg); $^1$H NMR (CDCl$_3$, TMS): $\delta$ 11.33–1.44 (m, 6H, 2-OCH$_2$CH$_3$), 4.28–4.39 (m, 4H, 2-OCH$_2$CH$_3$), 7.57–7.64 (m, 2H), 7.85–7.93 (m, 2H), 8.04–8.14 (m, 2H), 9.08 (s, 1H) ppm; $^{13}$C NMR (CDCl$_3$, TMS): 16.79 (d, $^3J_{CP} = 5.7$ Hz, 2-OCH$_2$CH$_3$), 64.52 (d, $^2J_{CP} = 7.3$ Hz, 2-OCH$_2$CH$_3$), 123.75–136.67, 169.90 (C$_{10}$H$_7$), 199.07 (d, $^1J_{CP} = 174.9$ Hz, C═O) ppm; IR (neat): $\nu$ 1655 (C═O), 1260 (P═O) cm$^{-1}$; MS: M$^+$ (292), M–P(O)(OEt)$_2$ (155); Elemental analysis for C$_{15}$H$_{17}$O$_4$P requires C 61.6%, H 5.8%; found: C 61.2%, H 5.3%.

**Diethyl 3-pridoyl phosphonate (2m).** B.p. 125–126°C/2 mmHg (lit.[21] b.p. 128°C/2 mmHg); $^1$H NMR (CDCl$_3$, TMS): $\delta$ 1.23–1.36 (m, 6H, 2-OCH$_2$CH$_3$), 4.14–4.30 (m, 4H, 2-OCH$_2$CH$_3$), 7.38–7.43 (m, 1H), 7.90 (d, 2H, $^2J_{HH} = 7.9$ Hz), 8.78 (d, 2H, $^2J_{HH} = 3.8$ Hz), 9.34 (s, 1H) ppm; $^{13}$C NMR (CDCl$_3$, TMS): 16.72 (d, $^3J_{CP} = 5.5$ Hz, 2-OCH$_2$CH$_3$), 64.72 (d, $^2J_{CP} = 7.5$ Hz, 2-OCH$_2$CH$_3$), 124.11, 131.96, 151.27, 154.90 (C$_5$H$_4$N), 199.18 (d, $^1J_{CP} = 183.5$ Hz, C═O) ppm; IR (neat): $\nu$ 1654 (C═O), 1245 (P═O) cm$^{-1}$; MS: M$^+$ (243), M–P(O)(OEt)$_2$ (106); Elemental analysis for C$_{10}$H$_{14}$NO$_4$P requires C 49.4%, H 5.8%; found: C 49.0%, H 5.4%.

**Diethyl 1-oxo-3-phenyl-2-propenylphosphonate (2n).** B.p. 108–109°C/0.05 mmHg; $^1$H NMR (CDCl$_3$, TMS): $\delta$ 1.30 (t, 6H, $^2J_{HH} = 7.1$ Hz, 2-OCH$_2$CH$_3$), 4.14 (dq, 4H, $^2J_{PH} = 7.1$ Hz, $^2J_{HH} = 7.1$ Hz, 2-OCH$_2$CH$_3$), 7.38–7.43 (m, 1H), 8.45–8.48 (m, 1H), 8.77–8.78 (m, 1H), 9.34 (s, 1H)





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ppm; $^{13}$C NMR ($CDCl_3$, TMS): 16.72 (d, $^3J_{CP} = 5.7$ Hz, 2-OCH$_2$<u>C</u>H$_3$), 64.72 (d, $^2J_{CP} = 7.5$ Hz, 2-O<u>C</u>H$_2$CH$_3$), 124.11, 137.34, 151.27, 154.90 ($-C_5H_5N$), 199.18 (d, $^1J_{CP} = 195.5$ Hz, C═O) ppm; IR (neat): $\nu$ 1655 (C═O), 1260 (P═O) cm$^{-1}$; MS: $M^+$ (268), M−P(O)(OEt)$_2$ (131); Elemental analysis for $C_{13}H_{17}O_4P$ requires C 58.2%, H 6.3%; found: C 58.0%, H 6.1%.

**Diethyl 1-oxo-2-butenylphosphonate (2o).** B.p. 105°C/10 mmHg; (lit.[2d] b.p. 109°C/10 mmHg); $^1$H NMR ($CDCl_3$, TMS): $\delta$ 1.18–1.33 (m, 6H, 2-OCH$_2$C<u>H</u>$_3$), 1.90–1.96 (m, 3H, CH$_3$), 4.02–4.20 (m, 4H, 2-OC<u>H</u>$_2$CH$_3$), 6.27–6.42 (m, 1H), 7.38–7.53 (m, 1H) ppm; $^{13}$C NMR ($CDCl_3$, TMS): 16.71 (d, $^3J_{CP} = 5.5$ Hz, 2-OCH$_2$<u>C</u>H$_3$), 18.18 (CH$_3$), 63.14 (d, $^2J_{CP} = 7.3$ Hz, 2-O<u>C</u>H$_2$CH$_3$), 126.10, 129.78 (CH═CH), 198.08 (d, $^1J_{CP} = 189.5$ Hz, C═O) ppm; IR (neat): $\nu$ 1665 (C═O), 1265 (P═O) cm$^{-1}$; MS: $M^+$ (206), M−P(O)(OEt)$_2$ (69); Elemental analysis for $C_8H_{15}O_4P$ requires C 46.46%, H 7.3%; found: C 46.41%, H 7.1%.

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