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A simple, solvent and catalyst-free green synthetic protocol for α-amino phosphonates

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ABSTRACT

A simple and efficient method for the synthesis of α-amino phosphonates has been developed by using aromatic aldehydes, amines, and trimethyl/triethyl phosphite, under catalyst and solvent free conditions, with the formation of the product in good to excellent yields. This method involves milder reaction conditions, easy work-up, and cleaner reaction profiles, and may have wide spread application in organic synthesis.

1. Introduction

α-Amino phosphonates are an important class of compounds in pharmaceutical chemistry with potential biological activity of medicinal importance, and act as enzyme inhibitors [1], such as HIV protease [2], antibiotics [3], herbicides, fungicides, insecticides [4], plant growth regulators [5], antithrombotic agents [6], as well as peptidases and proteases [7]. Several one pot syntheses of α-amino phosphonates have been reported in recent literature and amongst these nucleophilic addition of phosphite to imines is the most convenient route usually acheived by Lewis acid catalysis, carried out by a wide spectrum of catalysts such as lanthanide triflate [8], samarium diiodide [9], $InCl_3$ [10], $TaCl_5$–SiO_2 [11], (bromodimethyl)sulfonium bromide [12], $LiClO_4$ [13], montmorillonite KSF [14], $ZrCl_4$ [15], alumina-supported reagents [16], ionic liquids [17], $H_3PW_{12}O_{40}$ [18], oxalic acid [19], and TiO_2 [20]. Recently, Perumal *et al*., developed $KHSO_4$ catalyzed synthesis of α-amino phosphonates from ferrocene-1-carboxaldehyde, aniline and diethyl phosphite under neat conditions [21]. Bhattacharya and Rana reported Amberlite-IR 120 catalyzed synthesis of α-amino phosphonates from various aromatic aldehydes, aniline and diethyl phosphite under micro wave conditions [22]. However, many of these reported methodologies are associated with several disadvantages like use of inflammable organic solvents, additional reagents, longer reaction times, and expensive moisture sensitive catalysts. Performing organic reactions under neat conditions gained significance because of added advantages of minimized use of organic solvents/catalysts, making it economically viable and environmentally benign. These synthetic protocols have also been demonstrated to be simple, and efficient with remarkable decrease in reaction times, increased yields and easy workup.

2. Experimental

2.1. Instrumentation and material

All chemicals were purchased from Fluka and S. D. Fine Chemicals and directly used for the synthesis. All reactions were carried out without any special precautions in an atmosphere of air. Analytical Thin Layer Chromatography (TLC) was carried out by using silica gel 60 F254 pre-coated plates. Visualization was accomplished with UV lamp and by I_2 staining. All products were characterized by their NMR and mass spectra. ^{1}H NMR and ^{13}C NMR were recorded on 200 or 300 MHz, in $CDCl_3$ using TMS as the internal standard and chemical shifts were reported in parts per million (ppm, δ) downfield from the tetramethylsilane. ^{1}H NMR Spectra: Varian 200 or Avance 300 spectrometer; in $CDCl_3$; δ in ppm, J in Hz, Mass spectra: *VG* Autospec; in *m/z*. M.p.: Fischer-Johns melting-point apparatus; uncorrected.

2.2. General procedure for the synthesis of diethyl (phenyl (phenylamino)methyl)phosphonate

Benzaldehyde (1 mmol) and aniline (1 mmol) were mixed and stirred for few minutes, followed by the addition of triethyl phosphite (1 mmol), after which the reaction mixture was heated at 80–85 ^{0}C until completion of the reaction as indicated by TLC. The reaction mixture was cooled to room temperature and treated with water. The aqueous phase was extracted with ethyl acetate (3 x 10 mL) and the organic layers were washed with water, saturated brine solution, and dried over anhydrous Na_2SO_4.

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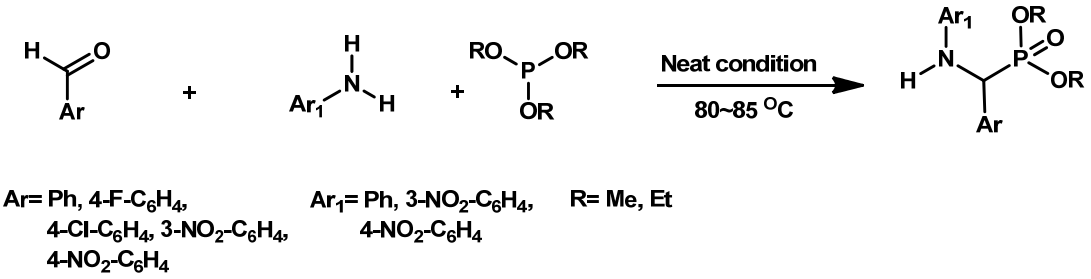


Scheme 1

The combined organic layers were evaporated under reduced pressure and the resulting crude product was purified by column chromatography by using ethyl acetate and hexane (7:3) as eluent to give the corresponding diethyl (phenyl(phenylamino)methyl)phosphonate as pure product in 90% yield. The identity of the product was confirmed by IR, ^{1}H and ^{13}C NMR, and mass spectra. Compound characterization data and spectral data of new compounds are available in the supporting information (Scheme 1).

Diethyl naphthalene-1yl(pyridine-2ylamino) methyl phosphonate (Table 1, Entry 1): Yellow semisolid. Yield: 88%. IR (KBr, cm^{-1}): 3301. ^{1}H NMR (200 MHz, $CDCl_3$, δ, ppm): 1.22-1.39 (m, 6H), 3.98-4.22 (m, 4H), 5.48 (d, 1H, *J* = 8.3 Hz), 5.84 (t, 1H, *J* = 6.0 Hz), 6.38-6.52 (m, 3H, arom), 7.23-7.58 (m, 3H, arom), 7.72-7.84 (m, 3H, arom), 8.01 (d, 1H, *J* = 5.2 Hz), 8.33 (d, 1H, *J* = 9.0 Hz). ^{13}C NMR (75 MHz, $CDCl_3$, δ, ppm): 15.6, 45.8, 47.9, 62.8, 95.6, 108.4, 112.8, 123.4, 126.2, 136.2, 136.7, 147.4, 156.6. MS (m/z, ESI): 371 $(M+H)^+$. Anal. calcd. for $C_{20}H_{23}N_2O_3P$: C, 64.86; H, 6.26; N, 7.56. Found: C, 64.82; H, 6.21; N, 7.51 %.

Diethyl naphthalene-1yl (phenylamino) methylphosphonate (Table 1, Entry 2): White semisolid. Yield: 89%. IR (KBr, cm^{-1}): 3302. ^{1}H NMR (200 MHz, $CDCl_3$, δ, ppm): 11.25-1.36 (m, 6H), 3.06-4.22 (m, 4H), 5.57 (d, 1H, *J* = 24.1 Hz), 6.47-6.61 (m, 3H), 6.98 (t, 2H, arom, *J* = 7.5 Hz), 7.39-7.60 (m, 3H, arom), 7.74 (d, 2H, arom, *J* = 10.0 Hz), 8.85 (d, 1H, *J* = 7.9 Hz), 8.20 (d, 1H, *J* = 8.4 Hz). ^{13}C NMR (75 MHz, $CDCl_3$, δ, ppm): 1515.7, 49.5, 47.9, 52.5, 62.9, 95.8, 113.2, 117.8, 122.5, 125.2, 125.8, 128.7, 131.7, 133.4, 146.0. MS (m/z, ESI): 371 370 $(M+H)^+$. Anal. calcd. for $C_{21}H_{24}NO_3P$: C, 68.28; H, 6.55; N, 3.79. Found: C, 68.22; H, 6.51; N, 3.72 %.

Diethyl pheny1 (pyridine-2-ylamino) methylphosphonate (Table 1, Entry 3): White semisolid. Yield: 90%. IR (KBr, cm^{-1}): 3295. ^{1}H NMR (200 MHz, $CDCl_3$, δ, ppm): 11.10 (t, 3H, *J* = 14.1 Hz), 1.24 (t, 3H, *J* = 13.9 Hz), 3.62-3.75 (m, 1H), 3.85-4.19 (m, 3H), 5.55 (d, 1H, *J* = 9.2 Hz), 5.88 (t, 1H, *J* = 15.6 Hz), 6.43-6.52 (m, 2H), 7.19-7.31 (m, 4H, arom), 7.50 (t, 2H, arom, *J* = 7.7 Hz), 8.0 (d, 1H, arom, *J* = 4.9 Hz). ^{13}C NMR (75 MHz, $CDCl_3$, δ, ppm): 1515.7, 50.2, 95.3, 113.2, 126.9, 136.2, 147.0, 156.7. MS (m/z, ESI): 371 $(M+Na)^+$. Anal. calcd. for $C_{16}H_{21}N_2O_3P$: C, 59.99; H, 6.61; N, 8.75. Found C, 59.91; H, 6.58; N, 8.69 %.

Diethyl pheny1 ((S)-(-)-1-phenylethylamino) methyl phosphonate (Table 1, Entry 4): White oil. Yield: 87%. IR (KBr, cm^{-1}): 3458. ^{1}H NMR (200 MHz, $CDCl_3$, δ, ppm): 10.94-1.04 (m, 3H), 1.23-1.30 (m, 6H), 3.70-4.18 (m, 4H), 7.11-7.35 (m, 10H, arom). ^{13}C NMR (75 MHz, $CDCl_3$, δ, ppm): 1515.3, 21.6, 24.1, 53.9, 56.0, 58.9, 61.7, 126.7, 135.5, 144.5. MS (m/z, ESI): 371 348 $(M+H)^+$. Anal. calcd. for $C_{19}H_{26}NO_3P$: C, 65.69; H, 7.54; N, 4.03. Found: C, 65.64; H, 7.49; N, 3.96 %.

Diethyl (pheny1amino)(thiophen-2-yl) methylphosphonate (Table 1, Entry 5): Yellow semisolid. Yield: 88%. IR (KBr, cm^{-1}): 3306. ^{1}H NMR (200 MHz, $CDCl_3$, δ, ppm): 11.17-1.30 (m, 6H), 3.84-4.11 (m, 4H), 4.71 (s, 1H, -NH), 5.06 (d, 1H, *J* = 23.9 Hz), 6.67-7.17 (m, 8H, arom). ^{13}C NMR (75 MHz, $CDCl_3$, δ, ppm): 1515.2, 55.6, 62.5, 112.9, 118.0, 124.1, 126.3, 127.0, 130.0, 138.9. MS (m/z, ESI): 326 $(M+H)^+$. Anal. calcd. for $C_{15}H_{20}NO_3PS$: C, 55.37; H, 6.20; N, 4.30. Found: C, 55.31; H, 6.16; N, 4.26 %.

Diethyl (pyridine-2-ylamino) (thoiphene-2-yl) methyl phosphonate (Table 1, Entry 6): Yellow semisolid. Yield: 89%. IR (KBr, cm^{-1}): 3282. ^{1}H NMR (200 MHz, $CDCl_3$, δ, ppm): 11.16-1.36 (m, 6H), 3.82-4.19 (m, 4H), 5.95 (d, 1H, *J* = 9.8 Hz), 6.48-6.57 (m, 2H, arom), 6.91 (t, 1H, arom, *J* = 4.5 Hz), 7.15-7.35 (m, 3H, arom), 8.04 (d, 1H, arom, *J* = 4.5 Hz). ^{13}C NMR (75 MHz, $CDCl_3$, δ, ppm): 1516.3, 29.8, 46.2, 49.0, 96.4, 108.6, 113.9, 124.8, 126.7, 137.6, 148.3, 156.4. MS (m/z, ESI): 349 $(M+Na)^+$. Anal. calcd. for $C_{14}H_{19}N_2O_3PS$: C, 51.52; H, 5.87; N, 8.58. Found: C, 51.48; H, 5.83; N, 8.52 %.

Diethylfurae-2-yl (phenylamino) methylphosphonate (Table 1, Entry 7): Yellow semisolid. Yield: 88%. IR (KBr, cm^{-1}): 3325. ^{1}H NMR (200 MHz, $CDCl_3$, δ, ppm): 11.25-1.37 (m, 6H), 4.05-4.15 (m, 4H), 6.31-6.35 (m, 1H, arom), 6.64 (d, 2H, arom, *J* = 7.7 Hz), 7.04-7.16 (m, 2H), 7.26-7.37 (m, 1H), 7.51 (d, 1H, arom, *J* = 8.1 Hz). ^{13}C NMR (75 MHz, $CDCl_3$, δ, ppm): 1515.9, 29.7, 63.7, 96.1, 114.0, 120.3, 128.8, 142.9, 148.5. MS (m/z, ESI): 310 $(M+H)^+$. Anal. calcd. for $C_{15}H_{20}NO_4P$: C, 58.25; H, 6.52; N, 4.53. Found: C, 58.18; H, 6.47; N, 4.50 %.

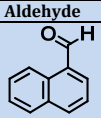
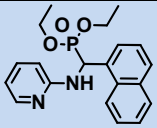
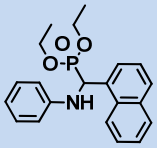
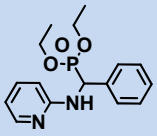
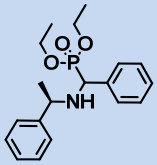
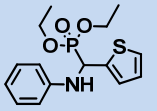
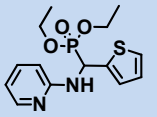
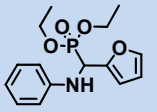
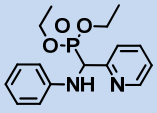
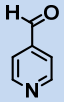
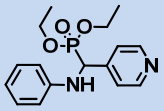
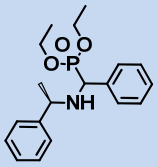
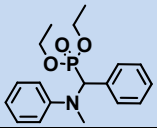
Diethyl (phenylamino)(pyridine-2-yl)methylphosphonate (Table 1, Entry 8): Light yellow semisolid. Yield: 89%. IR (KBr, cm^{-1}): 3356. ^{1}H NMR (200 MHz, $CDCl_3$, δ, ppm): 11.15 (t, 3H, *J* =14.5 Hz), 1.26 (t, 3H, *J* = 13.6 Hz), 3.83-4.15 (m, 4H), 4.92 (d, 1H, *J* = 21.8 Hz), 5.22 (s, 1H, -NH), 6.62-6.65 (m, 3H, arom), 7.06 (t, 2H, arom, *J* = 15.4 Hz), 7.16 (t, 1H, arom, *J* = 10.9 Hz), 7.46 (d, 1H, *J* = 7.2 Hz), 7.61 (t, 1H, arom, *J* = 15.4 Hz). ^{13}C NMR (75 MHz, $CDCl_3$, δ, ppm): 1516.6, 56.7, 58.9, 63.0, 96.3, 113.8, 114.4, 118.8, 122.9, 129.8, 136.6. MS (m/z, ESI): 321 $(M+H)^+$. Anal. calcd. for $C_{16}H_{21}N_2O_3P$: C, 59.99; H, 6.61; N, 8.75. Found: C, 59.91; H, 6.58; N, 8.70 %.

Diethyl (phenylamino)(pyridine-2-yl)methylphosphonate (Table 1, Entry 9): Light yellow semisolid. Yield: 90%. IR (KBr, cm^{-1}): 3356. ^{1}H NMR (200 MHz, $CDCl_3$, δ, ppm): 11.15 (t, 3H, *J* = 14.5 Hz), 1.26 (t, 3H, *J* = 13.6 Hz), 3.83-4.15 (m, 4H), 4.92 (d, 1H, *J* = 21.8 Hz), 5.22 (s, 1H, -NH), 6.62-6.65 (m, 3H, arom), 7.06 (t, 2H, arom, *J* = 15.4 Hz), 7.16 (t, 1H, arom, *J* = 10.9 Hz), 7.46 (d, 1H, *J* = 7.2 Hz), 7.61 (t, 1H, arom, *J* = 15.4 Hz). ^{13}C NMR (75 MHz, $CDCl_3$, δ, ppm): 1516.5, 56.5, 58.8, 63.0, 96.1, 113.5, 114.1, 118.2, 122.5, 129.3, 136.5. MS (m/z, ESI): 321 $(M+H)^+$. Anal. calcd. for $C_{16}H_{21}N_2O_3P$: C, 59.99; H, 6.61; N, 8.75. Found: C, 59.91; H, 6.58; N, 8.70 %.

Diethyl pheny1 ((R)-(+)-1-phenylethylamino) methyl phosphonate (Table 1, Entry 10): White oil. Yield: 87%. IR (KBr, cm^{-1}): 3458. ^{1}H NMR (200 MHz, $CDCl_3$, δ, ppm): 10.94-1.04 (m, 3H), 1.23-1.30 (m, 6H), 3.70-4.18 (m, 4H), 7.11-7.35 (m, 10H, arom). ^{13}C NMR (75 MHz, $CDCl_3$, δ, ppm): 1515.3, 21.6, 24.1, 53.9, 56.0, 58.9, 61.7, 126.7, 135.5, 144.5. MS (m/z, ESI): 348 $(M+H)^+$. Anal. calcd. for $C_{19}H_{26}NO_3P$: C, 65.69; H, 7.54; N, 4.03. Found: C, 65.64; H, 7.49; N, 4.00 %.

Diethyl (methyl(phenyl)amino)(phenyl)methylphosphonate (Table 1, Entry 11): Light yellow semisolid. Yield: 83%. IR (KBr, cm^{-1}): 3326.

Table 1. A simple, solvent and catalyst-free green synthesis of α-amino phosphonates with triethyl phosphite [a].

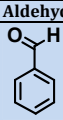
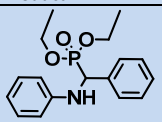
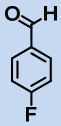
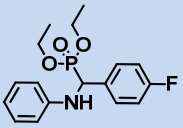
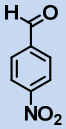
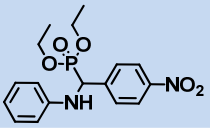
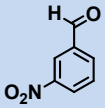
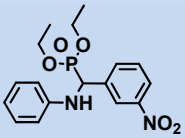
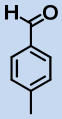
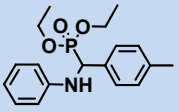
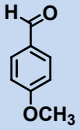
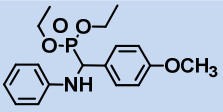
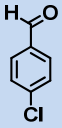
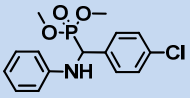
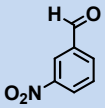
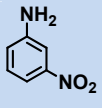
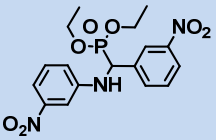
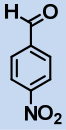
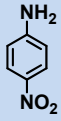
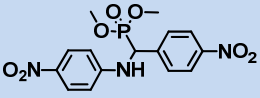
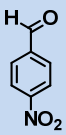
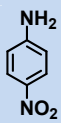
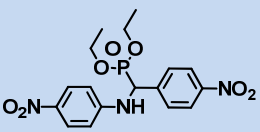
Sample no	Aldehyde	Amine	Product	Yield (%)[b]
1				88
2				89
3				90
4				87
5				88
6				89
7				88
8				89
9				90
10				87
11				83

[a] Reaction Conditions: Aldehyde (1 mmol), amine (1 mmol), triethyl phosphite (1 mmol), under neat conditions at 80-85 °C.
[b] Isolated yields.

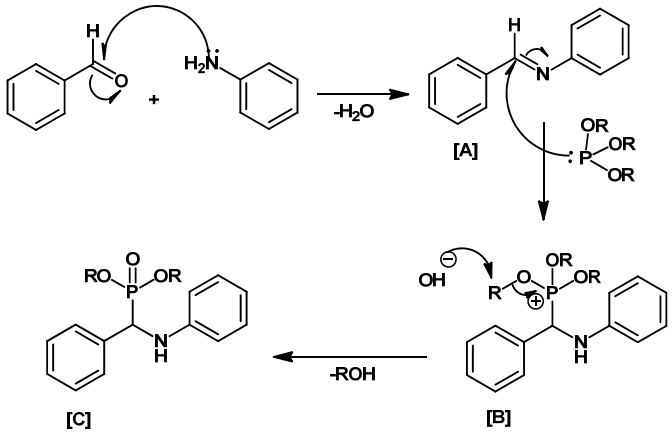
Table 2. The effect of the molar ratio of reagents and the temperature on the synthesis of diethyl phenyl (phenyl amino) methylphosphonate.

Entry	Triethyl phosphite : Aniline : Benzaldehyde (molar ration)	Reaction temperature (°C)	Yield, %
1	1:1:1	60-65	35
2	1:1:1	65-75	56
3	1:1:1	80-85	90
4	1:1:1	100-110	55
5	1:2:1	80-85	61
6	2:1:1	80-85	59

Table 3. Preparation of α-amino phosphonates with triethyl phosphite [a].

Sample no	Aldehyde	Amine	Product	Yield (%)[b]	Reference[c]
1				90	[24]
2				92	[22]
3				93	[20]
4				89	[22]
5				81	[22]
6				80	[22]
7				91	[23]
8				92	[25]
9				84	[26]
10				87	[26]

[a] Reaction Conditions: Aldehyde (1 mmol), amine (1 mmol), trimethyl/triethyl phosphite (1 mmol), under neat conditions at 80-85 °C.
[b] Yields refer to the pure isolated products.
[c] All known products have been characterized by comparison with IR and NMR spectra of authentic samples.



Scheme 2

^{1}H NMR (200 MHz, $CDCl_3$, δ, ppm): 11.18-1.25 (m, 6H), 2.94 (s, 3H), 4.02-4.24 (m, 4H), 5.34 (d, 1H, *J* = 24.9 Hz), 6.78 (t, 1H, arom, *J* = 7.1 Hz), 6.87 (d, 1H, arom, *J* = 8.3 Hz), 7.22-7.32 (m, 3H, arom), 7.45-7.62 (m, 3H, arom), 8.11 (d, 2H, *J* = 7.5 Hz). ^{13}C NMR (75 MHz, $CDCl_3$, δ, ppm): 1515.2, 38.5,60.3, 62.5, 115.3, 119.6, 127.5, 128.3, 129.6, 132.5. MS (m/z, ESI): 332 $(M+H)^+$. Anal. calcd. for $C_{18}H_{24}NO_3P$: C, 64.85; H, 7.26; N, 4.20. Found: C, 64.80; H, 7.18; N, 4.17 %.

3. Results and discussion

To the best of our knowledge, there have been no reports for the synthesis of α-amino phosphonates under catalyst and solvent-free conditions. In continuation of our current research interest to develop facile synthetic routes for biologically active heterocyclic compounds, utilising various green chemical approaches in organic synthesis, [27-31] herein, we report for the first time, a mild, simple and efficient one-pot three component synthesis of α-amino phosphonates under catalyst and solvent free conditions (Scheme 1). During the course of our efforts in developing the present methodology, an initial experiment was conducted for a possible reaction between benzaldehyde, aniline and trimethyl/triethyl phosphite at room temperature in the absence of any catalyst /solvent, which did not result in any product. The effect of reaction temperature was investigated on the present reaction, by conducting experiments at different ranges of temperature. When the reaction temperature was increased to 60-65, 65-75 and 80-85 °C, the yields varied from 35, 56 and 90%, respectively. However, no further improvement was observed in the yield, when temperature was increased beyond 85 °C (Table 2). The scope of this reaction was expanded to include various substituted aromatic aldehydes and anilines and the results are indicated in Tables 3 and 1.

The plausible mechanism for the synthesis of α-amino phosphonates involves the nucleophilic addition of amine with aldehyde leading to the formation of intermediate [A]. This imine reacts with phosphite to give phosphonium intermediate [B], which reacts with water to give the desired product [C] (Scheme 2).

4. Conclusion

In conclusion, we have developed a simple and efficient synthesis of α-amino phosphonates by the reaction of the corresponding aromatic aldehydes, amine, and triethylphosphite under neat conditions. These organic reactions are useful both from economical and environmental points of view. This methodology also prevents the formation of unwanted by-products, low yields, and use of hazardous solvents and high temperatures.

Acknowledgements

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