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Organocatalytic synthesis of α-hydroxy and α-aminophosphonates

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ABSTRACT

A new and highly flexible procedure is described for the synthesis of α-amino- and α-hydroxy phosphonates. In the presence of a catalytic amount of oxalic acid (10 mol %), trimethyl phosphite reacts with aldehydes or imines (generated in situ from an aldehyde and an amine) to yield the corresponding coupled products in good yield.

Organocatalysis[1] has emerged as an important area of research over the last decade. Compared with biocatalysts and metal catalysts, organocatalysts are usually more stable, more environmentally friendly, more readily available, less expensive and can be applied using less demanding reaction conditions, such as rigorously anhydrous or anaerobic conditions. Although organic molecules such as amino acids, peptides, carbenes, ureas, and phase-transfer agents have been used as catalysts in carbon–carbon, carbon–heteroatom bond-forming reactions, and 1,4 and 1,2 additions of trivalent P to carbonyl compounds,[2] they are still limited to specific reactions. Thus, new, more versatile organic catalysts are highly desirable.[3]

Since α-aminophosphonate derivatives are structural mimics of α-amino acids, some of these compounds exhibit very high potency in inhibiting enzymes that are involved in the metabolism of the corresponding amino acids. These compounds have already been found to act as antibacterial agents, neuroactive compounds, anticancer drugs, and pesticides, with some of them being commercialized.[4] The altered activity of such enzymes has been associated with HIV infections and several pathological disorders, including cancer and cataracts.[5] A number of synthetic methods for α-amino phosphonates have been developed.[6] Of these, the nucleophilic addition of phosphites to imines, catalyzed by a base or an acid, is the most convenient. Lewis acids such as $SnCl_4$,[7] $BF_3.OEt_2$,[8] $ZnCl_2$,[9] and $ZrCl_4$[10] have been used for this transformation. However, these reactions cannot be carried out in a one-pot operation with a carbonyl compound, an amine and a dialkyl phosphite because the amine and water present during imine formation can decompose or deactivate the Lewis acid.[11] This drawback has been overcome in some recent methods using lanthanide triflates/$MgSO_4$,[9] $InCl_3$,[12] $ZrCl_4$,[13] $TaCl_5$–SiO_2,[14] bismuth nitrate pentahydrate,[15] $MgClO_4$,[16] TiO_2,[17] Amberlite-IR 120,[18] sulfamic acid,[19] $H_3PW_{12}O_{40}$,[20] trimethylanilinium chloride,[21] lithium perchlorate,[22] and Amberlyst-15.[23] However, these catalysts have various drawbacks: reactions require a long time, and when the starting materials contain aliphatic amines, the reactions usually give uncharacterizable products. In addition, some of these catalysts are expensive or are difficult to prepare. It is well known that oxalic acid is a relatively stable, easy to handle solid that is insensitive to small amounts of air and moisture. Herein, we describe a mild and efficient protocol for the synthesis of α-aminophosphonates using a catalytic amount of oxalic acid under solvent-free conditions at 50 °C. We investigated the reaction between trimethyl phosphite and the imine generated in situ from benzaldehyde and aniline in the presence of a catalytic amount of oxalic acid (10 mol %) and isolated the desired amino phosphonate in a 98% yield within 40 min at 50 °C. After this success, reactions of several aldehydes (aliphatic, aromatic, heterocyclic, and conjugated), amines (primary and secondary), and trimethyl phosphite were examined in the presence of 10 mol % oxalic acid under solvent-free conditions. Benzaldehyde and electron-deficient aromatic aldehydes reacted with aromatic and aliphatic amines to give the corresponding α-aminophosphonates in high yields.

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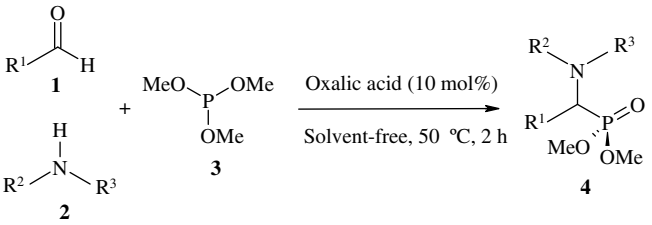
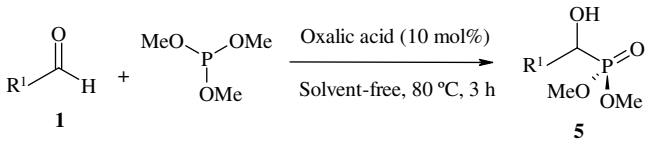
Sensitive functionalities such as CN, MeO, and Cl were unaffected during the reaction. In all cases, the reactions proceeded smoothly at 50 °C to afford α-aminophosphonates exclusively without any undesired side products. This method is even effective with aliphatic aldehydes, which normally produce low yields due to their intrinsic lower reactivity. The present method does not require any additives or promoters, and the results are summarized in Scheme 1.

In assessing the catalytic activity of oxalic acid, we were pleased to find that addition of trimethyl phosphite to aldehydes gave the corresponding α-hydroxy phosphonates in excellent yields. α-Hydroxy phosphonates have received attention as substrates for the preparation of other α-substituted phosphonates and because of their potential biological activity.[24] These compounds show antiviral,[25a] antibacterial,[25b] antivaccinia,[25c] anticancer,[25d] pesticide,[25e] renin inhibitory,[25f] HIV-protease,[25g] anti-HIV activities,[25h,25i] and enzyme inhibitor properties.[25j] Furthermore, α-hydroxy phosphonates are useful precursors for the preparation of α-functionalized phosphonates, such as α-amino,[26] α-keto,[27] α-halo,[28] and α-acetoxyphosphonates.[29] Recently, numerous activators have been developed for the synthesis of α-hydroxy phosphonates.[30] However, these methods often have disadvantages. For example, in the strongly alkaline medium used, α-hydroxy-alkanephosphonic esters are cleaved to regenerate the starting carbonyl compounds.[31] In addition, the yields are not always good and mixtures of products are sometimes obtained. Hence, there is a need to develop a convenient and environmentally benign method for the synthesis of α-hydroxy phosphonates. Herein, we report our results on the preparation of α-hydroxy phosphonates from aldehydes and trimethyl phosphite in the presence of oxalic acid under solvent-free conditions at 80 °C. The results are summarized in Scheme 2.



Entry	R^1	R^2	R^3	**4** (%)
a	Phenyl	Phenyl	H	98
b	2-Cl-C_6H_4	Phenyl	H	91
c	4-Cl-C_6H_4	Phenyl	H	91
d	4-CN-C_6H_4	Phenyl	H	94
e	Cinnamyl	Phenyl	H	83
f	2-Furyl	Phenyl	H	94
g	4-MeO-C_6H_4	Phenyl	H	89
h	4-HO-C_6H_4	Phenyl	H	87
i	*i*-Propyl	Phenyl	H	87
j	Phenyl	Benzyl	H	90
k	4-Cl-C_6H_4	Benzyl	H	90
l	Phenyl	Benzyl	Benzyl	87
m	2-Cl-C_6H_4	Benzyl	Benzyl	84
n	Phenyl	4-MeO-C_6H_4	H	87
o	Phenyl	4-Cl-C_6H_4	H	91

Scheme 1.



Entry	R^1	**5** (%)
a	Phenyl	98
b	2-Cl-C_6H_4	91
c	4-Cl-C_6H_4	91
d	4-CN-C_6H_4	94
e	Cinnamyl	83
f	2-Furyl	94
g	4-MeO-C_6H_4	89
h	4-OH-C_6H_4	87
i	*i*-Propyl	87
j	Cyclohexyl	90
k	*n*-Propyl	90
l	*n*-Pentyl	87
m	Tolyl	84

Scheme 2.

When we treated benzaldehyde with trimethyl phosphite in the absence of oxalic acid, only a low yield (<20%) of dimethyl 1-hydroxy-1-phenylmethylphosphonate was obtained, implying the role of oxalic acid in this reaction. As shown in Scheme 2, reaction of a mixture of aliphatic or aromatic aldehyde and trimethyl phosphite in the presence of oxalic acid at 80 °C afforded the desired products in good to high yields. α,β-Unsaturated aldehydes also afforded selectively the corresponding α-hydroxy phosphonates in good yield and with no byproduct formation. This reaction was performed in organic solvents such as diethyl ether, CH_2Cl_2, $CHCl_3$, MeCN, THF, dioxane, and methanol, however low yields (<30%) of the α-hydroxy phosphonates were obtained. Ketones and trimethyl phosphite did not react under these reaction conditions.

In conclusion, the present procedure using oxalic acid as catalyst provides an efficient one-pot synthesis of α-amino and α-hydroxy phosphonates under solvent-free conditions. The advantages of this procedure are operational simplicity, wide substrate scope, and high yields. In many cases, the products crystallized directly from the reaction mixture in high purity. We believe that this method presents a practical alternative to existing procedures for the synthesis of α-amino- and α-hydroxy phosphonates.

Typical procedure I: Solvent-free: a mixture of benzaldehyde (106 mg, 1 mmol), oxalic acid (20 mg, 10 mol %), aniline (93 mg, 1 mmol), and trimethyl phosphite (152 mg, 1 mmol) was stirred vigorously at 50 °C for approximately 2 h. The reaction mixture was then diluted with water and extracted with CH_2Cl_2. The CH_2Cl_2

extract, after being washed with brine and drying over sodium sulfate, was evaporated. The crude product was purified by silica gel column chromatography with EtOAc/hexane (1:6) as eluent to provide pure α-aminophosphonate (293 mg, 98%).

Typical procedure II: Solvent-free: a mixture of aldehyde (2 mmol), oxalic acid (10 mol %), and trimethyl phosphite (2.2 mmol) was stirred at 80 °C for 3 h. After completion of the reaction, as indicated by TLC, the reaction mixture was quenched with aq satd $NaHCO_3$ followed by brine solution and then extracted with CH_2Cl_2. The organic extracts were combined, dried ($MgSO_4$), and concentrated. The residue was purified by column chromatography on silica gel using hexane/ethyl acetate (4:1) to afford the pure α-hydroxy phosphonate.

The ^1H (500 MHz) and ^{13}C (125 MHz) NMR data reported below for selected products were determined on a Bruker Avance DRX 500 spectrometer. The spectroscopic and physical data for all compounds corresponded to those given in the literature: **4a**,[16,20] **4b**,[17] **4c**,[23] **4d**,[17] **4e**,[16,20] **4f**,[16] **4g**,[16] **4h**,[23] **4i**,[23] **4j**,[19] **4k**,[19] **4l**,[22] **4m**,[22] **4n**,[23] **4o**,[23] **5a**,[30e,j] **5b**,[30j] **5c**,[30j] **5d**,[30j] **5e**,[30j] **5f**,[30e] **5g**,[30j] **5h**,[30j] **5i**,[30i] **5j**,[30j] **5k**,[30i] **5l**,[30i] **5m**.[30j]

Spectral data for selected products: *Compound* (**4a**): White solid, mp 87 °C; ^1H NMR (500 MHz, $CDCl_3$): δ 3.51 (d, J = 10.5 Hz, 3H), 3.81 (d, J = 10.6 Hz, 3H), 4.82 (d, J = 24 Hz, 1H), 4.84 (br s, 1H), 6.64 (d, J = 8.0 Hz, 2H), 6.74 (t, J = 7.2 Hz, 1H), 7.1 (t, J = 7.7 Hz, 2H), 7.3 (t, J = 7.5 Hz, 1H), 7.39 (t, J = 7.4 Hz, 2H), 7.5 (d, J = 7.3 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 54.1 (d, $^2J_{p-c}$ = 7.0 Hz, OCH_3), 54.2 ($^2J_{p-c}$ = 6.8 Hz, OCH_3), 56.2 (d, $^1J_{p-c}$ = 150 Hz, CH), 68.59 (CH), 114.3 (CH), 119.0 (CH), 128.2 (d, $^3J_{p-c}$ = 5.8 Hz, CH), 128.4 (d, $^3J_{p-c}$ = 3.1 Hz, CH), 129.1 (CH), 131.2 (CH), 136.0 (C), 146.6 (d, $^2J_{p-c}$ = 14.5 Hz, C). *Compound* (**4c**): White solid, mp 60 °C; ^1H NMR (500 MHz, $CDCl_3$): δ 3.51 (m, 1H), 3.79 (d, J = 11.8 Hz, 3H), 3.83 (d, J = 10.1 Hz, 3H), 5.2 (d, J = 24 Hz, 1H), 6.8–7.28 (m, 5H), 7.3 (d, J = 8.5 Hz, 2H), 7.5 (d, J = 8.5 Hz, 2H); ^{13}C NMR (22.5 MHz, $CDCl_3$): δ 56.1 (d, $^2J_{p-c}$ = 7.0 Hz, OCH_3), 56.2 (d, $^2J_{p-c}$ = 6.8 Hz, OCH_3), 57.2 (d, $^1J_{p-c}$ = 150 Hz, CH), 114.3 (CH), 120.0 (CH), 128.2(d, $^3J_{p-c}$ = 5.8 Hz, CH), 128.4 (d, $^3J_{p-c}$ = 3.1 Hz, CH), 130.1 (CH), 131.2 (C), 140.0 (C), 146.6 (d, $^2J_{p-c}$ = 14.5 Hz, C). *Compound* (**4f**): Viscous yellowish oil; ^1H NMR (500 MHz, $CDCl_3$): δ 3.6 (d, J = 10.6 Hz, 3H), 3.8 (d, J = 10.6 Hz, 3H), 4.5 (br s, 1H), 5.0 (d, J = 23.8 Hz, 1H), 6.37–7.40 (m, 8H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 50 (d, $^1J_{p-c}$ = 159.6 Hz, CH), 54.1 (d, $^2J_{p-c}$ = 5.8 Hz, OCH_3), 54.4 (d, $^2J_{p-c}$ = 6.9 Hz, OCH_3), 109.4 (d, $^3J_{p-c}$ = 6.8 Hz, CH), 111.2 (CH), 114.4 (CH), 119.5 (CH), 129.9 (d, $^3J_{p-c}$ = 5.6 Hz, CH), 143.1 (CH), 146.3 (d, $^2J_{p-c}$ = 13.3 Hz, C),149.4 (C). *Compound* (**4h**): Viscous yellowish oil; ^1H NMR (90 MHz, $CDCl_3$): δ 3.49 (d, 3H, J = 10.5 Hz), 3.71 (d, 3H, J = 10.6 Hz), 4.71–4.79 (d, 1H, $^1J_{P-H}$ = 23.9 Hz), 6.5–7.25 (m, 9H); ^{13}C NMR (22.5 MHz, $CDCl_3$): δ 51.9 (CH), 54.03 (OMe), 54.3 (OMe), 114.0 (CH), 121.9 (CH), 125.7 (CH), 129.3 (CH), 130.1 (CH), 131.2 (C), 135.0 (C), 149.2 (C).

Compound **(5a):** White solid, mp 86 °C; ^1H NMR (500 MHz, $CDCl_3$): δ 3.6 (d, J = 10.3 Hz, 3H), 3.6 (d, J = 10.3 Hz, 3H), 5.0 (d, 1H, J = 13.2 Hz), 6.0 (s, 1H, OH), 7.3–7.5 (m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 53.7 (d, J_{CP} = 7.5 Hz), 54.2 (d, J_{CP} = 7.5 Hz), 69.1 (d, J_{CP} = 164.0 Hz), 128.8, 129.4, 131.1, 133.8 (d, J_{CP} = 2.9 Hz). *Compound* **(5c):** White solid, mp 69 °C; ^1H NMR (500 MHz, $CDCl_3$): δ 3.6–3.7 (m, 6 H), 5.1 (d, J = 13.4 Hz, 1H), 6.2 (s, 1H, OH), 7.4 (d, J = 8.5 Hz, 2H), 7.5 (d, J = 8.5 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 53.7 (d, J_{CP} = 7.1 Hz), 54.2 (d, J_{CP} = 7.5 Hz), 69.1 (d, J_{CP} = 161.1 Hz), 128.8, 129.4, 133.1 (d, J_{CP} = 3.9 Hz), 138.2. *Compound* **(5e):** Colorless solid, mp 82.6–83.3 °C; ^1H NMR (500 MHz, $CDCl_3$): δ 3.8 (d, J_{PH} = 10.3 Hz, 3H), 3.8 (d, J_{PH} = 10.3 Hz, 3H), 4.7 (s, 1H, OH), 4.8 (dd, J = 6.4, 15.9 Hz, 1H), 6.4 (dd, J = 6.4, 14 Hz, 1H), 6.8 (d, J = 14 Hz, 1H), 7.2–7.4 (m, 5H); ^{13}C NMR (500 MHz, $CDCl_3$): δ 53.7 (d, J_{PC} = 7.4 Hz), 53.9 (d, J_{PC} = 7.1 Hz), 69.2 (d, J_{PC} = 161.0 Hz), 128.4, 127.8, 126.5, 123.5 (d, J_{PC} = 4.3 Hz), 132.2 (d, J_{PC} = 13.0 Hz), 136.1 (d, J_{PC} = 2.9 Hz). *Compound* **(5k):** Colorless oil; ^1H NMR (90 MHz, $CDCl_3$): δ 1.0 (t, J = 7.4 Hz, 3H), 1.8–1.1 (m, 4H), 2.7 (m, 1H), 3.7 (d, $^3J_{PH}$ = 5.4 Hz, 3H), 3.8 (d, $^3J_{PH}$ = 5.4 Hz, 3H), 3.9 (s, 1H, OH); ^{13}C NMR (22.5 MHz, $CDCl_3$): δ 13.8 (d, $^4J_{PC}$ = 19.1 Hz, CH_3), 19.9 (d, $^3J_{PC}$ = 11.8 Hz, CH_2), 29.0 (d, $^2J_{PC}$ = 7.4 Hz, CH_2), 51.1 (d, $^2J_{PC}$ = 7.3 Hz, OCH_3), 52.2 (d, $^2J_{PC}$ = 7.3 Hz, OCH_3), 56.8 (d, $^1J_{PC}$ = 136.8 Hz, OCH_3).

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