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RESEARCH ARTICLE

A New Catalyst and Solvent-free Green Synthesis of *α*-Hydroxy Phosphonates and *α*-Aminophosphonates

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Abstract: A microwave-promoted easy, efficient and green synthesis of *α*-hyroxyphosphonates and *α*-aminophosphonates is reported from two-component reaction of an aldehyde and diethylphosphite and three component reactions of an aldehyde, diethylphosphite and aniline, respectively. The desired products were isolated in excellent yields and high purity under solvent and catalyst free conditions.

Keywords: Aniline, Aldehyde, Diethylphosphite, Microwave

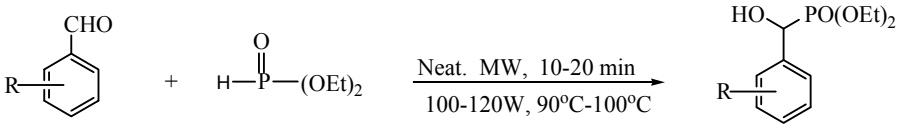
Introduction

The multi-component, one pot reactions are extremely important because of their wide range of applications in pharmaceutical chemistry for the production of structural scaffolds and combinatorial libraries for drug discovery[1]. The synthesis of *α*-hyroxyphosphonates and *α*-aminophosphonates has received great attention due to their potent biological activities, particularly in medicinal chemistry, such as peptide mimetics[2], enzyme inhibitors[3], anti-inflammatory[4], antibiotic[5], fungicides[6] and anti-HIV[7]. These compounds also serve as building blocks for the synthesis of pharmaceutically useful compounds[8].

The synthesis of *α*-hydroxyphosphonates have been reported to be promoted by several catalysts, such as CaO[9], various metal complexes, of aluminum, titanium, lanthanum, ytterbium, niobium complexes[10-14] and MoO_2Cl_2[15], while *α*-aminophosphonates were synthesized by several catalysts such as $InCl_3$[16], $ZrCl_4$[17], mesoporous aluminosilicate nano-cage[18], silica sulfuric acid[19], $Al(H_2PO_4)_3$[20], $CeCl_3.7H_2O$[21], $NbCl_5$[22] and Fe_3O_4 nanoparticle[23]. In most of the reactions, toxic solvents such as CH_3CN, THF and CH_2Cl_2 are used in thermal conditions.

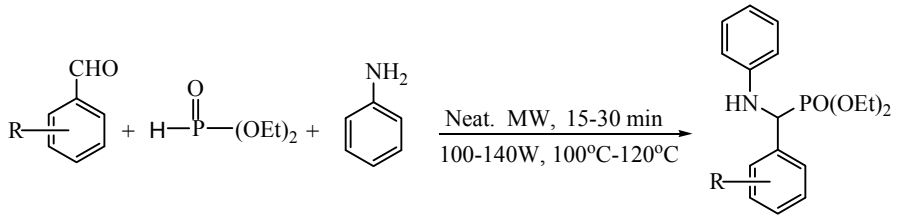
Considering the burgeoning importance of these compounds, development of new protocols for the efficient synthesis of titled compounds under the solvent- and catalyst-free conditions is a desirable goal. During the last few years, numerous organic reactions have been carried out under microwave irradiation with spectacular suceess[24-32]. Prompted by these studies, we report herein a new green protocol for the synthesis of a series of *α*- hydroxyl-

phosphonates and *α*-aminophosphonates from the corresponding aromatic aldehyde and/or aniline and diethylphosphite, under microwave radiation. It is worth mentioning that the synthesis of *α*-aminophosphonates has recently been described under ultrasound conditions[33], however, to the best of our knowledge, so far there is no report on the synthesis of the titled compounds under microwave conditions only and without the use of a catalyst (Scheme 1 and Scheme 2).



(R = -NO_2, -OH, -OCH_3, -Cl, -Br, -H, -CH_3)

Scheme 1. Two-component synthesis of α-hyroxyphosphonates



(R = -NO_2, -OH, -OCH_3, -Cl, -Br, -H, -CH_3)

Scheme 2. Three-component synthesis of α-aminophosphonates

Experimental

All chemicals were purchased from commercial suppliers, such as Sigma-Aldrich and Merck. Reactions were carried out in STAR D Microwave Digestion System (Power 1200 Watt). All the isolated compounds were characterized by spectroscopy such as their ^1H, $^{31}P\{^1H\}$ NMR, MASS, and IR spectra, and melting point determination. The IR spectra were recorded in the range of 4000-400 cm^{-1} on an FTIR Perkin 2000 Model spectrometer using KBr disk. Melting points were determined in sealed capillary tubes and therefore uncorrected. Purity of the compounds was checked by TLC on a silica gel alumina sheet using *n*-hexane and ethylacetate as eluent. The visualization was accomplished with UV lamps at 254 nm.

General procedure for the synthesis of the synthesis of α-hydroxyphosphonates (**1a-j**)

A mixture of aldehyde (1 mmol), diethylphosphite, (1 mmol), was placed in a Teflon pressure vessel and the vessel was closed with the help of "milestone TWISTER" and kept in a "STAR D Microwave Digestion System" under Pressure 5-6 bar, temperature 90-100 ^oC and microwave power 100-120 Watt for 10-20 minutes.

After completion, the reaction was cooled to room temperature and the vessel was opened with the help of "milestone TWISTER" then reaction mixture was analyzed by TLC. The reaction mixture was treated with water, aqueous phase was extracted with ethylacetate (2x10 mL) and the organic layers was washed with water, saturated brine solution and dried over anhydrous Na_2SO_4. The combined organic layers were evaporated under reduced pressure and the resulting crude product was purified by column chromatography by using ethylacetate and *n*-hexane. The identity of the product was confirmed by IR, ^1H and $^{31}P\{^1H\}$ NMR and Mass spectra. The spectroscopic data obtained on the synthesized compounds are given in below.

Spectroscopic data obtained on of *α*-hydroxyphosphonates

Diethyl (4-bromophenyl)(hydroxyl)methylphosphonate (**1a**)

White solid, ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.50-7.26 (m, 4H), 5.00 (s, 1H), 4.96 (d, 1H), 4.13-3.98 (m 4H), 1.35-1.22 (m, 6H). ^{31}P NMR ($CDCl_3$, 161.97 MHz): δ 20.51. IR (ν_{max} KBr); 1236 (P=O). EI-MS; *m/z* 322.17 (M^+).

Diethyl (hydroxyl)(4-nitrophenyl)methylphosphonate (**1b**)

Yellow solid, ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.15-7.39 (m, 4H), 5.19 (s, 1H), 4.79 (d, 1H) 4.33-4.18 (m 4H), 1.42-1.26 (m, 6H).^{31}P NMR ($CDCl_3$, 161.97 MHz): δ 20.19. IR (ν_{max} KBr); 1240 (P=O). EI-MS; *m/z* 279.13 (M^+).

Diethyl (hydroxyl)(phenyl)methylphosphonate (**1e**)

White solid, ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.42-7.28 (m, 4H), 5.07 (s, 1H), 4.80 (d, 1H) 4.29-4.00 (m 4H), 1.37-1.23 (m, 6H), ^{31}P NMR ($CDCl_3$, 161.97 MHz): δ 20.82, IR (ν_{max} KBr); 1243 (P=O). EI-MS; *m/z* 243.09 (M^+).

Diethyl (4-chlorophenyl)(hydroxyl)methylphosphonate (**1f**)

White solid, ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.39-7.18 (m, 5H), 5.30 (s, 1H), 4.53(d, 1H) 3.99-3.86 (m 4H), 1.23-1.19 (m, 6H). ^{31}P NMR ($CDCl_3$, 161.97 MHz): δ 22.29, IR (ν_{max} KBr); 1239 (P=O). EI-MS; *m/z* 276.84 (M^+).

Diethyl (hydroxyl)(4-methoxyphenyl)methylphosphonate (**1j**)

White solid, ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.35-7.10 (m, 5H), 5.22 (s, 1H), 4.12-4.02 (m, 4H), 3.80 (s, 3H), 1.26-1.18 (m, 6H). ^{31}P NMR ($CDCl_3$, 161.97 MHz): δ 20.26, IR (ν_{max} KBr); 1230 (P=O). EI-MS; *m/z* 272.28 (M^+).

General procedure for the synthesis of the synthesis of α-aminophosphonates **(2a-i)**

A mixture of aldehyde (1 mmol), diethyl Phosphite, (1 mmol) and aniline (1 mmol), was placed in a teflon pressure vessel and vessel was closed with the help of "milestone TWISTER" and kept in a "STAR D Microwave Digestion System" under Pressure 6-9 bar, temperature 100-120 ^{o}C and microwave power 100-130 Watt for 15-30 minutes.

After completion, the reaction was cooled to room temperature and vessel was opened with the help of "milestone TWISTER" then reaction mixture was analyzed by TLC. The reaction mixture was treated with water, aqueous phase was extracted with ethylacetate (2x10 mL) and the organic layers was washed with water, saturated brine solution and dried over anhydrous Na_2SO_4. The combined organic layers were evaporated under reduced pressure and the resulting crude product was purified by Column Chromatography by using ethylacetate and *n*-hexane. The identity of the product was confirmed by IR, ^{1}H and ^{31}P{^{1}H} NMR and mass spectra. The spectroscopic data obtained on the synthesized compounds are given in below.

Spectroscopic data of the *α*-aminophosphonates

Diethyl (4-bromophenyl)(phenylamino)methylphosphonate (**2a**)

White solid; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.82-7.58 (m, 4H), 7.39 (t, 2H), 7.00 (t, 1H), 6.69 (d, 2H), 5.99 (1H, br s), 5.02 (1H, d), 4.39-4.00 (4H, m), 3.98-3.76 (1H. m), 3.58- 3.39 (1H, m) 1.37 (3H, t), 1.20 (3H,t). ^{31}P NMR ($CDCl_3$, 161.97 MHz): δ 21.81. IR (ν_{max} KBr); 1249 (P=O). EI-MS; *m/z* 399.84 (M^+).

Diethyl (4-nitrophenyl)(phenylamino)methylphosphonate (**2b**)

Light yellow solid; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.29-7.48 (m, 4H), 7.11 (t, 2H), 6.70 (t, 1H), 6.53 (d, 2H), 5.22 (1H, br s), 4.98 (1H, d), 4.15-3.82 (4H, m), 1.29 (3H, t), 1.12 (3H, t). ^{31}P NMR ($CDCl_3$, 161.97 MHz): δ 20.94. IR (ν_{max} KBr); 1252 (P=O). EI-MS; *m/z* 366.16 (M^+).

Diethyl (4-methoxyphenyl)(phenylamino)methylphosphonate (**2c**)

Viscous colorless oil; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.29-7.08 (m, 4H), 6.79 (t, 2H), 6.52 (t, 1H), 6.49 (d, 2H), 5.09 (1H, br s), 4.68 (1H, d), 4.15-3.62- (4H, m), 3.12 (3H, s), 1.21 (3H, t), 1.08 (3H, t). ^{31}P NMR ($CDCl_3$, 161.97 MHz): δ 22.90. IR (ν_{max} KBr); 1254 (P=O). EI-MS; *m/z* 350.26 (M^+).

Diethyl (4-chlorophenyl)(phenylamino)methylphosphonate (**2d**)

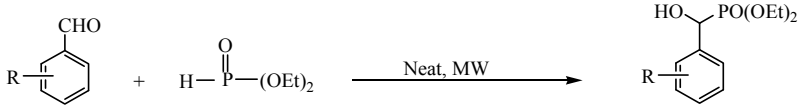
White solid; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.52-7.38 (m, 4H), 7.09 (t, 2H), 6.73 (t, 1H), 6.65 (d, 2H), 5.89 (1H, br s), 4.72 (1H, d), 4.20-4.00 (4H, m), 3.68-3.56 (1H. m), 3.48- 3.29 (1H, m) 1.30 (3H, t), 1.16 (3H,t). ^{31}P NMR ($CDCl_3$, 161.97 MHz): δ 22.05. IR (ν_{max} KBr); 1260 (P=O). EI-MS; *m/z* 354.19 (M^+).

Diethyl (4-hydroxyphenyl)(phenylamino)methylphosphonate (**2g**)

Viscous colorless oil; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.09-6.68 (m, 4H), 6.82 (t, 2H), 6.70-6.40 (m, 3H), 5.42 (1H, br s), 4.98 (1H,d), 4.55 (1H, d), 3.82-3.3.70 (2H, m), 3.73-3.62 (1H, m), 354-3.48 (1H, m), 1.09 (3H, t), 0.99 (3H, t). ^{31}P NMR ($CDCl_3$, 161.97 MHz): δ 22.63. IR (ν_{max} KBr); 1248 (P=O).EI-MS; *m/z* 334.19 (M^+).

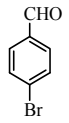
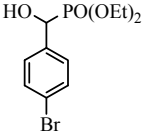
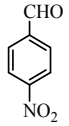
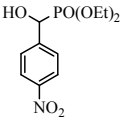
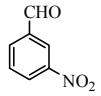
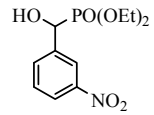
Results and Discussion

A series of *α*-hydroxyphosphonates and *α*-aminophosphonates were synthesized under catalyst and solvent free conditions under microwave as outlined in Scheme 1 (Table 1) and Scheme 2 (Table 2), respectively.



Scheme 1

Table 1. Synthesis of *α*-hydroxyphosphonates from aldehyde and diethylphosphite under microwave radiation

S. No.	Entry	Aldehyde	Product[a]	Time, min	%,Yield[b]	m.p. °C	m.p.[lit] °C
1	**1a**			10	94	76-79	77-78[34,35]
2	**1b**			14	90	85-87	87-88[36]
3	**1c**			13	88	81-83	81-82[34]

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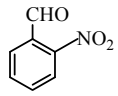
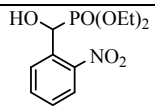
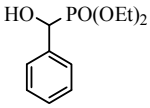
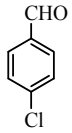
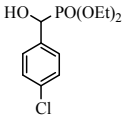
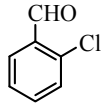
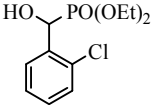
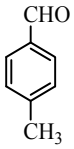
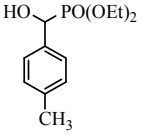
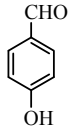
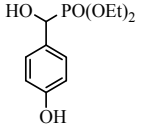
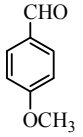
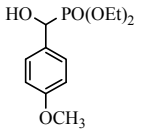
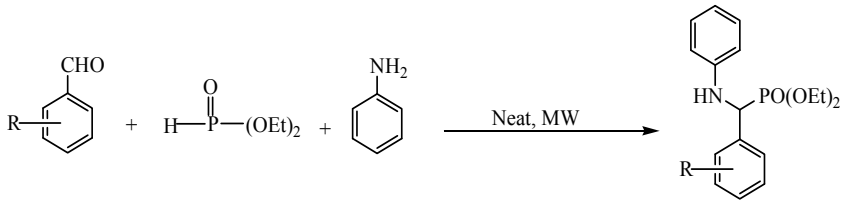
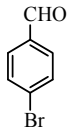
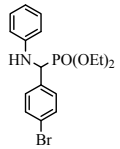
4	**1d**			15	84	115-117	114-116[34]
5	**1e**			18	91	74-76	75-76[34]
6	**1f**			12	95	66-68	67-68[35]
7	**1g**			17	93	74-76	74-75[35,36]
8	**1h**			11	89	94-96	94-95[35]
9	**1i**			20	79	73-75	75-76[36]
10	**1j**			16	93	120-122	120-121[34]

[a]Purity determined by TLC & [1]H and [31]P NMR. [b]Isolated yields.



Scheme 2

Table 2. Synthesis of *α*-aminophosphonates from aldehyde, aniline and diethylphosphite under microwave radiation

S. No.	Entry	Aldehyde	Product[a]	Time min	%, Yield[b]	mp °C	mp[lit] °C
1	**2a**			17	85	65-68	66-68[18]

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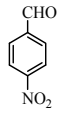
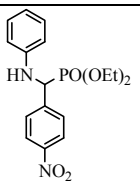
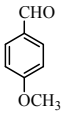
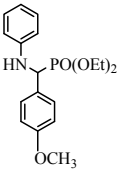
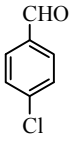
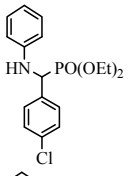
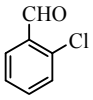
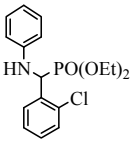
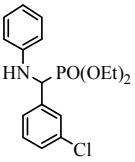
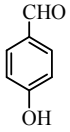
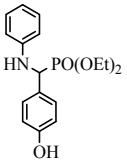
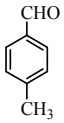
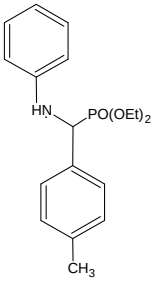
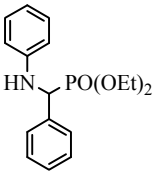
2	**2b**			15	97	120-122	120[37]
3	**2c**			24	90	oil	-
4	**2d**			22	87	58-59	60-62[37]
5	**2e**			25	93	86-88	88-90[17]
6	**2f**			30	94	88-90	90-91[18]
7	**2g**			20	93	oil	-
8	**2h**			18	87	59-61	61-63[37]
9	**2i**			16	91	88-90	90-91[18]

[a]Purity determined by TLC & [1]H and [31]P NMR. [b]Isolated yields

In order to find the optimum reaction conditions for the synthesis of diverse bioactive organophosphorus compounds, *i.e.* *α*- hyroxyphosphonates and *α*-aminophosphonates, initially, 4-bromobenzaldehyde and diethylphosphite were chosen under different temperature, pressure, power, and time for α-hyroxyphosphonates (Table 3, entry 1-10). For the synthesis of *α*-aminophosphonates, 4-nitrobenzaldehyde, diethylphosphite and aniline were chosen for optimization of reaction conditions (Table 4, entry 1-7).

Table 3. Effect of temperature and pressure, power and time on the synthesis of diethyl (4-bromophenyl)(hydroxyl)methylphosphonate

Entry	Time, min	Pressure, bar	Temperature, ^{o}C	Power, Watt	%, Yield*
1	5	1	80	70	trace
2	6	1	90	70	trace
3	7	2	90	70	57
4	8	2	90	80	65
5	8	3	90	80	72
6	9	3	90	80	75
7	9	4	90	90	84
8	10	5	90	100	94
9	15	6	100	100	93
10	15	6	100	110	89

**Isolated yields*

After optimizations of reaction conditions, the best yield of diethyl (4-bromophenyl)-(hydroxyl)methylphosphonate was obtained at a temperature 90 ^{o}C, pressure 5 bar, power 100 watt, and time 10 minute (Table 3, entry 8).

Table 4. Effect of temperature, pressure, power and time on the synthesis of diethyl (4-nitrophenyl)(phenylamino)methylphosphonate

Entry	Time, min	Pressure, bar	Temperature, ^{o}C	Power, Watt	%, Yield*
1	10	5	100	100	83
2	15	5	100	100	90
3	20	5	100	100	89
4	15	6	100	100	97
5	15	7	100	100	91
6	15	6	110	100	92
7	15	6	100	110	84

**Isolated yields*

As evident from Table 4, the best result was obtained for the synthesis of the diethyl (4-nitrophenyl)(phenylamino)methylphosphonate (Table 2, entry 1) at a temperature of 100 ^{o}C, pressure 6 bar, power 100 Watt and time 15 minute (Table 4, entry 4). Therefore, all reactions were performed under the optimized conditions.

Different protic and aprotic solvents such as water, dichloromethane, methanol acetonitrile, hexane, ethanol and toluene were screened for both type of reactions *i.e.* (Scheme 1, Table 5) and (Scheme 2, Table 6). As apparent from Table 5 and Table 6, the maximum yield of the products was obtained under solvent-free condition. Table 5 clearly indicates that the best results are obtained in solvent free condition (entry 8).

Table 5. Study of solvent effects on the reaction of 4-bromobenzaldehyde and diethylphosphite under microwave

Entry	Solvent	Time, min	%, Yield*
1	Dichloromethane	10	89
2	Acetonitrile	10	79
3	Water	10	66
4	Hexane	10	86
5	Ethanol	10	71
6	Methanol	10	79
7	Toluene	10	76
8	Solvent-free	10	94

**Isolated yields*

Table 6. Study of solvent effects on the reaction of 4-nitrobenzaldehyde, aniline and diethylphosphite under microwave

Entry	Solvent	Time, min	%,Yield*
1	Acetonitrile	15	82
2	Dichloromethane	15	76
3	Water	15	83
4	Hexane	15	85
5	Ethanol	15	73
6	Methanol	15	69
7	Toluene	15	73
8	Solvent-free	15	97

**Isolated yields*

The best yield (Table 6, entry 8) was obtained in solvent-free condition for the synthesis of diethyl (4-nitrophenyl)(phenylamino)methylphosphonate. The products were obtained as colourless/pale yellow solids or as viscous liquids. All compounds were characterized by IR, ^{1}H, ^{31}P{^{1}H} NMR and MASS Spectra. The spectra of synthesized compounds were compared with the literature valves[10-23]. All the spectroscopic data obtained were found to be in good agreement with the reported valves. The IR spectra of all synthesized compounds showed a characteristics band ranging from 1230 cm^{-1} to 1260 cm^{-1} corresponding to νP=O band, 3300 cm^{-1} to 3319 cm^{-1} for νN-H band[38], respectively.

The ^{31}P{^{1}H} NMR of all compounds in $CDCl_3$ exhibited a singlet, ranging from δ 20.19-22.90. The ^{31}P NMR value matches the literature values. The MASS spectra also showed a molecular ion peak (m/e) corresponding to the atomic mass of the compounds. The ^{1}H NMR of all *α*-amino- phosphonates compounds contained a board singlet at δ 5.09-5.99 due to –NH resonance[37] while *α*-hydroxyphosphonates compounds showed sharp singlet peak in range of δ 5.00-5.30 for OH proton. In general, the reaction of aldehydes bearing electron-withdrawing group (EWG) were accomplished in relatively less time than the aldehydes bearing electron-donating group (EDG).

Conclusion

In conclusion, we have developed a simple efficient, catalyst and solvent free synthesis of *α*-hydroxyphosphonates and *α*-aminophosphonates by the reaction of the corresponding aromatic amine and/ or aldehyde and diethylphosphite, under microwave conditions. These organic reactions are useful from both economical and environmental points of view. This methodology also prevents the formation of unwanted by-products and obviates the use of catalysts.

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