A facile and highly efficient route to α-amino phosphonates *via* three-component reactions catalyzed by $Mg(ClO_4)_2$ or molecular iodine

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Received 20th February 2006, Accepted 6th March 2006
First published as an Advance Article on the web 28th March 2006
DOI: 10.1039/b602536f

Three-component reactions of aldehydes, amines, and diethyl phosphite catalyzed by $Mg(ClO_4)_2$ or molecular iodine afforded the corresponding α-amino phosphonates in excellent yields under mild reaction conditions.

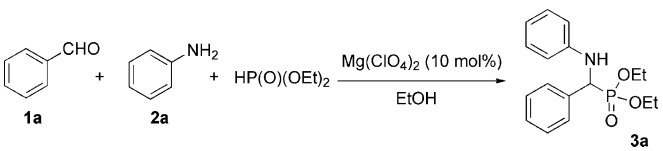
Introduction

In recent years, magnesium perchlorate has been utilized as a mild Lewis acid, imparting high regio-, chemo- and stereo-selectivity in various organic transformations.[1] Moreover, it has been found to retain its activity even in the presence of amines and also effectively activates nitrogen-containing compounds such as imines. Very recently, we also found that it was highly effective as a catalyst for the synthesis of quinolines *via* Friedländer annulation.[1a] Herein, we wish to report its application as a catalyst for the efficient synthesis of α-amino phosphonate *via* three-component reactions of aldehydes, amines, and diethyl phosphite under mild conditions.

α-Amino phosphonic acids, their phosphonate esters, and short peptides incorporating this unit are excellent inhibitors of a wide range of proteolytic enzymes.[2] In addition, α-amino phosphonate derivatives have broad applications due to their antibacterial[3] and antifungal[4] activity, and as inhibitors of phosphatase activity.[5] Lewis acid-catalyzed addition of diethyl phosphite to aldimine provides a useful method for the preparation of α-amino phosphonate.[6] Recently, three-component α-amino phosphonate syntheses starting from aldehydes, amines, and diethylphophite or triethyl phosphite catalyzed by Lewis acids[7] and Brønsted acid,[8] or under microwave conditions[9] have been reported. However, many of these procedures suffered from the use of stoichiometric and/or toxic, relatively expensive reagents. Since α-amino phosphonate derivatives are increasingly useful and important in pharmaceuticals and industry, the development of a simple, eco-benign, low cost protocol is still desirable. As α-amino phosphonate synthesis *via* three-component reactions is among the most important acid-mediated reactions, the development of a reaction that uses a catalytic amount of a readily available magnesium salt of low toxicity should be of great interest.

Results and discussion

An initial study was performed by the treatment of benzaldehyde **1a**, aniline **2a**, and diethyl phosphite in EtOH in the presence of a catalytic amount of $Mg(ClO_4)_2$ (10 mol%) at room temperature (Scheme 1). To our delight, we observed the formation of product **3a**. Complete conversion and 79% isolated yield were obtained after 24 hours. Further studies established that EtOH was the best choice of solvent among the solvents (EtOH, THF, CH_2Cl_2, CH_3CN, toluene) screened. Next, we surveyed the temperature for the reaction shown in Scheme 1. When the temperature was elevated to 40 °C, the reaction time was shortened to 16 hours. The result was dramatically improved when the reaction was performed at 50 °C or 60 °C. Only 5 hours were needed for completion and the isolation of desired compound **3a** in 84% yield. Then, we examined the catalytic requirement of $Mg(ClO_4)_2$ (1–10 mol%) for the reaction in ethanol at 50 °C. A similar result was obtained (5 hours, 85% yield) when a catalytic amount of 5 mol% magnesium perchlorate was employed in the reaction. Gratifyingly, 1 mol% of $Mg(ClO_4)_2$ was found to be sufficient for catalysis of α-amino phosphonate synthesis although a prolonged reaction time was needed for completion with slightly lower yield (1 mol% of $Mg(ClO_4)_2$, 12 hours, 60% yield). The result also provides evidence that there is no deactivation or inhibition of the magnesium catalyst, which is of interest considering that the reactants and/or the amine product might act as a Lewis base. Moreover, it is noteworthy that this reaction could be performed open to the air without loss of efficiency.



Scheme 1 Reaction of **1a**, **2a**, and diethyl phosphite in EtOH catalyzed by $Mg(ClO_4)_2$ (10 mol%).

To demonstrate the generality of this method, we next investigated the scope of this reaction under the optimized conditions (EtOH, 5 mol% of $Mg(ClO_4)_2$, air, 50 °C) and the results are summarized in Table 1. As shown in Table 1, this method is equally effective for both aromatic aldehydes and amines. Various substituted aromatic aldehydes **1a–1d** reacted smoothly with amines **2** to produce a range of α-amino phosphonate derivatives. Complete conversion and excellent isolated yields were observed for all substrates employed. This reaction is very clean and free from side reactions. For example, almost quantitative yields of products **3b** and **3c** were obtained when aldehyde **1a** reacted with anilines **2b** and **2c** (entries 2 and 3). The reactions also

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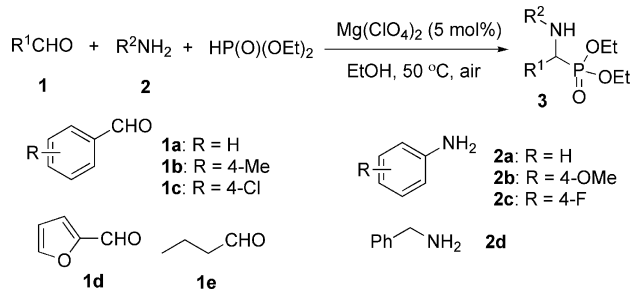
Table 1 Reaction of aldehyde **1**, amine **2**, and diethyl phosphite catalyzed by $Mg(ClO_4)_2$ (5 mol%) in EtOH[a]



Entry	Aldehyde **1**	Amine **2**	Reaction time/h	Yield (%)[b]
1	**1a**	**2a**	5	85 (**3a**)
2	**1a**	**2b**	6	99 (**3b**)
3	**1a**	**2c**	12	99 (**3c**)
4	**1a**	**2d**	12	99 (**3d**)
5	**1b**	**2a**	12	99 (**3e**)
6	**1b**	**2b**	6	99 (**3f**)
7	**1b**	**2c**	12	99 (**3g**)
8	**1b**	**2d**	12	99 (**3h**)
9	**1c**	**2b**	24	99 (**3i**)
10	**1c**	**2d**	24	96 (**3j**)
11	**1d**	**2b**	24	75 (**3k**)
12	**1d**	**2d**	12	99 (**3l**)
13	**1e**	**2a**	24	— (**3m**)
14	**1e**	**2d**	24	— (**3n**)

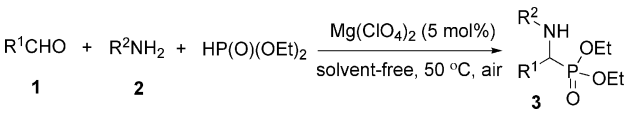
[a] Reaction conditions: aldehyde **1** (0.4 mmol), amine **2** (0.4 mmol, 1.0 eq.), diethyl phosphite (0.4 mmol, 1.0 eq.), $Mg(ClO_4)_2$ (5 mol%), EtOH (0.5 mL), 50 °C, 3–24 h. [b] Isolated yield.

proceeded smoothly when benzylamine was employed as the substrate (entries 4, 8, 10, and 12). However, no desired products were isolated with aliphatic aldehyde since the reaction systems were complicated (entries 13 and 14). We attribute this to the slow formation and unstable nature of the imine formed from the aliphatic aldehyde examined.

On the other hand, due to growing concern about the effect of organic solvents on the environment as well as on the human body, organic reactions without the use of conventional organic solvents have attracted the attention of synthetic organic chemists.[10,11] We also tried the solvent-free reaction of **1a**, **2a** and diethyl phosphite in the presence of $Mg(ClO_4)_2$ (5 mol%) at 50 °C and found that the desired product **3a** was generated in almost quantitative yield (5 h, 99% yield). Other substrates were then investigated and the results are shown in Table 2. From Table 2, it can be seen that the catalytic system under solvent-free conditions was highly effective and all the products were furnished in excellent yields.

Moreover, we turned our attention to other Lewis acid catalysts for this three-component reaction, such as molecular iodine. In recent years, iodine has emerged as a very effective Lewis acid catalyst for various organic transformations.[12,13] Iodine is relatively inexpensive compared to other Lewis acids including rare earth metal triflates, and is more tolerant in comparison to typical Lewis acids/bases. Iodine catalysis can also be easily adapted to commercial applications, since its handling does not require special precautions and it is readily reduced to relatively nontoxic iodide during work-up procedures. Gratifyingly, quantitative yield of product **3a** was obtained by treatment of aldehyde **1a**, aniline **2a**, and diethyl phosphite in EtOH in the presence of a catalytic amount of I_2 (5 mol%) at room temperature under an air atmosphere. Similar results were obtained for the reaction scope investigation (Table 3). Under solvent-free conditions, the reaction of aldehyde **1a**, aniline **2a**, and diethyl phosphite at room temperature also proceeded smoothly to afford the corresponding product **3a** in excellent yield (4 h, 99% yield).

Table 2 Reaction of aldehyde **1**, amine **2**, and diethyl phosphite catalyzed by $Mg(ClO_4)_2$ (5 mol%) under solvent-free conditions[a]



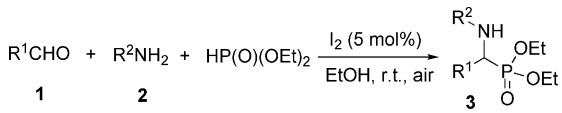
Entry	Aldehyde **1**	Amine **2**	Reaction time/h	Yield (%)[b]
1	**1a**	**2a**	5	99 (**3a**)
2	**1a**	**2b**	12	99 (**3b**)
3	**1a**	**2c**	5	99 (**3c**)
4	**1a**	**2d**	12	99 (**3d**)
5	**1d**	**2b**	24	90 (**3k**)
6	**1d**	**2d**	24	95 (**3l**)

[a] Reaction conditions: aldehyde **1** (0.4 mmol), amine **2** (0.4 mmol, 1.0 eq.), diethyl phosphite (0.4 mmol, 1.0 eq.), $Mg(ClO_4)_2$ (5 mol%), 50 °C, 3–24 h. [b] Isolated yield.

Conclusions

In conclusion, we have described a convenient and efficient synthetic protocol for the preparation of α-amino phosphonate derivatives utilizing $Mg(ClO_4)_2$ or molecular iodine as the catalyst *via* three-component reactions. This method not only provides an excellent complement to α-amino phosphonate synthesis *via* three-component reactions, but also avoids the use of hazardous acids or expensive/toxic Lewis acids and harsh reaction conditions.

Table 3 Reaction of aldehyde **1**, amine **2**, and diethyl phosphite catalyzed by molecular iodine (5 mol%) in EtOH[a]



Entry	Aldehyde **1**	Amine **2**	Reaction time/h	Yield (%)[b]
1	**1a**	**2a**	4	99 (**3a**)
2	**1a**	**2b**	3	93 (**3b**)
3	**1a**	**2c**	4	99 (**3c**)
4	**1a**	**2d**	4	93 (**3d**)
5	**1b**	**2a**	4	99 (**3e**)
6	**1b**	**2b**	3	88 (**3f**)
7	**1b**	**2c**	3	99 (**3g**)
8	**1b**	**2d**	3	99 (**3h**)
9	**1c**	**2b**	4	96 (**3i**)
10	**1d**	**2b**	3	75 (**3k**)
11	**1e**	**2a**	4	— (**3m**)
12	**1e**	**2d**	4	— (**3n**)

[a] Reaction conditions: aldehyde **1** (0.4 mmol), amine **2** (0.4 mmol, 1.0 eq.), diethyl phosphite (0.4 mmol, 1.0 eq.), I_2 (5 mol%), EtOH (0.5 mL), room temperature, 3–12 h. [b] Isolated yield.

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Experimental

All reactions were performed in test tubes under an air atmosphere at room temperature. Flash column chromatography was performed as described by Still *et al.*[14] using silica gel (60 Å pore size, 32–63 μm, standard grade, Sorbent Technologies). Analytical thin-layer chromatography was performed using glass plates precoated with 0.25 mm 230–400 mesh silica gel impregnated with a fluorescent indicator (254 nm). Thin layer chromatography plates were visualized by exposure to ultraviolet light. Organic solutions were concentrated on Büchi R-200 rotary evaporators at ~20 Torr (house vacuum) at 25–35 °C. Commercial reagents and solvents were used as received. Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded in parts per million from internal tetramethylsilane on the δ scale and are referenced from the residual protium in the NMR solvent ($CHCl_3$: δ 7.27, DMSO-*d*6: δ 2.50). Data is reported as follows: chemical shift [multiplicity (s = singlet, d = doublet, q = quartet, m = multiplet), coupling constant(s) in Hertz, integration, assignment].

General procedure

A mixture of aldehyde **1** (0.4 mmol), amine **2** (0.4 mmol, 1.0 eq.), diethyl phosphite (0.4 mmol, 1.0 eq.), and $Mg(ClO_4)_2$ or I_2 (5 mol%) in EtOH (0.5 mL) or under solvent-free conditions was stirred at 50 °C (Method **A**: $Mg(ClO_4)_2$) or at room temperature (Method **B**: I_2) under an air atmosphere. After completion of the reaction as indicated by TLC, the reaction mixture was quenched with water (10 mL) and extracted with EtOAc (2 × 10 mL). Evaporation of the solvent followed by purification (chromatography column on silica gel) afforded pure α-amino phosphonate **3**. (All the products are known compounds. The characterizations of these compounds are identical with the literature reports.[7–9])

Diethyl phenyl(phenylamino)methylphosphonate 3a. Colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 1.10 (t, J = 7.0 Hz, 3H), 1.27 (t, J = 7.0 Hz, 3H), 3.66–3.67 (m, 1H), 3.90–3.92 (m, 1H), 4.10–4.12 (m, 2H), 4.72–4.80 (m, 1H), 4.87–4.89 (m, 1H), 6.58–6.69 (m, 3H), 7.07–7.08 (m, 2H), 7.29–7.31 (m, 3H), 7.45–7.46 (m, 2H).

Diethyl (4-methoxyphenylamino)(phenyl)methylphosphonate 3b. Colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 1.11 (t, J = 7.0 Hz, 3H), 1.28 (t, J = 7.0 Hz, 3H), 3.68 (s, 3H), 3.70–3.72 (m, 1H), 3.91–3.93 (m, 1H), 4.08–4.14 (m, 2H), 4.56 (br s, 1H), 4.68 (d, J = 24.3 Hz, 1H), 6.55 (d, J = 9.2 Hz, 2H), 6.69 (d, J = 9.2 Hz, 2H), 7.30–7.32 (m, 3H), 7.45 (d, J = 7.3 Hz, 2H).

Diethyl (4-fluorophenylamino)(phenyl)methylphosphonate 3c. Colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 1.10 (t, J = 7.0 Hz, 3H), 1.28 (t, J = 7.0 Hz, 3H), 3.66–3.68 (m, 1H), 3.91–3.93 (m, 1H), 4.10–4.14 (m, 2H), 4.66–4.73 (m, 1H), 4.85–4.87 (m, 1H), 6.52–6.54 (m, 2H), 6.76–6.80 (m, 2H), 7.30–7.33 (m, 3H), 7.44–7.45 (m, 2H).

Diethyl (benzylamino)(phenyl)methylphosphonate 3d. Colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 1.12 (t, J = 7.0 Hz, 3H), 1.28 (t, J = 7.0 Hz, 3H), 2.36 (s, 2H), 3.53 (d, J = 13.2 Hz, 1H), 3.79–3.82 (m, 2H), 3.99 (m, 1H), 4.04–4.08 (m, 2H), 7.26–7.42 (m, 10H).

Diethyl (phenylamino)(*p*-tolyl)methylphosphonate 3e. Colorless liquid. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 1.13 (t, J = 7.0 Hz, 3H), 1.28 (t, J = 7.0 Hz, 3H), 2.30 (s, 3H), 3.68–3.70 (m, 1H), 3.92–3.95 (m, 1H), 4.08–414 (m, 2H), 4.71 (d, J = 24.0 Hz 1H), 4.75 (br s, 1H), 6.60 (d, J = 7.5 Hz, 2H), 6.66–6.69 (m, 1H), 7.07–7.13 (m, 4H), 7.33–7.35 (m, 2H).

Diethyl (4-methoxyphenylamino)(*p*-tolyl)methylphosphonate 3f. Colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 1.14 (t, J = 7.0 Hz, 3H), 1.28 (t, J = 7.0 Hz, 3H), 2.30 (s, 3H), 3.67 (s, 3H), 3.69–3.71 (m, 1H), 3.92–3.93 (m, 1H), 4.09–4.14 (m, 2H), 4.66 (d, J = 24.3 Hz, 1H), 4.80 (br s, 1H), 6.55 (d, J = 9.2 Hz, 2H), 6.68 (d, J = 9.2 Hz, 2H), 7.12 (d, J = 7.8 Hz, 2H), 7.31–7.34 (m, 2H).

Diethyl (4-fluorophenylamino)(*p*-tolyl)methylphosphonate 3g. Colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 1.12 (t, J = 7.0 Hz, 3H), 1.28 (t, J = 7.0 Hz, 3H), 2.31 (s, 3H), 3.67–3.70 (m, 1H), 3.91–3.92 (m, 1H), 4.10–4.14 (m, 2H), 4.63–4.70 (m, 1H), 4.83–4.85 (m, 1H), 6.52–6.54 (m, 2H), 6.75–6.80 (m, 2H), 7.12 (d, J = 7.8 Hz, 2H), 7.33 (d, J = 7.8 Hz, 2H).

Diethyl (benzylamino)(*p*-tolyl)methylphosphonate 3h. Colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 1.14 (t, J = 7.0 Hz, 3H), 1.27 (t, J = 7.0 Hz, 3H), 2.30 (s, 2H), 2.35 (s, 3H), 3.53 (d, J = 13.2 Hz, 1H), 3.78–3.82 (m, 2H), 3.96–4.06 (m, 3H), 7.26–7.31 (m, 9H).

Diethyl (4-chlorophenyl)(4-methoxyphenylamino)methylphosphonate 3i. Colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 1.16 (t, J = 7.0 Hz, 3H), 1.29 (t, J = 7.0 Hz, 3H), 3.69 (s, 3H), 3.80–3.81 (m, 1H), 3.94–4.03 (m, 1H), 4.09–4.14 (m, 2H), 4.51–4.53 (m, 1H), 4.62–4.70 (m, 1H), 6.50–6.70 (m, 4H), 7.29–7.39 (m, 4H).

Diethyl (benzylamino)(4-chlorophenyl)methylphosphonate 3j. Colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 1.25 (t, J = 7.0 Hz, 3H), 1.27 (t, J = 7.0 Hz, 3H), 3.50 (d, J = 13.2 Hz, 1H), 3.77 (d, J = 13.2 Hz, 1H), 3.97–4.10 (m, 6H), 7.23–7.37 (m, 9H).

Diethyl furan-2-yl(4-methoxyphenylamino)methylphosphonate 3k. Colorless liquid. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 1.20 (t, J = 7.0 Hz, 3H), 1.34 (t, J = 7.0 Hz, 3H), 3.70 (s, 3H), 3.87–3.89 (m, 1H), 4.03–4.07 (m, 1H), 4.16–4.20 (m, 2H), 4.23 (br s, 1H), 4.78 (d, J = 13.2 Hz, 1H), 6.30 (s, 1H), 6.36–6.37 (m, 1H), 6.62–6.64 (m, 2H), 6.72–6.74 (m, 2H), 7.37 (s, 1H).

Diethyl (benzylamino)(furan-2-yl)methylphosphonate 3l. Colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 1.22 (t, J = 7.0 Hz, 3H), 1.31 (t, J = 7.0 Hz, 3H), 3.59 (d, J = 13.2 Hz, 1H), 3.85–3.88 (m, 2H), 4.03–4.15 (m, 5H), 6.37–6.38 (m, 2H), 7.29–7.30 (m, 6H).

Acknowledgements

Financial support from the National Natural Science Foundation of China (20502004), Ministry of Education of China, the Science and Technology Commission of Shanghai Municipality, and Fudan University is gratefully acknowledged.

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