

Ammonium metavanadate: an effective catalyst for synthesis of α -hydroxyphosphonates

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Abstract

Ammonium metavanadate (NH_4VO_3) is an inexpensive, efficient and mild catalyst for the synthesis of α -hydroxyphosphonate derivatives by the reaction of various aryl or heteroaryl aldehydes with triethylphosphite at room temperature. This method affords the α -hydroxyphosphonates in short reaction times, under solvent-free conditions, and in high yield.

Keywords: Ammonium metavanadate (NH_4VO_3), α -hydroxyphosphonate, aldehyde, triethyl phosphite, solvent-free

Introduction

Phosphonates functionalized with hydroxy and amino groups have attracted considerable attention for their role in biologically relevant processes¹ and wide range of applications.² α -Hydroxyphosphonates act as an inhibitor of a diverse group of enzymes including Renin,^{3a} FPTase,^{3b} HIV protease^{3c} and EPSP synthase.^{3d} Moreover, they show antibacterial activity with the quinoline nucleus.⁴ In addition, α -hydroxyphosphonates serve as attractive precursors in the synthesis of various α -substituted phosphonates and phosphonic acids, such as α -aminophosphonates and α -aminophosphonic acids. These compounds have both medicinal and synthetic importance.⁵ α -Hydroxyphosphonates have been used for the synthesis of 1,2-diketones,⁶ α -halophosphonates, halosubstituted alkenes and alkynes,⁷ α -ketophosphonates.⁸ Recently α -hydroxy allylic phosphonates were used in the synthesis of (-)-Enterolactone and cyclopentenones.⁹

Various methods have been used to synthesize α -hydroxyphosphonates. However, most of them are just obvious modification of the old methods described by Abramov,¹⁰ Pudovik¹¹ and

Field.¹² These methods are based on the reaction of aldehydes or ketones with dialkyl phosphonates in the presence of various bases such as, sodium alkoxide,^{10,11} triethylamine,^{12,13} ethyl magnesium bromide,¹⁴ potassium or cesium fluoride,¹⁵ potassium fluoride on alumina,¹⁶ quinine,¹⁷ LDA,¹⁸ MgO,¹⁹ TMG,²⁰ DBU.²¹ There are some disadvantages over the use of base for the activation of dialkyl phosphonates.²²

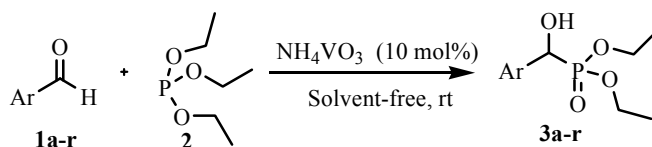
Acid catalyst like $\text{BF}_3 \cdot \text{Et}_2\text{O}$ and AlCl_3 or HCl ,²³ alumina,²⁴ TFA or TfOH ,²⁵ $\text{Ti}(\text{OPr}^i)^{26}$ have been reported for the activation of aldehydes and dialkyl phosphonates in the Abramov reaction. However, there are few reports describing the reaction of trialkyl phosphite with aldehydes or ketones in the presence of acid catalysts such as, TMSCl ,⁶ $\text{HCl} \cdot \text{Et}_2\text{O}$,²² $\text{LiClO}_4 \cdot \text{Et}_2\text{O}$ and TMSCl ,²⁷ guanidine hydrochloride.²⁸ One report explains a direct approach to α -hydroxyphosphonic acids by the reduction of bis-acylphosphonic acids.²⁹ In most cases these reactions suffer from the long reaction time or exotic reaction conditions.

In recent years, solvent-free organic synthesis have offered more advantages as compared to their homogeneous counterparts due to the growing concern for the influence of organic solvent on the environment as well as on human body, economical demands and simplicity in the processes.³⁰

Hence the search continues for a better catalyst in the synthesis of α -hydroxyphosphonates in terms of operational simplicity and economic viability. Herein we report the use of ammonium metavanadate (NH_4VO_3) as a water soluble, inorganic acid³¹ that meets the demand for a economic catalyst. It is employed similar to vanadium pentoxide³² and as a catalyst in oxidation reactions with other cocatalysts.³³ It is a reagent used in analytical chemistry, the photographic industry, and the textile industry.³² This is the first report of utilizing ammonium metavanadate as a catalyst for the synthesis of α -hydroxyphosphonates.

Results and Discussion

In continuation of our research devoted to phosphorus chemistry^{4,33} and interest in the development of novel synthetic methodologies,³⁴ herein, we report a simple, efficient, and rapid method for the synthesis of α -hydroxyphosphonates catalyzed by ammonium metavanadate (Scheme 1).



Scheme 1. Reaction of aldehyde with triethyl phosphite.

In our search for an efficient catalyst and the best experimental reaction conditions in the preparation of α -hydroxyphosphonates, we have determined that the reaction of 2-chloroquinoline-3-carbaldehyde **1a** with triethyl phosphite **2** under solvent-free conditions at room temperature is the standard model reaction. We screened a number of different catalysts, such as FeCl₃, CdCl₂, ZnCl₂, *p*-toluene sulphonic acid (*p*-TSA), sulphamic acid, acidic alumina and NH₄VO₃. Employing FeCl₃, CdCl₂, or ZnCl₂ afforded the desired product in poor yields 23-42% (Table 1, Entry 1-3). The use of *p*-TSA, sulphamic acid and acidic alumina provided the product in moderate yields 54-71% (Table 1, Entry 4-6). However, NH₄VO₃ provided the best results, yielding 94% of product yield within 5 min (Table 1, Entry 7).

Table 1. Screening of catalysts^a

Entry	Catalyst	Time (min)	Yield ^b (%)
1	FeCl ₃	60	23
2	CdCl ₂	60	36
3	ZnCl ₂	60	42
4	<i>p</i> -TSA	60	54
5	Sulphamic acid	60	67
6	Acidic alumina	60	71 ^c
7	NH ₄ VO ₃	5	94

^aReaction Conditions: **1a** (2.5 mmol), **2** (4 mmol), Catalyst (10 mol%), solvent-free at rt.

^bIsolated yields. ^cCatalyst (mg).

To evaluate the effect of solvent, various solvents such as water, dichloromethane, tetrahydrofuran, toluene, and ethanol were used for the standard model reaction. Predictably, it was observed that the use of solvent retarded the reaction rate and afforded the desired product in much lower yields (Table 2, Entry 2-5). When water is used as the solvent no product was observed (Table 2, Entry 1).

Table 2. Screening of solvents^a

Entry	Solvents	Time (hr)	Yield ^b (%)
1	Water	24	No reaction
2	Dichloromethane	24	10
3	Tetrahydrofuran	24	10
4	Toluene	24	15
5	Ethanol	24	20

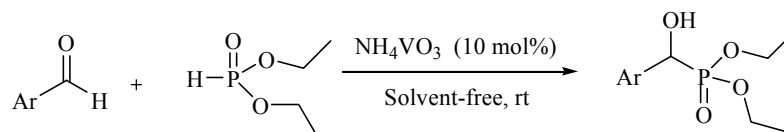
^aReaction Conditions: **1a** (2.5 mmol), **2** (4 mmol), NH₄VO₃ (10 mol%), solvent (10 mL) at rt.

^bIsolated yields.

To establish generality with respect to the reaction of carbonyl compounds; triethyl phosphite was treated with various aldehydes and ketones under the influence of NH_4VO_3 (Table 5). It was observed that substituted 2-chloroquinoline-3-carbaldehydes reacted faster than other aldehydes, providing excellent yields 90-94% (Table 5, Entry 1-5). The substituted 4-oxo-4*H*-chromene-3-carbaldehydes formed the corresponding hydroxy phosphonates in 10-12 min in good yields 83-90% (Table 5, Entry 6-10). In comparison with these results, aryl aldehydes formed their respective hydroxyphosphonates, requiring longer time, but also in good yields (80-90%, Table 5, Entry 11-17). In case of cinnamaldehyde, the addition of triethyl phosphite selectively occurs at the carbonyl carbon (Table 5, Entry 18). Unfortunately the reaction of aliphatic aldehydes and aliphatic or aromatic ketones does not show any conversion after 24 hrs, even on increasing the concentration of NH_4VO_3 (Table 5, Entry 19-22).

The reaction was compatible with various substituents such as Cl, OH, NO_2 , Me, OMe and OEt. No competitive nucleophilic ether cleavage was observed for the substrate having an aryl OMe or OEt groups. In case of aryl aldehydes, electron donating substituents resulted in longer reaction times whereas electron withdrawing substituents requires shorter time for the complete reaction (Table 5, Entry 12-17). However, no significant substituent effect was found in case of heteroaryl aldehydes.

We also examined the reaction of diethyl phosphonate with three principal aldehydes (Scheme 2, Table 3) by applying the same experimental conditions. Only the benzaldehyde gives their hydroxyphosphonate in trace amount (Table 3, Entry 3), whereas heteroaryl aldehydes do not show any conversion after 24 hrs (Table 3, Entry 1-2).



Scheme 2. Reaction of aldehyde with diethylphosphonate.

Table 3. Synthesis of α -hydroxyphosphonates using dialkyl phosphonates^a

Entry	Aldehyde	Time (hr)	Yield ^b (%)
1		24	No reaction
2		24	No reaction
3		24	5

^aReaction Conditions: Aldehyde (2.5 mmol), diethyl phosphonate (5 mmol), NH_4VO_3 (10 mol%), solvent-free at rt. ^bIsolated yields.

A mechanism for the action of NH_4VO_3 has been proposed (Figure 1), whereby the aldehyde carbonyl oxygen binds with the vacant 'd' orbital of vanadium to form complex (I). This interaction increases the reaction rate tremendously to shorten the overall reaction time.

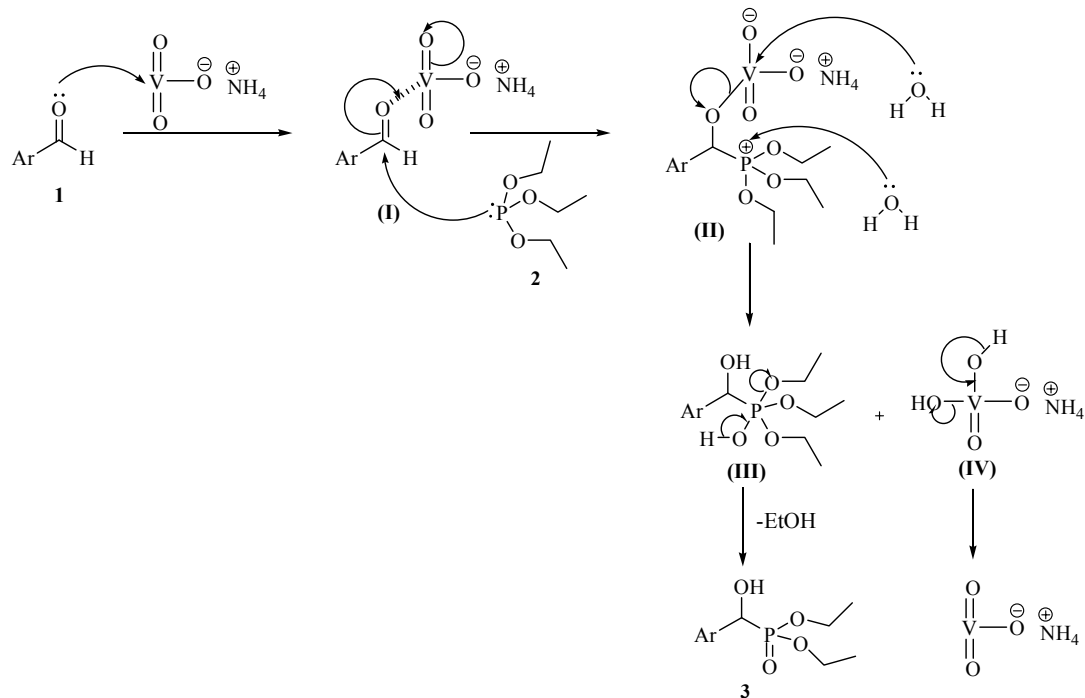


Figure 1. Proposed reaction mechanism.

In order to show the merit of NH_4VO_3 in comparison with the other catalyst used for the similar reaction, a side by side comparison was run with some of the more common catalysts used for this chemistry. The results are presented in Table 4. It is evident from these results, NH_4VO_3 was found to be an effective catalyst for the synthesis of α -hydroxyphosphonates.

Table 4. Comparison with reported procedure

Entry	Catalyst	Catalyst Conc.	Solvent/ Medium	Temp (°C)	Time	Yield ^e (%)	Reference
1	TMSCl	1 eq.	-	120	8 hr	92 ^a	6
2	Guanidine·HCl	5 mol%	H ₂ O	50	2 hr	95 ^b	28
3	HCl·Et ₂ O	1 eq.	DCM	-10	1 hr	74 ^a	22
4	TMSCl	1 eq.	LiClO ₄ ·Et ₂ O	rt	5 min	98 ^a	27
5	NH ₄ VO ₃	20 mol%	-	rt	15 min	90 ^a	Present work
6	TMSCl	2 eq.	Toluene	Reflux	20 min	76 ^c	4
7	NH ₄ VO ₃	20 mol%	-	rt	5 min	92 ^c	Present work
8	TMSCl	2 eq.	MW/150W	-	10 min	85 ^d	33b
9	NH ₄ VO ₃	20 mol%	-	rt	10 min	88 ^d	Present work

^aReaction of benzaldehyde with triethyl phosphite. ^bReaction of benzaldehyde with trimethyl phosphite. ^cReaction of 2-chloroquinoline-3-carbaldehyde with triethyl phosphite. ^dReaction of 4-oxo-4H-chromene-3-carbaldehyde with triethyl phosphite. ^eIsolated yields based upon starting aldehyde.

With the optimized conditions, we have carried out the reaction of various aryl and heteroaryl aldehydes **1a-r** with triethyl phosphite **2**. The corresponding α -hydroxyphosphonates **3a-r** were formed in excellent yields (Table 5); confirmed by IR, ¹H NMR, Mass spectral data and elemental analysis conducted on the isolated product.

Table 5. Characterization data of α -hydroxyphosphonates **3**^a

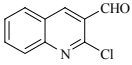
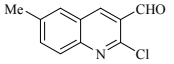
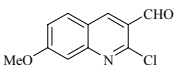
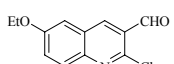
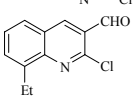
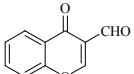
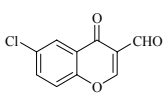
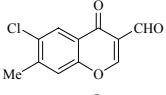
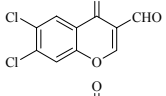
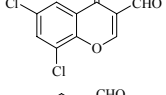
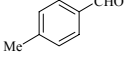
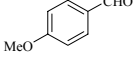
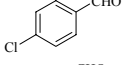
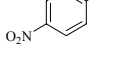
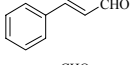
Entry	Compound	Aldehyde/Ketone	Time (min)	Yield (%) ^b	M.P. (°C)	
					Found	Literature
1	3a		5	94	122-124	124-126 ⁴
2	3b		6	93	146-148	145-147 ⁴
3	3c		5	90	154-156	154-156 ⁴
4	3d		5	91	166-168	168-170 ⁴
5	3e		7	92	145-146	145-147 ⁴
6	3f		10	88	170-172	172 ^{33b}
7	3g		12	87	179-180	180 ^{33b}
8	3h		10	90	178-180	178 ^{33b}
9	3i		10	85	221-222	220 ^{33b}
10	3j		12	83	190-192	190 ^{33b}
11	3k		15	90	76-78	75-77 ¹⁹
12	3l		20	84	94-95	94-95 ¹⁹
13	3m		25	80	119-120	120-121 ¹⁹
14	3n		20	82	96-97	97-98.5 ¹⁹
15	3o		12	88	67-68	67-68 ¹⁹
16	3p		15	83	75-77	74-75 ¹⁹
17	3q		10	90	86-88	87-88 ¹⁹
18	3r		40	80	105-107	105-106 ¹⁹
19	3s		24 ^c	No reaction	-	-
20	3t		24 ^c	No reaction	-	-

Table 5. Continued

21	3u		24 ^c	No reaction	-	-
22	3v		24 ^c	No reaction	-	-

^aReaction Conditions: **1** (2.5 mmol), **2** (4 mmol), NH₄VO₃ (10 mol%), solvent-free at rt.

^bIsolated yields. ^cTime in hr.

Conclusions

Ammonium metavanadate (NH₄VO₃) is a readily available, inexpensive, and efficient catalyst for the synthesis of variety of α -hydroxyphosphonate derivatives. The remarkable advantages offered by this method are solvent-free reaction conditions, room temperature reactions, short reaction times, ease of product isolations, and high yields. We believe that this method is a useful addition to the present methodology for the synthesis of α -hydroxyphosphonates.

Experimental Section

General Procedures. All the melting points were determined in open capillaries in paraffin bath and are uncorrected. IR spectra were recorded on a Perkin-Elmer FTIR using KBr discs. ¹H NMR spectra were recorded on Mercury Plus Varian in DMSO or CDCl₃ at 400 MHz using TMS as an internal standard. Mass spectra were recorded on Micromass Quattro II using electrospray Ionization technique. The elemental analysis was carried out on Flash EA 1112, 50/60 Hz, 1400 VA CHNS analyzer. The progress of the reactions was monitored by TLC.

Typical experimental procedure

For Scheme 1: A mixture of aldehyde (2.5 mmol), triethyl phosphite (4 mmol) and NH₄VO₃ (10 mol%) was stirred magnetically at room temperature. After the completion of reaction as monitored by TLC; 20 mL ice cold water was added to the reaction mixture. The crude product was extracted with chloroform and purified by column chromatography on silica gel by petroleum ether: ethyl acetate (8:2) as an eluent.

For Scheme 2: A mixture of aldehyde (2.5 mmol), diethyl phosphonate (5 mmol) and NH₄VO₃ (10 mol%) was stirred magnetically at room temperature. 20 mL ice cold water was added to the reaction mixture after 24 hr. The crude product was extracted by chloroform and purified by column chromatography on silica gel by petroleum ether: ethyl acetate (8:2) as an eluent. Only the benzaldehyde forms their hydroxy phosphonate in 5% yield.

Diethyl(2-chloroquinolin-3-yl)(hydroxy)methylphosphonate (3a). IR (KBr, $\nu_{\max}/\text{cm}^{-1}$): 3240 (OH), 1230 (P=O), 1015 (P-O-C). ^1H NMR δ_{H} (400 MHz, CDCl_3 , Me_4Si): 1.22 (t, 3H, $J = 7.2$ Hz, CH_3), 1.33 (t, 3H, $J = 7.2$ Hz, CH_3), 2.6 (brs, 1H, OH), 4.03-4.14 (m, 2H, O- CH_2), 4.15-4.26 (m, 2H, O- CH_2), 5.66 (d, 1H, $J = 11.6$ Hz, P-CH), 7.56 (t, 1H, $J = 7.6$, 6.8 Hz, Ar-H), 7.35 (t, 1H, $J = 8.0$, 7.6 Hz, Ar-H), 7.84 (d, 1H, $J = 8.0$ Hz, Ar-H), 8.01 (d, 1H, $J = 8.4$ Hz, Ar-H), 8.55 (d, 1H, $J = 3.4$ Hz, Ar-H). MS: m/z 330. Elemental analysis: $\text{C}_{14}\text{H}_{17}\text{ClNO}_4\text{P}$ Calcd.: C: 51.00%, H: 5.20%, N: 4.25%. Found: C: 50.96%, H: 5.15%, N: 4.21%.

(Diethyl(6-chloro-7-methyl-4-oxo-4H-chromen-3-yl)(hydroxy)methylphosphonate (3h). IR (KBr, $\nu_{\max}/\text{cm}^{-1}$): 3250 (OH), 1690 (C=O), 1210 (P=O), 1020 (P-O-C). ^1H NMR δ_{H} (400 MHz, $\text{DMSO}-d_6$, Me_4Si): 1.11 (t, 3H, $J = 7.2$ Hz, CH_3), 1.19 (t, 3H, $J = 7.2$, CH_3), 2.4 (s, 3H, Ar- CH_3), 3.93-3.99 (m, 2H, O- CH_2), 4.01-4.08 (m, 2H, O- CH_2), 5.16 (dd, 1H, $J = 12.4$, 6.8 Hz, P-CH), 6.27 (brs, 1H, OH), 7.73 (s, 1H, Ar-H), 7.97 (s, 1H, Ar-H), 8.31 (d, 1H, $J = 3.6$ Hz, Ar-H). MS: m/z 361. Elemental analysis: $\text{C}_{15}\text{H}_{18}\text{ClO}_6\text{P}$ Calcd.: C: 49.94%, H: 5.03%. Found: C: 49.90%, H: 4.99%.

Diethyl hydroxy(4-methoxyphenyl)methylphosphonate (3m). IR (KBr, $\nu_{\max}/\text{cm}^{-1}$): 3258 (OH), 1230 (P=O), 1061 P-O-C). ^1H NMR δ_{H} (400 MHz, CDCl_3 , Me_4Si): 1.21 (t, 3H, $J = 7.8$ Hz, CH_3), 1.27 (t, 3H, $J = 7.8$ Hz, CH_3), 3.80 (s, 3H, Ar-O- CH_3), 3.93-4.09 (m, 4H, O- CH_2), 4.95 (d, 1H, $J = 10$ Hz, P-CH), 6.89 (d, 2H, $J = 8.5$ Hz, Ar-H), 7.41 (dd, 2H, $J = 8.7$, 2.8 Hz, Ar-H). MS: m/z 275. Elemental analysis: $\text{C}_{12}\text{H}_{19}\text{O}_5\text{P}$ Calcd.: C: 52.55%, H: 6.98%. Found: C: 52.50%, H: 6.93%.

Diethyl 1-hydroxy-3-(4-methoxyphenyl)allylphosphonate (3r). IR (KBr, $\nu_{\max}/\text{cm}^{-1}$): 3240 (OH), 1210 (P=O), 1045 (P-O-C). ^1H NMR δ_{H} (400 MHz, $\text{DMSO}-d_6$, Me_4Si): 1.20 (t, 6H, $J = 7.2$ Hz, CH_3), 3.99-4.07 (m, 4H, O- CH_2), 4.53 (brs, 1H, OH), 5.92 (dd, 1H, $J = 12.8$, 6.0 Hz, P-CH), 6.29 (dt, 1H, $J = 16.4$, 6.0 Hz, C=CH-C), 6.69 (dd, 1H, $J = 16.4$, 3.6 Hz, Ar-CH=C), 7.23 (t, 1H, $J = 7.2$ Hz, Ar-H), 7.32 (t, 2H, $J = 7.6$ Hz, Ar-H), 7.41 (d, 2H, $J = 7.6$ Hz, Ar-H), MS: m/z 271. Elemental analysis: $\text{C}_{13}\text{H}_{19}\text{O}_4\text{P}$ Calcd.: C: 57.77%, H: 7.09%. Found: C: 57.73%, H: 7.04%.

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