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A new, efficient, and simple method for the one-pot synthesis of α-acetoxyphosphonates from aldehydes under solvent-free conditions

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Abstract—A simple, efficient, and new method has been developed for the synthesis of α-acetoxyphosphonates from aldehydes through a one-pot reaction of aldehydes with diethylphosphite in the presence of acetic anhydride under solvent-free conditions using magnesium oxide. This method is easy, rapid, and high yielding for the one-pot synthesis of α-acetoxyphosphonates from aldehydes.

Organophosphorus compounds have found a wide range of application in the areas of industrial, agricultural, and medicinal chemistry owing to their biological and physical properties as well as their utility as synthetic intermediates.[1] α-Functionalized phosphonic acids are valuable intermediates for the preparation of medicinal compounds and synthetic intermediates.[2–4] Among of α-functional phosphonic acids, α-acetoxyphosphonates and α-hydroxyphosphonates are an important class of compounds that exhibit a variety of interesting and useful properties. In recent years, the preparation of α-acetoxy and α-hydroxyphosphonates has attracted a great deal of attention due to their potential biological activities with broad applications as enzyme inhibitors or as dinucleotide analogues having antiviral properties.[5] In addition, they are useful intermediates in the synthesis of other phosphorus compounds.[6] These compounds may also be used as precursors for the synthesis of optically active α-hydroxyphosphonates.[7] Indeed, α-acetoxyphosphonates are also used as precursors for the synthesis of a variety of α-substituted phosphonates. In contrast to the widely studied α-hydroxyphosphonic acid derivatives,[8–10] relatively few papers have been reported on the chemistry of α-acetoxyphosphonates.[5] Many effective methods for the preparation of α-hydroxyphosphonates have been developed, but, to the best of our knowledge, few synthetic routes to α-acetoxyphosphonates have been reported. These methods involve prolonged heating of acyl phosphates with carbonyl compounds at 120 °C,[11] direct acetylation of α-hydroxyphosphonates with ketenes catalyzed by $BF_3.OEt$[12] or H_2SO_4,[13] and acetylation of α-hydroxyphosphonates with Ac_2O or AcCl in the presence of Et_3N or pyridine as a base.[5a,7,14] Recently, new methods have been reported using copper triflate as a catalyst and microwave irradiation for the preparation of α-acetoxyphosphonates from the reaction of α-hydroxyphosphonates with Ac_2O.[15] However, these methods have problems, including harsh reaction conditions, low yields, long reaction times, use of Lewis acids, and side reactions. On the other hand in all methods, each of the starting materials requires prior synthesis. Surface-mediated solid-phase reactions are of growing interest[16] because of their advantages of ease of set up, mild conditions, rapid reactions, selectivity, increased yields of the products, and low cost compared with their homogeneous counterpart. As part of our efforts to explore the utility of solid-phase reactions for the synthesis of organophosphorus compounds,[17] we report a new method for the one-pot synthesis of α-acetoxyphosphonates from the reaction of diethylphosphite with aldehydes in the presence of Ac_2O under solvent-free conditions, using MgO as a solid phase producing good to high yields of α-acetoxyphosphonates (Scheme 1, Table 1).

Keywords: Aldehydes; Magnesia; Solvent-free; Phosphorylation; Acetic anhydride.
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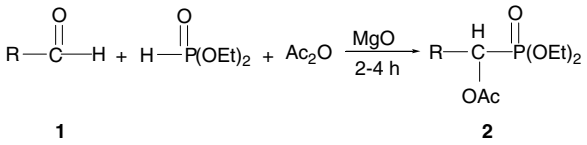

Scheme 1.

Table 1. Synthesis of α-acetoxyphosphonates from aldehydes using MgO under solvent-free condition

Compound	R	Reaction time (h)	Yield[a] (%), **2**
1a	C_6H_5–	2	90
1b	*p*-$CH_3OC_6H_4$–	2	86
1b	*p*-$CH_3C_6H_4$–	3	83
1c	*p*-ClC_6H_4–	2	80
1d	*p*-BrC_6H_4–	2	90
1c	*m*-ClC_6H_4–	2	75
1d	*m*-$CH_3OC_6H_4$–	3	87
1e	*m*-BrC_6H_4–	3	85
1f	*m*-$CH_3C_6H_4$–	3	81
1g	*o*-ClC_6H_4–	2	83
1h	*o*-$CH_3C_6H_4$–	4	80
1i	α-Naphthyl	3	65
1j	β-Naphthyl	2	75
1k	Ph–CH=CH–	3	72

[a] Isolated yields.

As shown in Scheme 1 and Table 1, the reaction of a mixture of diethylphosphite and aromatic aldehydes (**1a**–**1h**) with Ac_2O under solvent-free condition using MgO afforded the desired products in high yields (**2a**–**2h**). Naphthalene carbaldehydes as polynuclear aldehydes also reacted with diethylphosphite in the presence of Ac_2O using MgO, to give the desired compounds in high yields (**2i** and **2j**). Cinnamaldehyde (**1k**) also reacted to give the desired compound **2k** in good yield.

In all the reactions we have reported in this paper cleavage of C–P bond of the phosphonates was not detected and the conversion of the substrates to their corresponding acetyloxy compounds was clean. Work-up of the reaction mixture is very easy and gives highly pure products, which do not need further purification.[18]

In summary, in this paper, we have described a simple procedure for the high yielding synthesis of a variety of diethyl α-acetoxyphosphonates by one-pot reaction of aldehydes with diethylphosphite in the presence of acetic anhydride using magnesia. Simple work-up, solvent-free condition, fast reaction rates, mild reaction conditions, good to high yields, and the clean reactions with no tar formation make this method an attractive and a useful contribution to present methodologies.

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18. This solvent-free reaction is operationally simple. Magnesium oxide (1 g) was added to a stirred mixture of diethylphosphite (0.01 mol) and aldehyde (0.01 mol) at room temperature. Acetic anhydride (0.03 mol) was added to this mixture which was then stirred for 2–4 h at room temperature. The mixture was washed with ethyl acetate (4× 50 mL), dried with $CaCl_2$, and the solvent evaporated to give crude product. Chromatography on silica gel with EtOAc/*n*-hexane (3:7) and evaporation of the solvent under reduced pressure gave the pure products in 65–90% yields. All the products gave satisfactory spectral data in accordance with the assigned structures. Diethyl 1-acetoxyphenylmethylphosphonate (**2a**).[15] Colorless oil; ^{1}H NMR ($CDCl_3$/TMS—250 MHz): 1.13–1.32 (6H, m), 2.09 (3H, d, J = 2 Hz), 3.75–4.10 (4H, m), 6.06 (1H, d, J = 13.5 Hz), 7.21–7.43 (5H, m). ^{31}P NMR ($CDCl_3$/H_3PO_4—101.2 MHz):17.82 ppm; ^{13}C NMR ($CDCl_3$/TMS—62.9 MHz):16.2 (d, J_{PC} = 6.3 Hz), 16.3 (d, J_{PC} = 6.3 Hz), 20.8, 63.1–63.3, 67.6 (d, J_{PC} = 169.8 Hz), 127.8 (d, J_{PC} = 5.7 Hz), 128.4 (d, J_{PC} = 2.5 Hz), 128.6 (d, J_{PC} = 2.5 Hz), 133.4 (d, J_{PC} = 1.9 Hz), 169.3 (d, J_{PC} = 9.0 Hz). Diethyl 1-acetoxy(4-methoxyphenyl)methyl phosphonate (**2b**).[15] Colorless oil; ^{1}H NMR ($CDCl_3$/TMS—250 MHz): 1.13–1.22 (6H, m), 2.09 (3H, d, J = 1.2 Hz), 3.77 (3H, d, J = 1.5 Hz), 3.85–4.15 (4H, m), 6.05 (1H, d, J = 13.0 Hz), 6.86 (2H, d, J = 7.7 Hz), 7.41 (2H, d, J = 7.7 Hz). ^{31}P NMR ($CDCl_3$/H_3PO_4—101.2 MHz):18.22 ppm; ^{13}C NMR ($CDCl_3$/TMS—62.9 MHz):16.2 (d, J_{PC} = 5.8 Hz), 16.4 (d, J_{PC} = 5.7 Hz), 20.9, 55.2, 63.1–63.3, 70.0 (d, J_{PC} = 172.7 Hz), 113.9 (d, J_{PC} = 1.8 Hz), 125.4 (d, J_{PC} = 1.8 Hz), 129.5 (d, J_{PC} = 6.1 Hz), 159.9 (d, J_{PC} = 2.5 Hz), 169.3 (d, J_{PC} = 9.1 Hz). Diethyl 1-acetoxy(4-methylphenyl)methyl phosphonate (**2c**).[15] Colorless oil; ^{1}H NMR ($CDCl_3$/TMS—250 MHz): 1.15–1.30 (6H, m), 2.14 (3H, s), 2.32 (3H, s), 3.85–4.15 (4H, m), 6.09 (1H, d, J = 13.2 Hz), 7.16 (2H, d, J = 8.0 Hz), 7.38 (2H, d, J = 8.0 Hz). ^{31}P NMR ($CDCl_3$/H_3PO_4—101.2 MHz):18.09 ppm; ^{13}C NMR ($CDCl_3$/TMS—62.9 MHz):16.2 (d, J_{PC} = 5.8 Hz), 16.4 (d, J_{PC} = 5.7 Hz), 20.9, 21.2, 63.2 (d, J_{PC} = 6.8 Hz), 70.3 (d, J_{PC} = 171.0 Hz), 127.9 (d, J_{PC} = 6.0 Hz), 129.1 (d, J_{PC} = 2.1 Hz), 130.4 (d, J_{PC} = 2.0 Hz), 138.6 (d, J_{PC} = 3.0 Hz), 169.3 (d, J_{PC} = 9.0 Hz). Diethyl 1-acetoxy(4-chlorophenyl)methyl phosphonate (**2d**).[15] Colorless oil; ^{1}H NMR ($CDCl_3$/TMS—250 MHz): 1.13–1.30 (6 H, m), 2.13 (3H, s), 3.85–4.18 (4H, m), 6.05 (1H, d, J = 13.7 Hz), 7.30 (2H, d, J = 8.5 Hz), 7.39 (2H, d, J = 8.5 Hz). ^{31}P NMR ($CDCl_3$/H_3PO_4—101.2 MHz):17.20 ppm; ^{13}C NMR ($CDCl_3$/TMS—62.9 MHz):16.2 (d, J_{PC} = 6.3 Hz), 16.3 (d, J_{PC} = 6.3 Hz), 20.6, 63.2–63.3, 69.8 (d, J_{PC} = 171.1 Hz), 128.6 (d, J_{PC} = 1.9 Hz), 129.2 (d, J_{PC} = 5.7 Hz), 132.2 (d, J_{PC} = 1.9 Hz), 134.6 (d, J_{PC} = 3.1 Hz), 168.9 (d, J_{PC} = 8.8 Hz). Diethyl 1-acetoxy(4-bromophenyl)methyl phosphonate (**2e**). Colorless oil; ^{1}H NMR ($CDCl_3$/TMS—250 MHz): 1.15–1.30 (6H, m), 2.15 (3H, s), 3.80–4.08 (4H, m), 6.03 (1H, d, J = 13.7 Hz), 7.33 (2H, d, J = 8.2 Hz), 7.47 (2H, d, J = 8.2 Hz). ^{31}P NMR ($CDCl_3$/H_3PO_4—101.2 MHz):17.15 ppm; ^{13}C NMR ($CDCl_3$/TMS—62.9 MHz):16.3 (d, J_{PC} = 6.3 Hz), 16.4 (d, J_{PC} = 6.3 Hz), 20.8, 63.3–63.4, 69.8 (d, J_{PC} = 170.6 Hz), 122.9 (d,J_{PC} = 3.6 Hz), 129.5 (d, J_{PC} = 5.8 Hz), 131.6 (d, J_{PC} = 2.1 Hz), 132.6 (d, J_{PC} = 2.0 Hz), 169.2 (d, J_{PC} = 9.0 Hz). Anal. Calcd for $C_{13}H_{18}BrO_5P$: C, 42.74; H, 4.93. Found: C, 42.8; H, 5.1. Diethyl 1-acetoxy(3-chlorophenyl)methyl phosphonate (**2f**).[15] Colorless oil; ^{1}H NMR ($CDCl_3$/TMS—250 MHz): 1.10–1.25 (6H, m), 2.10 (3H, s), 3.85–4.18 (4H, m), 6.05 (1H, d, J = 14.0 Hz), 7.15–7.45 (4H, m). ^{31}P NMR ($CDCl_3$/H_3PO_4—101.2 MHz): 16.92 ppm; ^{13}C NMR ($CDCl_3$/TMS—62.9 MHz): 16.1 (d, J_{PC} = 5.6 Hz), 16.2 (d, J_{PC} = 5.6 Hz), 20.6, 63.2 (d, J_{PC} = 6.3 Hz), 63.3 (d, J_{PC} = 6.3 Hz), 69.8 (d, J_{PC} = 169.8 Hz), 125.9 (d, J_{PC} = 5.6 Hz), 127.7 (d, J_{PC} = 5.7 Hz), 128.7 (d, J_{PC} = 2.5 Hz), 129.6, 134.3, 135.6, 168.9 (d, J_{PC} = 8.2 Hz). Diethyl 1-acetoxy(3-methoxyphenyl)methyl phosphonate (**2g**).[7b] Colorless oil; ^{1}H NMR ($CDCl_3$/TMS—250 MHz): 1.15–1.29 (6H, m), 2.14 (3H,s), 3.78 (3H, d, J = 1.5 Hz), 3.85–4.15 (4H, m), 6.07 (1H, d, J = 13.7 Hz), 6.78–7.28 (4H, m). ^{31}P NMR ($CDCl_3$/H_3PO_4—101.2 MHz): 17.76 ppm; ^{13}C NMR ($CDCl_3$/TMS—62.9 MHz): 16.2 (d, J_{PC} = 5.8 Hz), 16.4 (d, J_{PC} = 5.9 Hz), 20.9, 55.2, 63.3 (d, J_{PC} = 5.9 Hz), 70.3 (d, J_{PC} = 170.1 Hz), 113.1 (d, J_{PC} = 5.5 Hz), 114.3 (d, J_{PC} = 2.7 Hz), 120.1 (d, J_{PC} = 5.8 Hz), 129.5, 134.8, 159.5, 169.2 (d, J_{PC} = 9.1 Hz). Diethyl 1-acetoxy(3-bromophenyl)methyl phosphonate (**2h**). Colorless oil; ^{1}H NMR ($CDCl_3$/TMS—250 MHz): 1.10–1.25 (6H, m), 2.10 (2H, d, J = 2.2 Hz), 3.85–4.18 (4H, m), 6.03 (1H, d, J = 13.7 Hz), 7.10–7.58 (4H, m). ^{31}P NMR ($CDCl_3$/H_3PO_4—101.2 MHz):17.03 ppm; ^{13}C NMR ($CDCl_3$/TMS—62.9 MHz):16.1 (d, J_{PC} = 5.7 Hz), 16.2 (d, J_{PC} = 5.7 Hz), 20.6, 63.2 (d, J_{PC} = 7.0 Hz), 63.3 (d, J_{PC} = 7.0 Hz), 69.4 (d, J_{PC} = 169.8 Hz), 122.2 (d, J_{PC} = 2.5 Hz), 126.3 (d, J_{PC} = 5.0 Hz), 129.8 (d, J_{PC} = 1.9 Hz), 130.4 (d, J_{PC} = 5.7 Hz), 131.5 (d, J_{PC} = 2.5 Hz), 135.6 (d, J_{PC} = 1.9 Hz), 168.8 (d, J_{PC} = 8.8 Hz). Anal. Calcd for $C_{13}H_{18}BrO_5P$: C, 42.74; H, 4.93. Found:C, 42.6; H, 5.1. Diethyl 1-acetoxy(3-methylphenyl)methyl phosphonate (**2i**). Colorless oil; ^{1}H NMR ($CDCl_3$/TMS—250 MHz): 1.15–1.30 (6H, m), 2.16 (3H, s), 2.34 (3H, s), 3.85–4.15 (4H, m), 6.09 (1H, d, J = 13.2 Hz), 7.10–7.45 (4H, m). ^{31}P NMR ($CDCl_3$/H_3PO_4—101.2 MHz):18.00 ppm; ^{13}C NMR ($CDCl_3$/TMS—62.9 MHz):16.2 (d, J_{PC} = 5.9 Hz), 16.4 (d, J_{PC} = 5.9 Hz), 20.9, 21.4, 63.1–63.3, 70.5 (d, J_{PC} = 170.1 Hz), 124.9 (d, J_{PC} = 5.8 Hz), 128.3 (d, J_{PC} = 2.2 Hz), 128.5 (d, J_{PC} = 5.9 Hz), 129.5 (d, J_{PC} = 2.8 Hz), 133.3, 138.1, 169.3 (d, J_{PC} = 8.9 Hz). Anal. Calcd for $C_{14}H_{21}O_5P$: C, 56.00; H, 7.00. Found:C, 56.2; H, 7.2. Diethyl 1-acetoxy(2-chlorophenyl)methyl phosphonate (**2j**).[15] Colorless oil; ^{1}H NMR ($CDCl_3$/TMS—250 MHz): 1.15 (3H, t, J = 7.0 Hz), 1.28 (3H, t, J = 7.0 Hz), 2.12 (3H, s), 3.80–4.21 (4H, m), 6.58 (1H, d, J = 13.8 Hz), 7.15–7.65 (4H, m). ^{31}P NMR ($CDCl_3$/H_3PO_4—101.2 MHz):17.24 ppm; ^{13}C NMR ($CDCl_3$/TMS—62.9 MHz):16.2 (d, J_{PC} = 5.7 Hz), 16.3 (d, J_{PC} = 5.7 Hz), 20.7, 63.2 (d, J_{PC} = 6.6 Hz), 66.8 (d, J_{PC} = 172.3 Hz), 127.0, 129.4, 129.6 (d, J_{PC} = 3.8 Hz), 129.8 (d, J_{PC} = 2.8 Hz), 131.9, 133.6 (d, J_{PC} = 7.9 Hz), 168.9 (d, J_{PC} = 9.6 Hz). Diethyl 1-acetoxy(2-methylphenyl)methyl phosphonate (**2k**).[7b] Colorless oil; ^{1}H NMR ($CDCl_3$/TMS—250 MHz): 1.10–1.35 (6H, m), 2.14 (3H, s), 2.48 (3H, s), 3.85–4.18 (4H, m), 6.36 (1H, d, J = 13.7 Hz), 7.10–7.65 (4H, m). ^{31}P NMR ($CDCl_3$/H_3PO_4—101.2 MHz): 18.58 ppm; ^{13}C NMR ($CDCl_3$/TMS—62.9 MHz): 16.2 (d, J_{PC} = 5.6 Hz), 16.4 (d, J_{PC} = 5.6 Hz), 19.6, 20.92, 63.2 (d, J_{PC} = 6.9 Hz), 67.0 (d, J_{PC} = 171.7 Hz), 126.2, 128.1 (d, J_{PC} = 4.4 Hz), 128.6130.3, 132.1, 136.7 (d, J_{PC} = 7.5 Hz), 169.3 (d, J_{PC} = 10.0 Hz). Diethyl 1-acetoxy(1-naphthyl)methyl

phosphonate (**2l**).[15] Colorless oil; ^{1}H NMR ($CDCl_3$/TMS—250 MHz): 0.95 (3H, t, J = 7.0 Hz), 1.15 (3H, t, J = 7.0 Hz), 2.10 (3H, s), 3.58–4.21 (4H, m), 6.94 (1H, d, J = 14.2 Hz), 7.35–8.0 (6H, m), 8.22 (1H, d, J = 8.5 Hz). ^{31}P NMR ($CDCl_3/H_3PO_4$—101.2 MHz): 18.13 ppm; ^{13}C NMR ($CDCl_3$/TMS—62.9 MHz): 16.1 (d, J_{PC} = 5.6 Hz), 16.3 (d, J_{PC} = 5.6 Hz), 20.8, 63.2 (d, J_{PC} = 6.6 Hz), 67.1 (d, J_{PC} = 172.0 Hz), 123.7, 125.2 (d, J_{PC} = 3.8 Hz), 125.8, 126.5, 126.7 (d, J_{PC} = 5.9 Hz), 128.6, 129.4, 129.7, 133.6 (d, J_{PC} = 5.5 Hz), 133.6, 169.2 (d, J_{PC} = 9.0 Hz). Diethyl 1-acetoxy(2-naphthyl)methyl phosphonate (**2l**).[15,7b] Colorless oil; ^{1}H NMR ($CDCl_3$/TMS—250 MHz): 1.10 (3H, t, J = 7.0 Hz), 1.17 (3H, t, J = 7.0 Hz), 2.10 (3H, s), 3.75–4.15 (4H, m), 6.28 (1H, d, J = 13.7 Hz), 7.30–7.95 (7H, m). ^{31}P NMR ($CDCl_3/H_3PO_4$—101.2 MHz): 17.82 ppm; ^{13}C NMR ($CDCl_3$/TMS—62.9 MHz): 16.2 (d, J_{PC} = 5.7 Hz), 16.3 (d, J_{PC} = 5.7 Hz), 20.8, 63.2–63.3, 70.5 (d, J_{PC} = 169.8 Hz), 125.2 (d, J_{PC} = 4.4 Hz), 126.3, 126.5, 127.3 (d, J_{PC} = 7.5 Hz), 127.6, 128.1, 128.2 (d, J_{PC} = 1.9 Hz), 130.9 (d, J_{PC} = 2.5 Hz), 132.9 (d, J_{PC} = 2.5 Hz), 133.2 (d, J_{PC} = 2.5 Hz), 169.2 (d, J_{PC} = 8.8 Hz). Diethyl 1-acetoxy(2-phenylethenyl)methyl phosphonate (**2j**).[15] Colorless oil; ^{1}H NMR ($CDCl_3$/TMS—250 MHz): 1.15–1.35 (6H, m), 2.11 (3H, s), 3.95–4.30 (4H, m), 5.80 (1H, ddd, J = 1.0, J = 7.2 and J = 14.0 Hz), 6.10–6.25 (1H, m), 6.58 (1H, dd, J = 3.5 and J = 15.7 Hz), 7.15–7.45 (5H, m). ^{31}P NMR ($CDCl_3/H_3PO_4$—101.2 MHz): 6.72 ppm; ^{13}C NMR ($CDCl_3$/TMS—62.9 MHz): 16.2–16.3, 20.8, 63.1–63.4, 69.2 (d, J_{PC} = 171.4 Hz), 120.1 (d, J_{PC} = 4.5 Hz) 126.7 (d, J_{PC} = 1.3 Hz), 128.6, 135.0, 135.6 (d, J_{PC} = 2.8 Hz), 169.2 (d, J_{PC} = 7.9 Hz).