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An efficient synthesis of α-hydroxy phosphonates and 2-nitroalkanols using $Ba(OH)_2$ as catalyst

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ABSTRACT

The α-hydroxy phosphonates have been synthesized using simple, inexpensive, and commonly available $Ba(OH)_2 \cdot 8H_2O$ at room temperature and quantitative yields were obtained in just 15 min for most of the reactions. On applying the same reaction condition to aqueous mediated Henry reaction, 2-nitroalkanols were obtained in good to excellent yield within 15 min.

1. Introduction

The addition of dialkyl phosphites to carbonyl compounds has become one of the most desired methods for the synthesis of α-hydroxy phosphonates [1]. The importance of α-hydroxy phosphonates has been well-recognized [2]. They are used as antibacterial agents [3], herbicides [4], inhibitors of different enzymes [5], and anti-HIV agents [6]. Many other biologically significant molecules are also synthesized from α-hydroxy phosphonates such as α-acetoxy phosphonates [7], α-amino phosphonates [8], α-keto phosphonates [9], α-halo phosphonates [10] and α-hydrazinoalkyl phosphonates [11].

The wide range of applications publicized by this class of compounds resulted in an extensive development of competent methodologies for synthesis of α-hydroxy phosphonates. This challenge was initially met using stoichiometric or super stoichiometric amounts of alumina [12], magnesium oxide [13], triethylamine [10] and pyridine [14]. Subsequently, catalytic amount (>0.2 equiv.) of titanium isopropoxide [15], potassium fluoride [16] and sodium ethoxide [17] were employed but yields were not superior. Conversely, tetramethylguanidine catalyzed reaction required large excess of dialkylphosphite (>30 equiv.) [18]. The synthesis of α-hydroxy phosphonates has also been achieved at higher temperature with catalysts such as molybdenum dichloride dioxide [19], and triethylamine [20] and even without any catalyst [21]. It has been reported that some of the α-hydroxy phosphonates decomposed to the corresponding starting materials when sodium ethoxide or higher temperature reaction condition is employed. Recently, tetracoordinated lanthanide amide $[(Me_3Si)_2N)]_3Ln(\mu\text{-}Cl)Li(THF)_3$, a chloride-bridged "ate" complex [22] derived from $Ln[N(SiMe_3)_2]_3$, LiCl and THF was used as catalyst for this purpose. Based on the existing methods, it is clear that the reaction requires either stoichiometric or catalytic amount of reagents under harsh reaction conditions to proceed. Therefore, the development of a new catalytic system, which is inexpensive, commonly available, easy to handle and time resolved, is highly desirable.

We have been interested in the development of cost-effective and readily accessible catalysts for the synthesis of optically active α-hydroxy ketones [23–25] and α-hydroxy esters [26]. In this context, we wish to report simple, commonly available, inexpensive $Ba(OH)_2 \cdot 8H_2O$ as an efficient catalyst for the synthesis of α-hydroxy phosphonates and 2-nitroalkanols (Scheme A1).

2. Experimental

2.1. General

$Ba(OH)_2 \cdot 8H_2O$ LR (NLT 97%, Product No.: B0040) was purchased from Rankem Chemicals, India and the bottle was opened a month before use. Dialkyl phosphite was purchased from Aldrich chemicals and was used as received. All the aldehydes were purified by washing with saturated $NaHCO_3$ prior to use. Thin-layer

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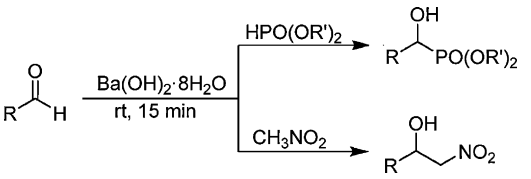


Scheme A1. Synthesis of α-hydroxy phosphonates and 2-nitroalkanols.

chromatography (TLC) was performed using Merck silica gel 60 F_{254} precoated plates (0.25 mm) and visualized by UV fluorescence quenching. Silica gel for column chromatography (particle size 100–200 mesh) was purchased from SRL India. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker 400 MHz instrument. ^{1}H NMR spectra are reported relative to Me_4Si (δ 0.0 ppm) or residual $CDCl_3$ (δ 7.26 ppm). ^{13}C NMR spectra are reported relative to $CDCl_3$ (δ 77.16 ppm). IR spectra are recorded on a Nicolet 4100 spectrometer and are reported in frequency of absorption (cm^{-1}). High resolution mass spectra (HRMS) were recorded on Q-TOF Micro mass spectrometer. ^{1}H, ^{13}C NMR and HRMS spectral data have been included for all compounds.

2.2. General procedure for synthesis of α-hydroxy phosphonates

A mixture of diethyl phosphite (1.2 mmol), aldehyde (1 mmol) and $Ba(OH)_2{\cdot}8H_2O$ (2–7 mol%) in THF (3 mL) was taken in a reaction tube and stirred at room temperature for 15 min. The reaction mixture was then concentrated under reduced pressure and the resulting residue was purified by silica gel column chromatography (eluents: hexanes-ethyl acetate) to isolate α-hydroxy phosphonate.

Characterization data for representative α-hydroxy phosphonate: diethyl hydroxy(4-nitrophenyl)methylphosphonate (Table A2, entry 1): Yellow solid, mp: 89–91 °C. R_f 0.40; (hexanes: ethyl acetate, 20:80, v/v): ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.20–1.32 (m, 6H), 4.00–4.17 (m, 4H), 5.16 (d, J = 12.4 Hz, 1H), 5.55 (s, 1H), 7.66 (d, J = 8.8 Hz, 2H), 8.19 (d, J = 8.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 16.5 (t, J = 4.7 Hz), 63.4 (d, J = 7.5 Hz), 64.1 (d, J = 7.0 Hz), 70.1 (d, J = 157.9 Hz), 123.4, 127.8 (d, J = 4.9 Hz), 144.6, 147.6; IR (Neat): 740, 1025, 1265, 3271 cm^{-1}; HRMS (m/z): $[M+H]^+$ calcd for $C_{11}H_{17}NO_6P$, 290.0794; found, 290.0802.

2.3. General procedure for synthesis of 2-nitroalkanols

A mixture of nitroalkane (10 mmol), aldehyde (1 mmol) and $Ba(OH)_2$ (5 mol%) in H_2O (3 mL) was taken in a reaction tube and stirred at room temperature for 15 min. The reaction mixture was then extracted three times with ethyl acetate. The combined organic layer was dried over anhydrous sodium sulfate and concentrated in vacuo. The resulting residue was purified by silica gel column chromatography (eluents: hexanes-ethyl acetate) to isolate 2-nitroalkanol.

Characterization data for representative 2-nitroalkanols: 2-nitro-1-(4-nitrophenyl)ethanol (Table A3, entry 1): Yellow solid, mp: 85–87 °C. R_f 0.28; (hexanes: ethyl acetate, 80:20, v/v): ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.29 (s, 1H), 4.58–4.65 (m, 2H), 5.57–5.65 (m, 1H), 7.62 (d, J = 8.8 Hz, 2H), 8.25 (d, J = 8.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 70.1, 80.8, 124.2, 127.1, 145.5, 148.0; IR (Neat) 1345, 1523, 3439 cm^{-1}; HRMS (m/z): $[M+Na]^+$ calcd for $C_8H_8N_2O_5Na$, 235.0331; found, 235.0324.

3. Results and discussion

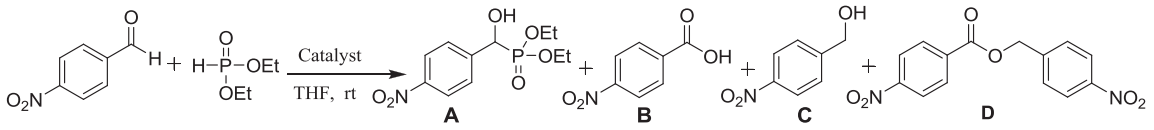
Initially, 4-nitrobenzaldehyde was chosen as the model substrate and was reacted with 1.2 equiv. of diethyl phosphite in the presence of 10 mol% of NaOH in THF at room temperature. The starting material was completely consumed in just 15 min and produced 58% yield for corresponding α-hydroxy phosphonate **A** along with other side products (**B**, **C** and **D**), which are due to Cannizzaro and Tishchenko reactions (Table A1, entry 1). The reaction with LiOH slightly increased the yield (Table A1, entry 2) while other bases such as KOH and CsOH decreased the yield and also increased the reaction time (entries 3–4).

Interestingly, when $Ba(OH)_2{\cdot}8H_2O$ was used instead of NaOH, the yield was increased from 58% to 93% without altering the reaction time and no other side products were observed (entry 1 vs 5). While this result appeared promising, further optimization with different catalytic amount of $Ba(OH)_2{\cdot}8H_2O$ using various solvents was even more enlightening. On reducing the $Ba(OH)_2{\cdot}8H_2O$ loading from 10 mol% to 1 mol% and 1.5 mol%, the reaction of fered more or less same yield with slightly increased reaction time (entries 6 and 8). The reaction with 2 mol% of $Ba(OH)_2{\cdot}8H_2O$ was found to be most efficient as it gave 98% yield for corresponding α-hydroxy phosphonate within 15 min (entry 7). In the same reaction, substitution of $Ba(OH)_2{\cdot}8H_2O$ with milder or stronger bases such as K_2CO_3 or NaOMe led to significantly lower yields (entries 9 and 10). Regeneration of aldehyde and phosphite may be the reason for the lower yield of α-hydroxy phosphonates in case of NaOMe as reported earlier [17]. It is interesting to note that the side reactions (Cannizzaro and Tishchenko reactions), observed in case of other bases, were not observed in case of $Ba(OH)_2{\cdot}8H_2O$. However, in the absence of the catalyst $Ba(OH)_2{\cdot}8H_2O$, no product formation was observed (entry 15).

The solvent screening revealed that non-polar solvent such as toluene could be a suitable reaction medium as it provided 92% yield on allowing longer reaction time (entry 11). Similarly, polar solvent such as ethanol was also efficient and furnished 89% yield in 15 min (entry 14). Although the reaction proceeded in other solvents such as chloroform and acetonitrile, the yields were low even after longer reaction time (entries 12 and 13). Solvent study clearly proved that THF was the solvent of choice in terms of reaction rate as well as yield (entry 7 vs 11–14). The higher yield of the product in toluene can be explained by the fact that the reactivity of nucleophile is enhanced in a polar aprotic solvent. However, the longer reaction time may be due to the lesser solubility of the catalyst in toluene. On the other hand, ethanol being a polar protic solvent increases the solubility of the catalyst resulting in a shorter reaction time. Importantly, the high yield and faster reaction rate observed in case of THF could be attributed to the fair solubility of catalyst due to moderately polar aprotic nature of the solvent and its consequent ability to insulate the cation in the reaction medium which in turn activates the nucleophile.

In order to explore the scope of this reaction, the optimized reaction condition was applied for the synthesis of a number of α-hydroxy phosphonates from various aldehydes including aromatic, heterocyclic, aliphatic, and α,β-unsaturated aldehydes and even from different dialkyl phosphites and the results are summarized in Table A2. The reaction of 4-nitrobenzaldehyde with diethyl, dibutyl and dibenzyl phosphites proceeded effortlessly in the presence of 2 mol% of $Ba(OH)_2{\cdot}8H_2O$ in THF and produced the corresponding α-hydroxy phosphonates with excellent yields in just 15 min (Table A2, entries 1–3). However, the substituted aromatic aldehydes required 5 mol% of $Ba(OH)_2{\cdot}8H_2O$ for completion of the reaction with the nitro group being an exception. Irrespective of their position, *para*- or *meta*-substituents on aromatic aldehydes, in general, gave quantitative yields using 5 mol% of $Ba(OH)_2{\cdot}8H_2O$ in 15 min (entries 5–15). The nitro group, being highly electron withdrawing in nature, increases the reactivity of electrophile so that the completion of reaction requires only 2 mol% of catalyst. However, the nitro group at *ortho*-position requires 5 mol% of catalyst which may be due to steric effect. Other electron withdrawing

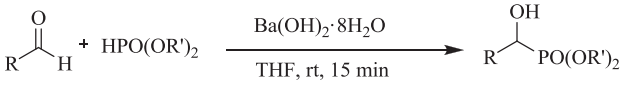
Table A1
Effect of catalysts and solvents on addition of diethyl phosphite to 4-nitrobanzaldehyde.[a].



Entry	Catalyst	Solvent	Catalyst (mol%)	Time	Yield (%)[b]			
					A	**B**	**C**	**D**
1	NaOH	THF	10	15 min	58	11	13	6
2	$LiOH{\cdot}H_2O$	THF	10	30 min	75	8	9	–
3	KOH	THF	10	20 h	51	13	14	6
4	$CsOH{\cdot}H_2O$	THF	10	20 h	43	18	15	8
5	$Ba(OH)_2{\cdot}8H_2O$	THF	10	15 min	93	–	–	–
6	$Ba(OH)_2{\cdot}8H_2O$	THF	1	30 min	91	–	–	–
7	$Ba(OH)_2{\cdot}8H_2O$	THF	2	15 min	98	–	–	–
8	$Ba(OH)_2{\cdot}8H_2O$	THF	1.5	30 min	90	–	–	–
9	K_2CO_3	THF	2	8 h	55[c]	–	–	–
10	NaOMe	THF	2	4 h	34[c]	–	–	–
11	$Ba(OH)_2{\cdot}8H_2O$	PhMe	2	4 h	92	–	–	–
12	$Ba(OH)_2{\cdot}8H_2O$	$CHCl_3$	2	8 h	67[c]	–	–	–
13	$Ba(OH)_2{\cdot}8H_2O$	CH_3CN	2	8 h	43[c]	–	–	–
14	$Ba(OH)_2{\cdot}8H_2O$	EtOH	2	15 min	89	–	–	–
15	–	THF	2	20 h	nr	–	–	–

[a] All the reactions were carried out with 1 mmol of aldehyde and 1.2 mmol of diethyl phosphite.
[b] Isolated yield.
[c] Remaining starting material was recovered.

Table A2
Addition of dialkyl phosphite to aldehydes using $Ba(OH)2{\cdot}8H_2O$ as catalyst.[a]



Entry	R	R′	$Ba(OH)_2{\cdot}8H_2O$ (mol%)	Yield (%)[b]
1	4-NO_2-C_6H_4	Et	2	98
2	4-NO_2-C_6H_4	^{n}Bu	2	92
3	4-NO_2-C_6H_4	Bn	2	90
4	3-NO_2-C_6H_4	Et	2	97
5	C_6H_5	Et	5	94
6	4-Me-C_6H_4	Et	5	92
7	3-Me-C_6H_4	Et	5	98
8	4-Br-C_6H_4	Et	5	92
9	3-Br-C_6H_4	Et	5	93
10	4-Cl-C_6H_4	Et	5	98
11	4-CN-C_6H_4	Et	5	99
12	3-CN-C_6H_4	Et	5	99
13	4-Et-C_6H_4	Et	5	91
14	4-F-C_6H_4	Et	5	99
15	3-F-C_6H_4	Et	5	98
16	2-NO_2-C_6H_4	Et	5	97
17	2-Me-C_6H_4	Et	5	97
18	2-Cl-C_6H_4	Et	5	98
19	2,6-Di-Cl-C_6H_3	Et	5	88
20	2-Furyl	Et	5	96
21	2-Thienyl	Et	5	88
22	2-Pyridyl	Et	7	90
23	3-Pyridyl	Et	7	97
24	4-Pyridyl	Et	7	99
25	4-OMe-C_6H_4	Et	7	84
26	2,3,4-Tri-OMe-C_6H_4	Et	7	87
27	1-Naphthyl	Et	7	93
28	2-Naphthyl	Et	7	95
29	9-Anthryl	Et	7	91
30	Cinnamyl	Et	7	94
31	Isobutyl	Et	7	72

[a] All the reactions were carried out with 1 mmol of aldehydes and 1.2 mmol of dialkyl phosphites
[b] Isolated yield

substituents were not strong enough to activate the electrophile, thereby, requiring 5 mol% of catalyst.

It is worth noting that *ortho*-substituted aromatic aldehydes including 2,6-dichlorobenzaldehyde which are considered as sterically hindered substrates also provided admirable yields for resultant α-hydroxy phosphonates (entries 16–19). Likewise, heterocyclic five membered aldehydes such as 2-furylaldehyde and 2-thienylaldehyde also provided the α-hydroxy phosphonates in

good to excellent yields (entries 20 and 21). In addition, 7 mol% of $Ba(OH)_2{\cdot}8H_2O$ was used for the synthesis of some α-hydroxy phosphonates which were obtained from notable aldehydes including highly electron rich 2,3,4-trimethoxybenzaldehyde (entries 22–29). Intriguingly, cinnamaldehyde (α,β-unsaturated aldehyde) and isobutraldehyde (aliphatic aldehyde) also reacted with diethyl phosphite to furnish corresponding α-hydroxy phosphonates (entries 30 and 31). The electron releasing group decreases the reactivity of electrophile leading to the reaction requiring 7 mol% of catalyst.

After developing an efficient method for synthesis of α-hydroxy phosphonates, the optimized reaction condition was then applied to aqueous mediated Henry reaction. Usually, base catalyzed Henry reaction is performed in organic solvent [27]. Only a few studies are known in which base has been used as a catalyst in aqueous mediated Henry reaction since the side reactions (Aldol and Cannizzaro reactions) and undesired nitroalkene, formed through elimination of water from 2-nitroalkanols, predominate over the targeted Henry product 2-nitroalkanols. Very important improvement has been made using sodium hydroxide in combination with cetyltrimethylammonium chloride (CTACl) to promote aqueous mediated Henry reaction [28]. In addition, stoichiometric amount of Et_3N has also been used for aqueous mediated Henry reaction [29]. Many other metal complexes and biocatalysts have also been reported to facilitate the Henry reaction in aqueous medium [30,31]. Herein, we report a simple, commonly available $Ba(OH)_2$ catalyzed aqueous mediated Henry reaction.

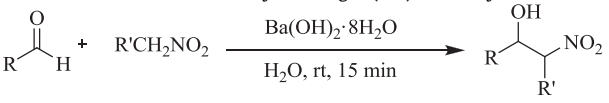
During the solvent screening of $Ba(OH)_2$ catalyzed synthesis of α-hydroxy phosphonates, nitromethane was used as a solvent which resulted in mixture of products such as α-hydroxy phosphonates and 2-nitroalkanol. This result induced us to investigate $Ba(OH)_2$ catalyzed Henry reaction. To begin, 4-nitrobenzaldehyde (1 mmol) was reacted with nitromethane (3 mL) in the presence of 5 mol% of $Ba(OH)_2$ at room temperature. The reaction took 2 h for completion and provided the corresponding 2-nitroalkanol (Henry product) in 81% yield (Table A3, entry 1). Similarly, the reaction of 4-nitrobenzaldehyde with 10 equiv. of nitromethane in THF produced 83% yield for 2-nitroalkanol in 2 h (entry 2).

It was fruitful to notice that water as a green solvent accelerated the reaction rate drastically. Thus, the reaction of 4-nitrobenzaldehyde with 10 equiv. of nitromethane in water yielded 91% of 2-nitroalkanol in just 15 min (entry 3). Since, further reduction of nitromethane to 5 equiv. resulted in lower yield (entry 4), the optimized condition (10 equiv. of nitromethane, 5 mol% of $Ba(OH)_2$ and water as solvent) was applied to a variety of aldehydes for the synthesis of substituted 2-nitroalkanols and the results are summarized in Table A3.

Aldehydes containing electron-withdrawing substituent generally responded well and furnished estimable yields. The reaction of 4-nitrobenzaldehyde with nitroethane and nitropropane provided 83% (threo:erythro/75:25) and 81% (threo:erythro/71:29) of respective products (entries 5 and 6). Likewise, simple benzaldehyde and 3-methyl benzaldehyde also reacted to give the corresponding 2-nitroalkanols in high yields (entries 8 and 9). The highly electron-rich substrate 2,3,4-trimethoxybenzaldehyde, however, required 7 mol% of $Ba(OH)_2$ to provide the corresponding 2-nitroalkanol in 72% yield (entry 22). On the other hand, regardless of five or six membered heterocyclic or aliphatic aldehydes, all reacted easily in the presence of 5 mol% of $Ba(OH)_2$ to produce corresponding 2-nitroalkanols in good to excellent yields (entries 18–21 and 23–24).

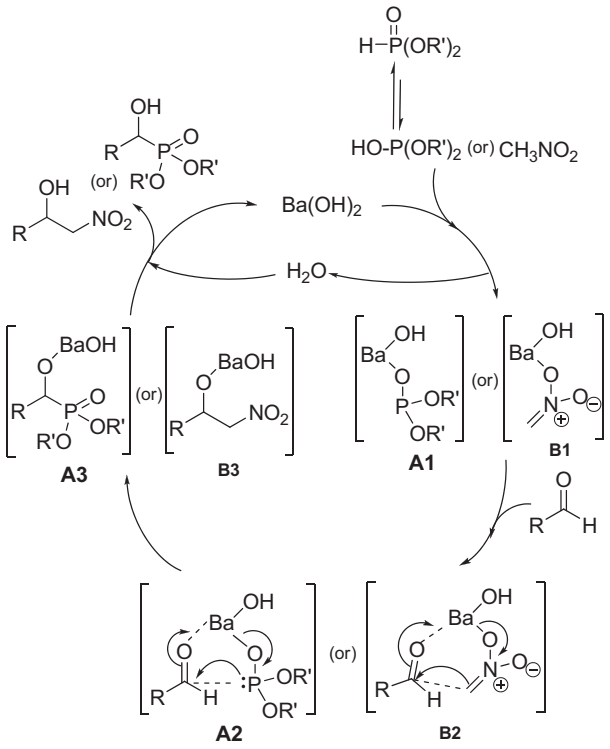
$Ba(OH)_2$ catalyzed synthesis of α-hydroxy phosphonates may possibly follow the mechanism as shown in Scheme A2.

Table A3
Addition of nitroalkane to aldehydes using Ba(OH)2 as catalyst.[a].



Entry	R	R′	$Ba(OH)_2{\cdot}8H_2O$ (mol%)	Yield[b]
1	4-NO_2-C_6H_4	H	5	81[c]
2	4-NO_2-C_6H_4	H	5	83[d]
3	4-NO_2-C_6H_4	H	5	91
4	4-NO_2-C_6H_4	H	5	71[e]
5	4-NO_2-C_6H_4	Me	5	83[f]
6	4-NO_2-C_6H_4	Et	5	81[g]
7	3-NO_2-C_6H_4	H	5	92
8	C_6H_5	H	5	80
9	3-Me-C_6H_4	H	5	88
10	4-Br-C_6H_4	H	5	76
11	2,6-Dichloro-C_6H_4	H	5	96
12	4-CN-C_6H_4	H	5	83
13	3-CN-C_6H_4	H	5	81
14	4-F-C_6H_4	H	5	84
15	3-F-C_6H_4	H	5	92
16	2-NO_2-C_6H_4	H	5	95
17	2,4-Di-NO_2-C_6H_3	H	5	98
18	2-Furyl	H	5	82
19	2-Pyridyl	H	5	96
20	3-Pyridyl	H	5	92
21	4-Pyridyl	H	5	98
22	2,3,4-Tri-OMe-C_6H_4	H	7	72
23	Isobutyl	H	5	82
24	n-Butyl	H	5	87

[a] All the reactions were carried out with 1 mmol of aldehydes and 10 mmol of nitromethane.
[b] Isolated yield.
[c] Nitromethane was used as solvent and reaction took 2 h for completion.
[d] THF was used instead of H_2O and reaction took 2 h for completion.
[e] 5 mmol of nitromethane was used.
[f] Diastereomeric ratio (threo:erythro/75:25) determined from 400 MHz ^1H NMR spectrometer.
[g] Diastereomeric ratio (threo:erythro/71:29).



Scheme A2. Plausible mechanism for $Ba(OH)_2{\cdot}8H_2O$ catalyzed synthesis of α-hydroxy phosphonates and 2-nitroalkanols.

Initially barium hydroxide may deprotonate the tautomeric form of dialkyl phosphite to become species **A1**, which further leads to species **A2** in the presence of aldehyde. The species **A2** favors the addition of phosphite to aldehydes and rearranges to species **A3**, which upon protonation releases the product α-hydroxy phosphonate and the catalyst is regenerated which enters into the next catalytic cycle. Similarly, in case of Henry reaction, deprotonation of nitromethane may follow the same pathway through species **B1**–**B3** and liberate Henry product 2-nitroalkanol.

4. Conclusion

In summary, the addition of dialkyl phosphite to aldehydes (Pudovik reaction) using $Ba(OH)_2$ as catalyst has been established for the synthesis of a large variety of α-hydroxy phosphonates. Further, the optimized reaction condition was successfully applied to aqueous mediated Henry reaction. In view of the inexpensive and commonly available catalyst, shorter reaction time (15 min), reactions at room temperature, excellent yields (up to 99%), operationally simple method (no dry setup), and water as reaction medium in case of Henry reaction, this methodology can be a desirable one for the synthesis of α-hydroxy phosphonates and 2-nitroalkanols.

Acknowledgements

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Appendix A.

See Schemes A1 and A2 and Tables A1–A3.

Appendix B. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.apcata.2012.07.011.

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