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Der Pharma Chemica, 2012, 4(6):2208-2213
(http://derpharmachemica.com/archive.html)

ISSN 0975-413X
CODEN (USA): PCHHAX

Synthesis, spectral characterization and antimicrobial activity of α-hydroxyphosphonates

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ABSTRACT

A simple and efficient method for the synthesis of α-hydroxyphosphonates ***(3a-j)*** *was accomplished by the reaction of aldehydes and dialkylphosphitesusing 1,4-dimethyl piperazineas a catalystunder solvent-free condition at room temperature.Their chemical structures were characterized by IR, NMR (*^{1}H*,* ^{13}C *&*^{31}P*), Mass spectral and elemental analysis. All the titled compounds were screened forInvitro antimicrobial activity.*

Keywords: α-Hydroxyphosphonates;phosphite; 1,4-dimethyl piperazine; antimicrobial activity;

INTRODUCTION

Phosphorus-carbon bond formation has attracted growing attention due to their novel applicationin organic synthesis and bio-organic chemistry. α-Functionalizedphosphonates are valuable intermediates for the preparation of medicinal compounds and synthetic intermediates [1-3]. Among these compounds α-amino and α-hydroxyphosphonates are important class of compounds that exhibit a variety of interesting and useful applications [4]. In recent years, the preparation of α-hydroxyphosphonates has attracted significant attention, due to their potential biological activities such as enzyme inhibitors, anti-HIV, anti-oxidant, antimicrobial and antiviral properties [5-7]. In addition, they are useful intermediates in the synthesis of other phosphorous compounds [8-10]. These compounds may also be used as precursors for the synthesis of organophosphorouspolymers possessing flame-resistant, corrosion-resistant, and ion-exchange properties [11-13]. Indeed, α-hydroxyphosphonates are also used as extractantsfor the recovery or separation of some metal ions [14]. Several different strategies for the synthesis of α-hydroxyphosphonates are known, the most common protocol is the reaction of aldehydes or ketones with dialkyl or trialkylphosphites in the presence of acidic or basic catalysts. Meanwhile, tris(trimethylsilyl)phosphite was also used to synthesize α-hydroxyphosphonates but it requires elevated temperature under anhydrous reaction conditions [15-17]. However, many of these methods are associated with variousdrawbacks such as use of metal catalysts, tedious experimental procedures, unsatisfactory yields, longreaction times and usage of expensive, moisture sensitivecatalysts. Hence, there is a need to develop a rapid and efficient protocol for the synthesis ofα-hydroxyphosphonates.

In continuation of our ongoing research work on the developmentof useful syntheticmethodologies [18-21], herein we report anefficient and practical method for the synthesis of α-hydroxyphosphonatesusing 1,4-dimethyl piperazineas a catalyst under solvent-free condition.

MATERIALS AND METHODS

2.1. Experimental

All chemicals were procured from Sigma-Aldrich and used without further purification. The melting points (mp) were determined in open capillary tubes on a Mel-Temp apparatus and are uncorrected. IR spectra were recorded in KBr pellets on a PerkinElmer 683 spectrophotometer.^{1}H, ^{13}C and ^{31}P NMR spectra were recorded on a Bruker instrument at 400 MHz in $CDCl_3$ using TMS as internal standard. ^{31}P NMR (202.44 MHz) was taken in $CDCl_3$ using 85% H_3PO_4 as external standard with broadband ^{1}H decoupling. Mass spectra were recorded on LCMS-2010A Shimadzu, Japan, spectrometer at University of Hyderabad, Hyderabad. Elementalanalysis was performed using EA 1112 Thermo Finnigan, France, instrument at University of Hyderabad, Hyderabad, India.

2.2. General Procedure for the Synthesis of α-Hydroxyphosphonates

A mixture of aldehyde (1 mmol),diethyl phosphite (1.5 mmol) and 1,4-dimethyl piperazine(20 mol %) undera neat condition was stirred at room temperature. After completion of thereaction as indicated by TLC, the contents were poured intowater and extracted with ethylacetate. The extract was dried withanhydrous. Na_2SO_4 and evaporated under vacuum. The crude product was subsequently purified by column chromatography on 60-120 mesh silica gel using ethyl acetate - hexane (1:4) as eluent. This procedure was applied successfully for the preparation of 3a-j.

2.2.1. Dimethyl hydroxy (4-hydroxy-3-nitrophenyl)methylphosphonate (3a):

Solid, Yield: 89 %, mp91-93 ºC. IR (KBr) (ν_{max} cm^{-1}): 3350 (brs, OH), 1232 (P=O), 1034 (P-O-C); ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.82-7.22 (m, 3H, Ar-H), 5.55 (s, 1H, OH), 3.85 (s, 1H, OH), 4.46 (d, J = 10.5 Hz, 1H, PCH), 3.62-3.45 (m, 3H, $POCH_3$) 3.42-3.24 (m, 3H, $POCH_3$); ^{13}C NMR ($CDCl_3$, 100.57 MHz) δ: 152.5 (C-4), 137.0 (C-3), 134.5 (C-6), 129.5 (C-1), 125.1 (C-2), 120.2 (C-5), 70.3 (d, J = 157.0 Hz, P-CH), 53.7 (d, J = 6.0 Hz, $POCH_3$), 53.6 (d, J = 6.0 Hz, $POCH_3$);^{31}P NMR ($CDCl_3$, 161.9 MHz): δ 22.82; ESI-MS: m/z 278 $(M+H)^+$; Anal. calcd. for $C_9H_{12}NO_7P$: C, 39.00; H, 4.36; N, 5.05; Found: C, 38.58; H, 4.20, N, 5.01;

2.2.2.Diethyl hydroxy(4-hydroxy-3-nitrophenyl)methylphosphonate (3b):

Solid, Yield: 94 %,mp 112-114 ºC. IR (KBr) (ν_{max} cm^{-1}): 3272 (brs, OH), 1243 (P=O), 1040 (P-O-C); ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.46-7.23 (m, 3H, Ar-H), 5.15 (s, 1H, OH), 4.79 (d, J = 10.9 Hz, 1H, PCH), 4.32-4.17 (m, 2H, $POCH_2$), 4.12-3.99 (m, 2H, $POCH_2$), 3.52 (s, 1H, OH), 1.35-1.24 (m, 3H, CH_3), 1.20-1.12 (m, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100.57 MHz) δ: 152.2 (C-4), 137.5 (C-3), 133.2 (C-6), 128.3 (C-1), 124.2 (C-2), 121.5 (C-5), 71.2 (d, J = 158.2 Hz, P-CH), 53.5 (d, J = 6.5 Hz, $POCH_2$), 53.6 (d, J = 6.4 Hz, $POCH_2$), 16.9 (d, J = 5.8 Hz, CH_3), 16.4 (d, J = 5.8 Hz, CH_3);^{31}P NMR ($CDCl_3$, 161.9 MHz): δ 20.8; ESI-MS: m/z 306 $(M+H)^+$; Anal. calcd. for $C_{11}H_{16}NO_7P$: C, 43.29; H, 5.28; N, 4.59; Found: C, 43.18; H, 5.21; N, 4.48;

2.2.3. Dibutyl hydroxy(4-hydroxy-3-nitrophenyl)methylphosphonate (3c):

Solid, Yield: 84%,mp 88-90 ºC. IR (KBr) (ν_{max} cm^{-1}): 3254 (brs, OH), 1235 (P=O), 1035 (P-O-C); ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.48-7.21 (m, 3H, Ar-H), 5.46 (s, 1H, OH), 4.75 (d, J = 11.2 Hz, 1H, PCH), 4.32-4.17 (m, 2H, $POCH_2$), 4.12-3.99 (m, 2H, $POCH_2$), 3.46 (s, 1H, OH), 1.71-1.55 (m, 4H, CH_2), 1.50-1.37 (m, 4H, CH_2), 1.32-1.21 (m, 3H, CH_3), 1.21-1.13 (m, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100.57 MHz) δ: 153.5 (C-4), 139.7 (C-3), 131.2 (C-6), 129.5 (C-1), 126.8 (C-2), 120.8 (C-5), 72.8 (d, J = 154.4 Hz P-CH), 54.8 (d, J= 6.5 Hz, $POCH_2$), 54.2 (d, J = 6.2 Hz, $POCH_2$), 30.2 (CH_2), 30.1 (CH_2), 18.2 (CH_2), 18.0 (CH_2), 16.8 (d, J = 5.8 Hz, CH_3), 16.2 (d, J = 5.8 Hz, CH_3); ^{31}P NMR ($CDCl_3$, 161.9 MHz): δ 22.4; ESI-MS: m/z 362 $(M+H)^+$; Anal. calcd. for $C_{15}H_{24}NO_7P$: C, 49.86; H, 6.69; N, 3.88; Found: C, 49.78; H, 6.62; N, 3.79;

2.2.4. Diphenyl hydroxy(4-hydroxy-3-nitrophenyl)methylphosphonate (3d):

Solid, Yield: 84 %, mp 87-89 ºC. IR (KBr) (ν_{max} cm^{-1}): 3332 (brs, OH), 1249 (P=O), 1038 (P-O-C); ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.46-7.21 (m, 13H, Ar-H), 5.26 (s, 1H, OH), 4.61 (d, J = 10.8 Hz, 1H, PCH), 4.32 (s, 1H, OH); ^{13}C NMR ($CDCl_3$, 100.57 MHz) δ: 155.9 (C-4), 150.2 (C-1′), 149.8 (C-1″), 138.5 (C-3), 134.2 (C-6), 131.7 (C-3′ & C-5′), 130.9 (C-3″ & C-5″), 130.1 (C-1), 126.8 (C-2), 122.4 (C-4′), 122.1 (C-4″), 120.9 (C-5), 120.4 (C-2′ & C-6′), 120.0 (C-2″ & C-6″), 75.8 (d, J = 152.8 Hz P-CH); ^{31}P NMR ($CDCl_3$, 161.9 MHz): δ 22.4; ESI-MS: m/z 402 $(M+H)^+$; Anal. calcd. for $C_{19}H_{16}NO_7P$: C, 56.87; H, 4.02; N, 3.49; Found: C, 56.81; H, 3.95; N, 3.37;

2.2.5. Dibenzyl hydroxy(4-hydroxy-3-nitrophenyl)methylphosphonate (3e):

Solid, Yield: 88 %, mp 103-105 ºC. IR (KBr) (ν_{max} cm^{-1}): 3235 (brs, OH), 1252 (P=O), 1028 (P-O-C); ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.44-7.18 (m, 13H, Ar-H), 5.34 (s, 2H, Ph-CH_2), 5.30 (s, 2H, Ph-CH_2), 5.28 (s, 1H, OH), 4.49

(d, *J* = 10.4 Hz, 1H, PCH), 4.42 (s, 1H, OH); ^{13}C NMR ($CDCl_3$, 100.57 MHz) δ: 156.8 (C-4), 138.5 (C-3), 136.2 (C-1′), 135.8 (C-1″), 134.8 (C-6), 130.2 (C-1), 129.4 (C-3′ & C-5′), 129.0 (C-3″ & C-5″), 128.4 (C-2′ & C-6′), 128.0 (C-2″ & C-6″), 127.2 (C-4′), 121.8 (C-4″), 124.7 (C-2), 120.5 (C-5), 76.2 (d, *J* = 154.8 Hz P-CH), 54.8 (d, *J*= 6.2 Hz, $POCH_2$), 54.2 (d, *J* = 6.2 Hz, $POCH_2$); ^{31}P NMR ($CDCl_3$, 161.9 MHz): δ 20.2; ESI-MS: m/z 430 $(M+H)^+$; Anal. calcd. for $C_{21}H_{20}NO_7P$: C, 58.74; H, 4.70; N, 3.26; Found: C, 58.62; H, 4.61; N, 3.18;

2.2.6. Dimethyl (4-chloro-3-nitrophenyl)(hydroxy)methylphosphonate (3f):
Solid, Yield: 86 %, mp 75-77 ºC. IR (KBr) (ν_{max} cm^{-1}): 3321 (brs, OH), 1238 (P=O), 1032 (P-O-C); ^{1}H NMR ($CDCl_3$, 400 MHz) *δ*: 7.96-7.24 (m, 3H, Ar-H), 4.42 (d, *J* = 10.2 Hz, 1H, PCH), 3.69 (s, 1H, OH), 3.60-3.42 (m, 3H, $POCH_3$) 3.40-3.22 (m, 3H, $POCH_3$); ^{13}C NMR ($CDCl_3$, 100.57 MHz) *δ*: 144.8 (C-3), 134.5 (C-6), 133.5 (C-1), 131.2 (C-5), 127.0 (C-4), 124.4 (C-2), 72.8 (d, *J* = 152.8 Hz, P-CH), 53.8 (d, *J* = 6.4 Hz, $POCH_3$), 53.6 (d, *J* = 6.2 Hz, $POCH_3$);^{31}P NMR ($CDCl_3$, 161.9 MHz): δ 21.23; ESI-MS: m/z 296 $(M+H)^+$; Anal. calcd. for $C_9H_{11}ClNO_6P$: C, 36.57; H, 3.75; N, 4.74; Found: C, 36.51; H, 3.68; N, 4.65;

2.2.7. Diethyl (4-chloro-3-nitrophenyl)(hydroxy)methylphosphonate (3g):
Solid, Yield: 92 %,mp 118-120 ºC. IR (KBr) (ν_{max} cm^{-1}): 3330 (brs, OH), 1232 (P=O), 1048 (P-O-C); ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.49-7.18 (m, 3H, Ar-H), 4.72 (d, *J* = 10.2 Hz, 1H, PCH), 4.28-4.20 (m, 2H, $POCH_2$), 4.12-4.02 (m, 2H, $POCH_2$), 3.65 (s, 1H, OH), 1.30-1.22 (m, 3H, CH_3), 1.19-1.12 (m, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100.57 MHz) δ: 147.4 (C-3), 134.2 (C-6), 133.8 (C-1), 130.2 (C-5), 126.4 (C-4), 124.8 (C-2), 74.2 (d, *J* = 152.4 Hz, P-CH), 53.5 (d, *J* = 6.4 Hz, $POCH_2$), 53.2 (d, *J* = 6.4 Hz, $POCH_2$), 16.8 (d, *J* = 6.2 Hz, CH_3), 16.4 (d, *J* = 6.0 Hz, CH_3); ^{31}P NMR ($CDCl_3$, 161.9 MHz): δ 21.6; ESI-MS: m/z 324 $(M+H)^+$; Anal. calcd. for $C_{11}H_{15}NO_7P$: C, 40.82; H, 4.67; N, 4.33; Found: C, 40.72; H, 4.61; N, 4.24;

2.2.8. Dibutyl (4-chloro-3-nitrophenyl)(hydroxy)methylphosphonate (3h):
Solid, Yield: 92%,mp 95-97 ºC. IR (KBr) (ν_{max} cm^{-1}): 3252 (brs, OH), 1228 (P=O), 1032 (P-O-C); ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.52-7.20 (m, 3H, Ar-H), 4.72 (d, *J* = 11.4 Hz, 1H, PCH), 4.30-4.21 (m, 2H, $POCH_2$), 4.18-4.08 (m, 2H, $POCH_2$), 3.40 (s, 1H, OH), 1.70-1.58 (m, 4H, CH_2), 1.52-1.37 (m, 4H, CH_2), 1.34-1.26 (m, 3H, CH_3), 1.22-1.16 (m, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100.57MHz) δ: 147.8 (C-3), 135.2 (C-6), 134.8 (C-1), 132.2 (C-5), 126.9 (C-4), 124.9 (C-2), 76.6 (d, *J* = 150.8 Hz, P-CH), 56.8 (d, *J*= 6.8 Hz, $POCH_2$), 56.2 (d, *J* = 6.4 Hz, $POCH_2$), 32.2 (CH_2), 31.8 (CH_2), 18.4 (CH_2), 18.2 (CH_2), 16.6 (d, *J* = 6.0 Hz, CH_3), 16.3 (d, *J* = 5.8 Hz, CH_3); ^{31}P NMR ($CDCl_3$, 161.9 MHz): δ 20.8; ESI-MS: m/z 380 $(M+H)^+$; Anal. calcd. for $C_{15}H_{23}NO_6P$: C, 47.44; H, 6.10; N, 3.69; Found: C, 47.38; H, 6.02; N, 3.60;

2.2.9. Diphenyl hydroxy(4-hydroxy-3-nitrophenyl)methylphosphonate (3i):
Solid, Yield: 88%, mp 83-85 ºC. IR (KBr) (ν_{max} cm^{-1}): 3342 (brs, OH), 1240 (P=O), 1030 (P-O-C); ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.32-7.28 (m, 13H, Ar-H), 4.62 (d, *J* = 10.2 Hz, 1H, PCH), 4.38 (s, 1H, OH); ^{13}C NMR ($CDCl_3$, 100.57 MHz) δ: 150.2 (C-1′), 150.0 (C-1″),147.2 (C-3), 134.8 (C-1), 134.2 (C-6), 132.2 (C-5), 131.8 (C-3′ & C-5′), 130.8 (C-3″ & C-5″), 126.8 (C-4), 124.8 (C-2), 123.4 (C-4′), 123.0 (C-4″), 120.4 (C-2′ & C-6′), 120.1 (C-2″ & C-6″), 76.6 (d, *J* = 150.2 Hz P-CH); ^{31}P NMR ($CDCl_3$, 161.9 MHz): δ 21.8; ESI-MS: m/z 420 $(M+H)^+$; Anal. calcd. for $C_{19}H_{15}NO_6P$: C, 54.37; H, 3.60; N, 3.34; Found: C, 54.30; H, 3.52; N, 3.24;

2.2.10. Dibenzyl hydroxy(4-hydroxy-3-nitrophenyl)methylphosphonate (3j):
Solid, Yield: 88 %, mp 125-127 ºC. IR (KBr) (ν_{max} cm^{-1}): 3232 (brs, OH), 1242 (P=O), 1030 (P-O-C); ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.25-7.24 (m, 13H, Ar-H), 5.32 (s, 2H, Ph-CH_2), 5.30 (s, 2H, Ph-CH_2), 4.42 (d, *J* = 10.2 Hz, 1H, PCH), 4.32 (s, 1H, OH); ^{13}C NMR ($CDCl_3$, 100.57 MHz) δ: 148.5 (C-3), 135.2 (C-1′), 135.0 (C-1″), 134.2 (C-1), 134.0 (C-6), 132.4 (C-5), 128.4 (C-3′ & C-5′), 128.1 (C-3″ & C-5″), 127.4 (C-2′ & C-6′), 127.2 (C-2″ & C-6″), 126.8 (C-4), 126.4 (C-4′), 126.2 (C-4″), 124.2 (C-2), 74.6 (d, *J* = 152.8 Hz P-CH)64.2 (d, *J*= 6.2 Hz, $POCH_2$), 64.0 (d, *J* = 6.2 Hz, $POCH_2$);^{31}P NMR ($CDCl_3$, 161.9 MHz): δ 20.2; ESI-MS: m/z 448 $(M+H)^+$; Anal. calcd. for $C_{21}H_{19}NO_6P$: C, 56.32; H, 4.28; N, 3.13; Found: C, 56.24; H, 4.20; N, 3.04;

2.3. Antimicrobial Activity
Antibacterial activity [22] of **3a-j** was tested against the growth of *Staphylococcus aureus* (ATCC 25923) (gram +ve) and *Escherichia coli* (ATCC 25922) (gram –ve) by disc diffusion method at various concentrations (50, 100 ppm) and results were summarized in**Table 1**. Penicillin was used as the reference compound. The compounds 3a-j showed moderate activity against Staphylococcus aureus and Escherichia coli. The highlight is that the three compounds **3e, 3g** and **3j** were more effective.

Table 1: Antibacterial activity of compounds 3a-j (µg/mL)

Compound	Zone of inhibition (%)			
	Escherichia coli		*Staphylococcus aureus*	
	50	100	50	100
3a	5	8	6	8
3b	6	9	5	7
3c	6	8	5	8
3d	6	9	6	7
3e	7	10	7	9
3f	5	7	5	8
3g	7	10	7	9
3h	6	9	7	8
3i	7	8	5	6
3j	7	10	7	9
Penicillin[a]	8	12	7	10

[a]*Reference Compound*

They were also screened for antifungal activity [22] against *Aspergillusniger* (ATCC 16404) and *Helminthosporiumoryzae* (ATCC 11000) species along with the standard fungicide Griseofulvin by the disc diffusion method at two different concentrations (50, 100 ppm)and results were summarized in**Table 2**. It is gratifying to observe that the majority of the compounds (3a-j) exhibited higher antifungal activity against both tested fungal strains when compared with that of griseofulvin. The significant results are that **3e** and **3j** exhibited higher activities than the standard griseofulvin against both the fungi.

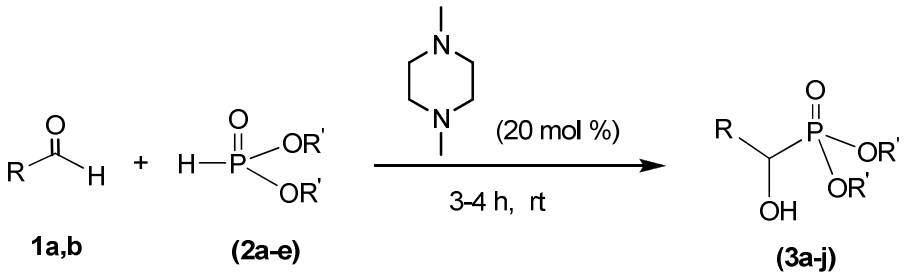
Table 2: Antifungal activity of compounds 3a-j (µg/mL)

Compound	Zone of inhibition (%)			
	Aspergillusniger		*Helminthosporiumoryzae*	
	50	100	50	100
3a	6	9	7	9
3b	5	8	7	8
3c	6	9	7	8
3d	6	9	8	9
3e	8	13	9	12
3f	5	9	5	9
3g	6	9	8	9
3h	5	8	7	10
3i	7	10	8	12
3j	8	13	9	13
Griseofulvin[a]	7	12	9	12

[a]*Reference Compound*

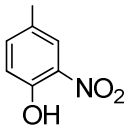
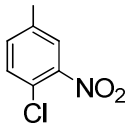
RESULTS AND DISCUSSION

Initially we have synthesiszedα-hydroxyphosphonates**(3a-j)**by the reaction of aldehydes**(1a,b)** anddialkylphosphites**(2a-e)** in thepresence of 1,4-dimethyl piperazine(20 mol %) as catalyst under solvent-free conditions at room temperature**(Scheme 1)**.



Scheme 1: Synthesis of α-Hydroxyphosphonates (3a-j)

Compound	R'
2a, 3a & 3f	CH_3
2b, 3b & 3g	C_2H_5
2c, 3c & 3h	C_4H_7
2d, 3d & 3i	C_6H_5
2e, 3e & 3j	CH_2-C_6H_5

Compound	R
1a, 3a-e	
1b, 3f-j	

In initial endeavour we carried out the reaction of 4-hydroxy-3-nitrobenzaldehyde and dimethyl phosphite in the absence of 1,4-dimethyl piperazine. It was observed that there is no formation of product even after 6 hours of reaction time. After that by the addition of 1,4-dimethyl piperazine to the reaction mixture in catalytic amount (20 mol %) the reaction proceeded smoothly and afforded 88 % yield of the product with in 3 h of reaction time. Which indicates that 1,4-dimethyl piperazineis necessary for this transformation. After that we extended this process with aldehydes and various dialkylphosphitesto synthesize 3a-j.It was observed that all the reactions were successfully completed within 3-4 hours and gave the corresponding α-hydroxyphosphonatesin 84–93% yields. The chemical structures of allthe products were fully characterized by IR, ^{1}H, ^{13}C&^{31}P NMRandmass spectral data.The antimicrobial activity of the title compounds was evaluated by the standard methods and the results were summarized in **Table 1 & 2**.

CONCLUSION

In conclusion, 1,4-dimethyl piperazinewas found to be an efficient catalyst for the synthesis of α-hydroxyphosphonates by reaction of aldehydes and dialkylphosphite under solvent-free condition at room temperature. The main advantages of the present synthetic protocol are mild, solvent-free conditions and easy work-up procedure. It is expected that the present methodology will find application in organic synthesis. All the titled compounds were screened for antimicrobial activity and some of the compounds (3a-j) were exhibit high activity compared to reference standard.

Acknowledgments
The authors express their grateful thanks to Prof. C. D. Reddy, Department of Chemistry, Sri Venkateswara University, Tirupati and also thankful to UGC for providing financial assistance in the form of UGC-BSR One Time Grant (F.4-10/2010, BSR).

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