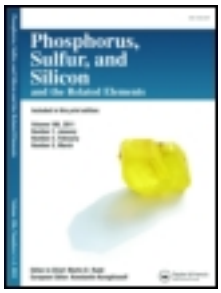

Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gpss20

PREPARATION OF α-KETOPHOSPHONATES BY OXIDATION OF α-HYDROXYPHOSPHONATES WITH PYRIDINIUM CHLOROCHROMATE (PCC)

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Published online: 16 Aug 2010.

To cite this article: Habib Firouzabadi , Nasser Iranpoor & Sara Sobhani (2004) PREPARATION OF α-KETOPHOSPHONATES BY OXIDATION OF α-HYDROXYPHOSPHONATES WITH PYRIDINIUM CHLOROCHROMATE (PCC), Phosphorus, Sulfur, and Silicon and the Related Elements, 179:8, 1483-1491, DOI: 10.1080/10426500490463925

To link to this article: http://dx.doi.org/10.1080/10426500490463925

Phosphorus, Sulfur, and Silicon, 179:1483–1491, 2004

ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426500490463925

PREPARATION OF α-KETOPHOSPHONATES BY OXIDATION OF α-HYDROXYPHOSPHONATES WITH PYRIDINIUM CHLOROCHROMATE (PCC)

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(Received December 18, 2003; accepted December 18, 2003)

Various types of diethyl α-hydroxyphosphonates were converted efficiently to their corresponding diethyl α-ketophosphonates by pyridiinum chlorochromate (PCC) without cleavage of C(O)—P bond in the absence of solvent or in solution in high yields.

Keywords: α-Hydroxyphosphonates; α-ketophosphonates; chlorochromates; oxidation

INTRODUCTION

Organophosphorus compounds have found wide applications in chemistry, medicinal chemistry, and biology. Phosphonates, as a class of organophosphorus compounds, are interesting complements to phosphates in terms of biological activity and have been well documented in the literature.[1] α-Ketophosphonates are an important subdivision of this class of compounds. The adjacent phosphorus substituents and carbonyl functional groups in α-ketophosphonates are the main reason that makes them interesting compounds in organic synthesis.[2] For instance, it is possible to prepare α,α-difluorophosphonates[3] and oximes[4] from their carbonyl functional groups, to reduce enantioselectively α-ketophosphonates to their corresponding α-hydroxyphosphonates,[5] and use them in hetero Diels Alder[6] and Wittig reactions.[7] For several years it has been known that the carbonyl of a α-ketophosphonate is activated towards attack by nucleophiles and that the carbon-phosphorus bond is readily cleaved.[8] This property makes α-ketophosphonates

The authors are thankful to the Shiraz University Research Council for the partial support of this work.

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potentially useful acylating agents but also susceptible to hydrolysis and difficult to handle.[8]

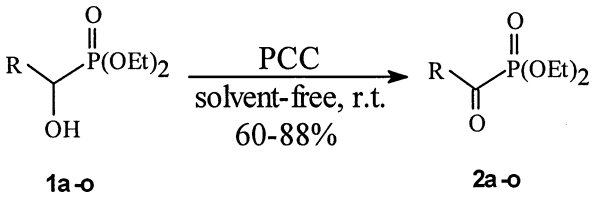
The Michael-Arbuzov reaction is a general method for the preparation of these compounds from acyl chlorides and trialkylphosphites.[9] This method works well for the less-complex acyl chlorides but shows less success in the preparation of α-keto-β,γ-unsaturated phosphonates, where multiple addition products are often observed.[9] An alternative method for the preparation of α-ketophosphonates is the oxidation of easily prepared and stable α-hydroxyphosphonates.[10] A literature survey indicates that in contrast to the existing methods for the conversion of alcohols to carbonyl compounds, few methods are known for the preparation of diethyl α-ketophosphonates from their corresponding diethyl α-hydroxysphonates. Oxidation by known reagents requires long reaction times, high molar ratios of the oxidant/substrate, or special treatment for the activation of the reagent.[3,11]

In recent years, we have started studies on the development of new methods for the preparation of diethyl α-functionalized phosphonates from diethyl α-hydroxyphosphonates. Along this line, we have reported mild oxidation, silylation, halogenation, and azidation procedures for the preparation of diethyl α-keto and α-trimethylsilyloxy, α-halo and α-azidophosphonates in high yields.[12]

RESULTS AND DISCUSSION

Our recent report on the oxidative transformation of organic functional groups by pyridiinum chlorochromate (PCC)[13] in the absence of solvent[14] prompted us to apply this reagent to the important oxidation of diethyl α-hydroxyphosphonates under solvent-free conditions. Under such reaction conditions, various types of diethyl α-hydroxyphenyl, 2-naphthyl, 3-pyridyl, and β,γ-unsaturated phosphonates (**1a–h** and **1l–o**) were oxidized easily at room temperature in 65–88% yields (Table I). Higher temperature (40°C) was needed for the oxidation of *o*-, *m*-, and *p*-substituted nitro derivatives of diethyl α-hydroxy-(phenylmethyl)phosphonates (**1i–k**) to produce the desired products in 60–75% yields (Scheme 1 and Table I).

We have also tried similar oxidations in the presence of (nicotinium dichromate) NDC,[15] (nicotinium chlorochromate) NCC,[16] (isonicotinium dichromate) INDC,[17] and (pyridinium dichromate) PDC[18] as the analogs of (pyridinium chlorochromate) PCC under solvent-free conditions. Surprisingly, we observed that none of the oxidants were effective for this purpose and the starting materials were isolated intact after long reaction times.



SCHEME 1

We have also studied oxidation of diethyl α-hydroxyphosphonates in the presence of PCC in solvent. In order to optimize the reaction conditions, we studied the oxidation of **1a** to **2a** in dry CH_3CN, CH_2Cl_2, $CHCl_3$, and CCl_4. We have found that **1a** was oxidized well by PCC to **2a** in dry CH_2Cl_2 at room temperature. Therefore, we applied similar conditions for the oxidation of other diethyl α-hydroxyphosphonates (**1b–o**) by PCC (Table I). As shown in Table I, various types of diethyl α-hydroxy-(phenylmethyl)phosphonates (**1a–k**) were cleanly converted into their corresponding diethyl α-keto-(phenylmethyl) phosphonates (**2a–k**) in excellent yields (65–87% by PCC). Diethyl α-hydroxy-2-naphthyl, 3-pyridyl, and β,γ-unsaturated phosphonates (**1l–o**) were also oxidized efficiently

TABLE I Oxidation of α-Hydroxyphosphonates to α-Ketophosphonates by PCC

Product **2**	R—	Time (h)	Yield[a,b] (%)	Time (h)	Yield[a,c] (%)
a	C_6H_5—	5.4	88	2	87
b	4-$CH_3C_6H_4$—	6	85	2.4	85
c	4-$CH_3OC_6H_4$—	8.4	71	2	65
d	2,4,6-$(CH_3)_3C_6H_2$—	5.5	73	3.5	70
e	2-ClC_6H_4—	8	68	2.5	71
f	3-ClC_6H_4—	8.5	72	3.5	65
g	4-ClC_6H_4—	7.5	76	3	67
h	2,6-$Cl_2C_6H_3$—	4	86	3.5	78
i	2-$O_2NC_6H_4$—	10	70	3	81[d]
j	3-$O_2NC_6H_4$—	9.5	60	3.5	79[d]
k	4-$O_2NC_6H_4$—	12	75	3.75	80[d]
l	2-naphthyl	11	67	8.5	68
m	3-pyridyl	4.5	65	1.75	71
n	PhCH=CH—	6	76	6.5	80
o	CH_3CH=CH—	12	79	9.5	60

[a]PCC/substrate = 1/1, isolated yields, room temperature. All compounds were characterized by comparison of their spectral data with authentic samples.
[b]CH_2Cl_2, [c]solvent-free, and [d]40°C.

to their corresponding diethyl α-ketophosphonates (**2l–o**) in 60–80% yields.

CONCLUSION

In general, conversion of α-hydroxyphosphonates to their α-ketophosphonates using PCC as an oxidant proceeded well in solution or under solvent-free conditions. Our results show that reactions in solution proceeded with higher yields and required longer reaction times in comparison with those under solvent–free conditions. Workup of the reaction mixtures is easy, and by a simple vacuum distillation pure products are isolated in good-to-excellent yields. Lack of cleavage of C(O)—P bond in both solvent–free conditions and in solution is a strong practical advantage of the method.

EXPERIMENTAL

General

Chemicals were either prepared in our laboratories or were purchased from Fluka and Merck Companies. Products were identified by comparison of their IR, NMR, and mass spectra with those reported for the authentic samples. Progress of the reactions was followed by TLC using silica-gel polygrams SIL G/UV 254 plates or by GC using a Shimadzu gas chromatograph GC-14A, equipped with a flame ionization detector and a glass column packed with DC-200 stationary phase and nitrogen as the carrier gas. IR spectra were record on a Perkin-Elmer 781 spectrophotometer. NMR spectra were run on a Bruker Avance DPX 250 MHz instrument. Mass spectra were recorded by GCMS-QP 1000 EX at 20 eV (Shimadzu).[23]

General Procedure for the Preparation of Diethyl α-Ketophosphonates by the Oxidation of Diethyl α-Hydroxyphosphonates with PCC under Solvent-Free Conditions

Pyridinium chlorochromate (1.077 g, 5 mmol) and substrate (5 mmol) were ground in a mortar and left at room temperature or in an oven (40°C) without further grinding for the appropriate reaction times (Table I). The reaction mixture was washed with CCl_4 (4 × 25 ml) and dried over Na_2SO_4. After evaporation of the solvent, the pure product was obtained by bulb-to-bulb vacuum distillation in 60–88% yields.

General Procedure for the Preparation of Diethyl α-Ketophosphonates by Oxidation of Diethyl α-Hydroxyphosphonates with PCC

To a solution of the α-hydroxyphosphonate (5 mmol) in dry CH_2Cl_2 (50 ml), the PCC (5 mmol) was added. The resulting mixture was stirred at room temperature for the appropriate time (Table I). After completion of the reaction (monitoring by TLC or GC), the mixture was filtered and the solid material was washed with the same reaction solvent (2 × 25 ml). Evaporation of the solvent under reduced pressure and then bulb-to-bulb vacuum distillation afforded the desired α-ketophosphonates in 80–92% yields (Table I).

Spectral Data of α-Ketophosphonates

*Diethyl benzoyl phosphonate (**2a**).* Yield = 97–99%; b.p. = 125–126°C, 0.05 mmHg (reported b.p. = 106–109°C, 0.01 mmHg);[2a] ^{1}H NMR ($CDCl_3$, TMS): δ 1.37–1.68 (t, 6H, $^2J_{HH}$ = 7.1 Hz, 2-OCH$_2$C$\underline{H}_3$), 4.08–4.28 (dq, 4H, $^2J_{PH}$ = 7.1 Hz, $^2J_{HH}$ = 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, $^3J_{CP}$ = 5.7 Hz, 2-OCH$_2$C$\underline{H}_3$), 64.31 (d, $^2J_{CP}$ = 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, $^1J_{CP}$ = 177.5 Hz, C=O) ppm; IR (neat): ν 1650 (C=O), 1267 (P=O) cm^{-1}; MS: M$^+$ (242), M–P(O)(OEt)$_2$ (105); **$C_{11}H_{15}O_4P$** requires: C, 54.5; H, 6.2. Found: C, 54.2; H, 6.0.

*Diethyl 4-methyl-benzoyl phosphonate (**2b**).* Yield = 90–96%; b.p. = 130–131°C, 0.05 mmHg (reported b.p. = 116–117°C, 0.03 mmHg);[2a] ^{1}H NMR ($CDCl_3$, TMS): δ 1.29–1.42 (t, 6H, $^2J_{HH}$ = 7.1 Hz, 2-OCH$_2$C$\underline{H}_3$), 2.35 (s, 3H, –CH$_3$), 4.11–4.16 (dq, 4H, $^2J_{PH}$ = 7.1 Hz, $^2J_{HH}$ = 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, $^3J_{CP}$ = 5.7 Hz, 2-OCH$_2$C$\underline{H}_3$), 22.18 (–CH$_3$), 64.24 (d, $^2J_{CP}$ = 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, $^1J_{CP}$ = 176.6 Hz, C=O) ppm; IR (neat): ν 1650 (C=O), 1261 (P=O) cm^{-1}; MS: M$^+$ (256), M–P(O)(OEt)$_2$ (119); **$C_{12}H_{17}O_4P$** requires: C, 56.2; H, 6.6. Found: C, 56.0; H, 6.1.

*Diethyl 4-methoxy-benzoyl phosphonate (**2c**).* Yield = 90–94%; b.p. = 166–167°C, 0.05 mmHg (reported b.p. = 175–179°C, 1.5 mmHg);[2a] ^{1}H NMR ($CDCl_3$, TMS): δ 1.11–1.29 (t, 6H, $^2J_{HH}$ = 7.1 Hz, 2-OCH$_2$C$\underline{H}_3$), 3.80 (s, 3H, –CH$_3$), 3.90–4.10 (dq, 4H, $^2J_{PH}$ = 7.1 Hz, $^2J_{HH}$ = 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, $^3J_{CP}$ = 5.7 Hz, 2-OCH$_2$C$\underline{H}_3$), 55.59 (–CH$_3$), 63.46 (d, $^2J_{CP}$ = 7.5 Hz, 2-0$\underline{C}$H$_2$CH$_3$), 114.03, 128.82, 129.21, 159.78 (–C$_6$H$_4$), 198.01 (d, $^1J_{CP}$ = 176.2 Hz, C=O) ppm; IR (neat): ν 1655 (C=O), 1265 (P=O) cm^{-1}; MS: M$^+$ (272), M–P(O)(OEt)$_2$ (135); **$C_{12}H_{17}O_5P$** requires: C, 52.9; H, 6.2. Found: C, 52.2; H, 5.9.

*Diethyl 2,4,6-trimethyl-benzoyl phosphonate (**2d**).* Yield = 88–95%; b.p. = 108–109°C, 0.07 mmHg (reported b.p. = 131–132°C, 0.3 mmHg);[2a] ^{1}H NMR ($CDCl_3$, TMS): δ 1.25–1.32 (t, 6H, $^2J_{HH}$ = 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, $^2J_{PH}$ = 7.1 Hz, $^2J_{HH}$ = 7.1 Hz, 2-OC$\underline{H}_2$CH$_3$), 6.83 (s, 2H) ppm; ^{13}C NMR ($CDCl_3$, TMS): 16.81 (d, $^3J_{CP}$ = 5.7 Hz, 2-OCH$_2$C$\underline{H}_3$), 21.17 (2,6-diCH$_3$), 21.38 (4-CH$_3$), 63.12 (d, $^2J_{CP}$ = 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, $^1J_{CP}$ = 177.0 Hz, C=O) ppm; IR (neat): ν 1665 (C=O), 1250 (P=O) cm^{-1}; MS: M$^+$ (284), M–P(O)(OEt)$_2$ (142); **C$_{14}$H$_{21}$O$_4$P** requires: C, 59.1; H, 7.4. Found: C, 59.3; H, 7.6.

*Diethyl 2-chloro-benzoyl phosphonate (**2e**).* Yield = 87–97%; b.p. = 105–106°C, 0.05 mmHg (reported b.p. = 158–160°C, 2.3 mmHg);[19] ^{1}H NMR ($CDCl_3$, TMS): δ 1.58 (t, 6H, $^2J_{HH}$ = 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, $^3J_{CP}$ = 5.7 Hz, 2-OCH$_2$C$\underline{H}_3$), 64.82 (d, $^2J_{CP}$ = 7.4 Hz, 2-0$\underline{C}$H$_2$CH$_3$), 126.84, 127.10, 130.64–132.07, 132.68–133.85, 134.16–135.98 (–C$_6$H$_4$), 200.53 (d, $^1J_{CP}$ = 182.0 Hz, C=O) ppm; IR (neat): ν 1650 (C=O), 1245 (P=O) cm^{-1}; MS: M$^+$ (276), M+2 (279), M–P(O)(OEt)$_2$ (139); **C$_{11}$H$_{14}$ClO$_4$P** requires: C, 47.8; H, 5.1. Found: C, 47.5 H, 4.9.

*Diethyl 3-chloro-benzoyl phosphonate (**2f**).* Yield = 89–98%; b.p. = 101–102°C, 0.06 mmHg (reported b.p. = 127°C, 0.4 mmHg);[20] ^{1}H NMR ($CDCl_3$, TMS): δ 1.28–1.34 (m, 6H, 2-OCH$_2$C$\underline{H}_3$), 4.16–4.27 (m, 4H, 2-OC$\underline{H}_2$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$_2$C$\underline{H}_3$), 66.45 (d, $^2J_{CP}$ = 7.4 Hz, 2-0$\underline{C}$H$_2$CH$_3$), 130.15–139.50 (–C$_6$H$_4$), 201.46 (d, $^1J_{CP}$ = 182.0 Hz, C=O) ppm; IR (neat): ν 1650 (C=O), 1267 (P=O) cm^{-1}; MS: M$^+$ (276), M+2 (279), M–P(O)(OEt)$_2$ (139); **C$_{11}$H$_{14}$ClO$_4$P** requires: C, 47.8; H, 5.1. Found: C, 47.4; H, 4.7.

*Diethyl 4-chloro-benzoyl phosphonate (**2g**).* Yield = 93–95%; b.p. = 142–143°C, 0.06 mmHg (reported b.p. = 112–113°C, 0.01 mmHg);[2a] ^{1}H NMR ($CDCl_3$, TMS): δ 1.13–1.42 (t, 6H, $^2J_{HH}$ = 7.1 Hz, 2-OCH$_2$C$\underline{H}_3$), 4.15–4.33 (dq, 4H, $^2J_{PH}$ = 7.1 Hz, $^2J_{HH}$ = 7.1 Hz, 2-OC$\underline{H}_2$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$_2$C$\underline{H}_3$), 64.49 (d, $^2J_{CP}$ = 7.5 Hz, 2-O$\underline{C}$H$_2$CH$_3$), 129.62, 131.58, 133.72, 141.85 (–C$_6$H$_4$), 198.09 (d, $^1J_{CP}$ = 180.0 Hz, C=O) ppm; IR (neat): ν 1650 (C=O), 1260 (P=O) cm^{-1}; MS: M$^+$ (277), M+2 (279), M–P(O)(OEt)$_2$ (139); **C$_{11}$H$_{14}$ClO$_4$P** requires: C, 47.8; H, 5.1. Found: C, 47.9; H, 5.3.

*Diethyl 2,6-dichloro-benzoyl phosphonate (**2h**).* Yield = 92–99%; b.p. = 150–151°C, 0.05 mmHg; ^{1}H NMR ($CDCl_3$, TMS): δ 1.04–1.24 (t,

6H, $^2J_{HH}$ = 7.1 Hz, 2-OCH$_2$C$\underline{H}_3$), 3.95–4.23 (dq, 4H, $^2J_{PH}$ = 7.1 Hz, $^2J_{HH}$ = 7.1 Hz, 2-OC$\underline{H}_2$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$_2$C$\underline{H}_3$), 64.85 (d, $^2J_{CP}$ = 7.5 Hz, 2-O$\underline{C}$H$_2$CH$_3$), 128.06, 128.56, 131.51, 132.07 (–C$_6$H$_3$), 204.36 (d, $^1J_{CP}$ = 195.5 Hz, C=O) ppm; IR (neat): ν 1691 (C=O), 1264 (P=O) cm^{-1}; MS: M$^+$ (311), M+2 (313), M+4 (315), M–P(O)(OEt)$_2$ (174); **C$_{11}$H$_{13}$Cl$_2$O$_4$P** requires: C, 42.4; H, 4.2. Found: C, 42.0; H, 4.0.

*Diethyl 2-nitro-benzoyl phosphonate (**2i**).* Yield = 89–91%; b.p. = 146–147°C, 0.05 mmHg; ^{1}H NMR (CDCl$_3$, TMS): δ 1.34 (t, 6H, $^2J_{HH}$ = 7.0 Hz, 2-OCH$_2$C$\underline{H}_3$), 4.20–4.32 (dq, 4H, $^2J_{PH}$ = 7.2 Hz, $^2J_{HH}$ = 7.3 Hz, 2-OC$\underline{H}_2$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, 2-OCH$_2$C$\underline{H}_3$), 64.92 (d, $^2J_{CP}$ = 7.2 Hz, 2-O$\underline{C}$H$_2$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): ν 1655 (C=O), 1260 (P=O) cm^{-1}; MS: M$^+$ (287), M–P(O)(OEt)$_2$ (150); **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**).* Yield = 88–91%; b.p. = 149–150°C, 0.05 mmHg; ^{1}H NMR (CDCl$_3$, TMS): δ 1.15–1.43 (m, 6H, 2-OCH$_2$C$\underline{H}_3$), 4.10–4.20 (q, 2H, $^2J_{HH}$ = 7.1 Hz, 2-OC$\underline{H}_2$CH$_3$), 4.30–4.39(q, 2H, $^2J_{HH}$ = 7.1 Hz, 2-OC$\underline{H}_2$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$_2$C$\underline{H}_3$), 65.12 (d, $^2J_{CP}$ = 7.5 Hz, 2-O$\underline{C}$H$_2$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): ν 1650 (C=O), 1260 (P=O) cm^{-1}; MS: M$^+$ (287), M–P(O)(OEt)$_2$ (150); **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**).* Yield = 87–90%; m.p. = 1140.141°C (reported m.p. = 142–143°C);[21] ^{1}H NMR (CDCl$_3$, TMS): δ 1.23–1.321 (m, 6H, 2-OCH$_2$C$\underline{H}_3$), 4.00–4.18 (m, 2H, 2-OC$\underline{H}_2$CH$_3$), 7.66 (d, 2H, $^2J_{HH}$ = 7.5 Hz), 8.7 (d, 2H, $^2J_{HH}$ = 8.7 Hz) ppm; IR (KBr): ν 1650 (C=O), 1260 (P=O) cm^{-1}; MS: M$^+$ (287), M–P(O)(OEt)$_2$ (150); **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**).* Yield = 87–91%; b.p. = 152–153°C, 0.07 mmHg (reported b.p. = 188–191°C, 1.2 mmHg);[19] ^{1}H NMR (CDCl$_3$, TMS): δ 11.33–1.44 (m, 6H, 2-OCH$_2$C$\underline{H}_3$), 4.28–4.39 (m, 4H, 2-OC$\underline{H}_2$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$_2$C$\underline{H}_3$), 64.52 (d, $^2J_{CP}$ = 7.3 Hz, 2-O$\underline{C}$H$_2$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): ν 1655 (C=O), 1260 (P=O) cm^{-1}; MS: M$^+$ (292),

M–P(O)(OEt)$_2$ (155); **$C_{15}H_{17}O_4P$** requires: C, 61.6; H, 5.8. Found: C, 61.2; H, 5.3.

*Diethyl 3-pridoyl phosphonate (**2m**).* Yield = 96–97%; b.p. = 125–126°C, 2 mmHg (reported b.p. = 128°C, 2 mmHg);[22] ^{1}H NMR ($CDCl_3$, TMS): δ 1.23–1.36 (m, 6H, 2-OCH$_2$C$\underline{H}_3$), 4.14–4.30 (m, 4H, 2-OC$\underline{H}_2$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$_2$C$\underline{H}_3$), 64.72 (d, $^2J_{CP}$ = 7.5 Hz, 2-OC$\underline{H}_2$CH$_3$), 124.11, 131.96, 151.27, 154.90 (C_5H_4N), 199.18 (d, $^1J_{CP}$ = 183.5 Hz, C=O) ppm; IR (neat): ν 1654 (C=O), 1245 (P=O) cm^{-1}; MS: M$^+$ (243), M–P(O)(OEt)$_2$ (106); **$C_{10}H_{14}NO_4P$** requires: C, 49.4; H, 5.8. Found: C, 49.0; H, 5.4.

*Diethyl 1-oxo-3-phenyl-2-propenylphosphonate (**2n**).* Yield=90–95%; b.p.=108–109°C, 0.05 mmHg; ^{1}H NMR ($CDCl_3$, TMS): δ 1.30 (t, 6H, $^2J_{HH}$ = 7.1 Hz, 2-OCH$_2$C$\underline{H}_3$), 4.14 (dq, 4H, $^2J_{PH}$ = 7.1 Hz, $^2J_{HH}$ = 7.1 Hz, 2-OC$\underline{H}_2$CH$_3$), 7.38–7.43 (m, 1H), 8.45–8.48 (m, 1H), 8.77–8.78 (m, 1H), 9.34 (s, 1H) ppm; ^{13}C NMR ($CDCl_3$, TMS): 16.72 (d, $^3J_{CP}$ = 5.7 Hz, 2-OCH$_2$C$\underline{H}_3$), 64.72 (d, $^2J_{CP}$ = 7.5 Hz, 2-OC$\underline{H}_2$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): ν 1655 (C=O), 1260 (P=O) cm^{-1}; MS: M$^+$ (268), M–P(O)(OEt)$_2$ (131); **$C_{13}H_{17}O_4P$** requires: C, 58.2; H, 6.3. Found: C, 58.0; H, 6.1.

*Diethyl 1-oxo-2-butenylphosphonate (**2o**).* Yield = 85–88%; b.p. = 105–105°C, 10 mmHg; (reported b.p. = 109°C, 10 mmHg);[2d] ^{1}H NMR ($CDCl_3$, TMS): δ 1.18–1.33 (m, 6H, 2-OCH$_2$C$\underline{H}_3$), 1.90–1.96 (m, 3H, CH$_3$), 4.02–4.20 (m, 4H, 2-OC$\underline{H}_2$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$_2$C$\underline{H}_3$), 18.18 (CH$_3$), 63.14 (d, $^2J_{CP}$ = 7.3 Hz, 2-OC$\underline{H}_2$CH$_3$), 126.10, 129.78 (CH=CH), 198.08 (d, $^1J_{CP}$=189.5 Hz, C=O) ppm; IR (neat): ν 1665 (C=O), 1265 (P=O) cm^{-1}; MS: M$^+$ (206), M–P(O)(OEt)$_2$ (69); **$C_8H_{15}O_4P$** requires: C, 46.46; H, 7.3. Found: C, 46.41; H, 7.1.

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[23] 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.