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$In(OTf)_3$ catalysed simple one-pot synthesis of α-amino phosphonates

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Abstract

A new efficient one-pot synthesis of α-amino phosphonates derived from nitro substituted anilines, aldehydes and diethyl phosphite has been carried out by employing 5 mol% of $In(OTf)_3$. The method is equally effective for the generation of α-amino phosphonates from various carbonyl compounds and other amines.

Keywords: One-pot synthesis; $In(OTf)_3$; Catalysed; α-amino phosphonate

1. Introduction

Because of their pharmacological and medicinal importance [1] the synthesis of α-amino phosphonates, the structural analogues of α-amino acids, has received increased attention during the last two decades. Their potential as peptidomimetics [2], enzyme inhibitors [3] (including HIV protease [4]), herbicides [5], insecticides [6], fungicides [7], antiviral agents [8] as well as their role for antibody generation [9] is well documented. Of the variety of reported methods [10–12] for the synthesis of α-amino phosphonates most are based on nucleophilic addition of phosphites to imines catalysed by protic [10a] or Lewis acids like BF_3-etherate [11a,b], $ZnCl_2$ [11c], $MgBr_2$ [11c], $SnCl_4$ [11a], etc. or by base [12]. However, these methods are not devoid of their limitations as many imines are hygroscopic and are not sufficiently stable for isolation.

The first one-pot synthesis of α-amino phosphonates has been achieved recently by the reaction of phosphite in the presence of lanthanide triflate [13] with the imines generated in situ from aldehydes and amines using $MgSO_4$ or molecular sieves as the dehydrating agent. Subsequent one-pot variations involved $InCl_3$ [14], $TaCl_5$–SiO_2 [15], montmorillonite KSF [16a], $ZrCl_4$ [16b] and surface mediated reactions on Al_2O_3 [17] based on diethyl phosphite or triethylphosphite [18]. Syntheses of a few chiral α-amino phosphonates have also been documented [10d,11a,19].

In connection with some other studies we required some α-amino phosphonates incorporating nitro substituted aromatic amines. Surprisingly, only two such α-amino phosphonates have been recorded in the literature [15,17b]. Although attempted preparation of α-amino phosphonates from *m*- or *p*-nitroanilines by the reported methodologies [13,14] failed but under modification provided the desired products to the extent of 24–41% depending upon the substrates (Table 1).

In continuation to our interest towards In(III) mediated organic reactions [20], we were prompted to explore the effectiveness of $In(OTf)_3$ as a catalyst for the generation of α-amino phosphonates. Thus, reaction of diethyl phosphite with the in situ generated imines from benzaldehyde and *m*- or *p*-nitroaniline in refluxing THF using $MgSO_4$ as the internal desiccant in the presence of catalytic amount of $In(OTf)_3$ afforded the corresponding α-amino phosphonates in very good yields (Scheme 1, Table 2). It may be noted that although, metal triflates have received considerable attention in numerous organic transformations [21], $In(OTf)_3$ has only been very recently used [20d,22]. To the best of our knowledge, this is the first demonstration of $In(OTf)_3$ catalysed synthesis of α-amino phosphonates.

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Table 1
One-pot synthesis of α-amino phosphonates

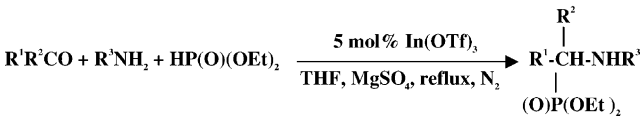
Catalyst (10 mol%)/solvent	R^1	R^2	R^3	Product	Yield (%)[a]
$InCl_3$/THF	Ph	H	*p*-NO_2–C_6H_4	**3d**	24
$InCl_3$/THF	*m*-NO_2–C_6H_4	H	*m*-NO_2–C_6H_4	**6d**	20
$Yb(Otf)_3$/(CH_2Cl_2)	Ph	H	*p*-NO_2–C_6H_4	**3d**	35
$Yb(Otf)_3$/(CH_2Cl_2)	*m*-NO_2–C_6H_4	H	*m*-NO_2–C_6H_4	**6d**	41

[a] Reaction mixtures were refluxed for 40 h; no products were formed at room temperature.

Table 2
$In(OTf)_3$ catalysed one-pot synthesis of α-amino phosphonates

Entry	R^1	R^2	R^3	Time (h)	Products[a]	Yields (%)[b]
1	Ph	H	Ph	21	**1d** [14]	79
2	Ph	H	*m*-NO_2–C_6H_4	25	**2d** [17b]	82
3	Ph	H	*p*-NO_2–C_6H_4	35	**3d**	79
4	Ph	H	$PhCH_2$	24	**4d** [14]	85
5	*m*-NO_2–C_6H_4	H	Ph	21	**5d** [18c]	70
6	*m*-NO_2–C_6H_4	H	*m*-NO_2–C_6H_4	13	**6d**	99
7	*p*-NO_2–C6H4	H	Ph	32	**7d** [14]	18
8	*m*-OH–C_6H_4	H	Ph	12	**8d** [14]	84
9	*p*-Cl–C_6H_4	H	Ph	18	**9d** [18a]	88
10	*p*-Cl–C_6H_4	H	*m*-NO_2–C_6H_4	46	**10d**	77
11	*p*-Cl-C_6H_4	H	*p*-NO_2–C_6H_4	32	**11d**	83
12	*p*-OMe-C_6H_4	H	Ph	12	**12d** [13]	97
13	*p*-OMe–C_6H_4	H	*p*-OMe–C_6H_4	32	**13d** [15]	60
14	*p*-OMe–C_6H_4	H	*m*-NO_2–C_6H_4	18	**14d**	80
15	*p*-OMe–C_6H_4	H	*p*-NO_2–C_6H_4	31	**15d**	92
16	Trans-C_6H_5CHCH	H	Ph	36	**16d** [14]	64
17	Me_2CH	H	*m*-NO_2–C_6H_4	50	**17d**[c]	88
18	Me_2CH	H	$PhCH_2$	54	**18d** [14][c]	45
19	C_9H_{19}	H	$PhCH_2$	50	**19d** [13]	16
20	Cyclohexanone		Ph	27	**20d** [15]	47
21	Cyclohexanone		$PhCH_2$	35	**21d** [14]	83

[a] All new compounds were characterized by IR, NMR (^{1}H- and ^{13}C-), mass and/or elemental analysis.
[b] Isolated yields.
[c] Reaction mixtures were stirred at 60 °C.



Scheme 1.

2. Experimental

2.1. Materials and methods

$In(OTf)_3$ (Catalog No. 44,215-1; Batch No. 10716BI) was purchased from Aldrich.

Infrared (IR) spectra were recorded on a Perkin-Elmer 297 spectrophotometer. ^{1}H NMR spectra were recorded on Bruker DPX-300 (300 MHz) spectrometer using $CDCl_3$ as solvent and TMS as the internal standard. ^{13}C NMR spectra were recorded on Bruker DPX-300 (75 MHz) spectrometer. Elemental analyses were performed on a Perkin-Elmer autoanalyzer 2400 II. Mass spectrometric data were taken on GCMS-QP5000 (Shimadzu). All melting points are uncorrected. All known compounds were characterized by comparing their physical data with those in the literature.

2.2. General experimental procedure

To a mixture of aldehyde (0.90–0.95 mmol), amine (0.95–1.00 mmol), diethyl phosphite (1.2–1.5 mmol) and $MgSO_4$ (400 mg) in dry THF (5 ml) was added $In(OTf)_3$ (5 mol%) and the reaction mixture was refluxed under nitrogen for the appropriate period (Table 2). After completion of the reaction (checked by TLC on silica gel), THF was removed under reduced pressure. The residue taken in CH_2Cl_2 (5 ml) was filtered through celite bed and washed well with CH_2Cl_2 (4 × 3 ml). The combined filtrate and washings were washed with water (2 × 15 ml), the pooled organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude residue was purified by column chromatography on silia gel with EtOAc-pet. ether (60–80°) to afford the product.

Representative physical and chemical data of products:

3d: yield 79%. Cream coloured crystals (EtOAc-pet. ether, 60–80°), mp 143–144°. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.12 (t, J 6.9 Hz, 3H), 1.31 (t, J 7.0 Hz, 3H), 3.57–3.65 (m, 1H), 3.89–3.97 (m, 1H), 4.12–4.20 (m, 2H), 4.83 (dd, $^1J_{PH}$ 24.0 Hz, J_{HH} 7.7 Hz, 1H), 6.10 (t, J 8.13 Hz, 1H), 6.60 (d, J 9.15 Hz, 2H), 7.28–7.49 (m, 5H), 8.01 (d, J 9.12 Hz, 2H). ^{13}C NMR (proton decoupled, $CDCl_3$, 75.4 MHz): 16.56 (d, $^3J_{PC}$ 4.20 Hz), 16.83 (d, $^3J_{PC}$ 4.28 Hz), 55.91 (d, $^1J_{PC}$ 150.74 Hz), 63.78 (d, $^2J_{PC}$ 7.04 Hz), 64.28 (d, $^2J_{PC}$ 6.78 Hz), 112.81 (s), 126.47 (s), 128.16 (d, $^4J_{PC}$ 5.1 Hz), 128.90 (s), 129.29 (s), 135.0 (s), 139.33 (s), 152.36 (d, $^2J_{PC}$ 13.42 Hz). IR (KBr): cm^{-1} 3250, 3050, 2970, 1600, 1490. Major mass peaks (CI–MS): m/e 364 (M^+), 228, 227 (base peak), 181, 103, 76. Anal. calcd. for $C_{17}H_{21}O_5N_2P$ (364.337): C 56.04%; H 5.81%; N 7.68%; found C 56.26%; H 5.98%; N 7.95%.

6d: yield 99%. Canary yellow crystals (EtOAc-pet. ether, 60–80°), mp 158°. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.20 (t, J 7.0 Hz, 3H), 1.33 (t, J 7.0 Hz, 3H), 3.87–3.95 (m, 1H), 4.03–4.11 (m, 1H), 4.18–4.22 (m, 2H), 4.92 (d, $^1J_{PH}$ 24.4 Hz, 1H), 5.62 (bs, 1H), 6.85–6.88 (dd, J 1.63 and 8.07 Hz, 1H), 7.25 (t, J 8.1 Hz, 1H), 7.43 (s, 1H), 7.53–7.58 (m, 2H), 7.84 (d, J 7.5 Hz, 1H), 8.16 (d, J 7.9 Hz, 1H), 8.36 (s, 1H). ^{13}C NMR (proton decoupled, $CDCl_3$, 75.4 MHz): 16.27 (s), 16.43 (s), 55.4 (d, $^1J_{PC}$ 151.2 Hz), 63.89 (s), 108.0 (s), 113.54 (s), 119.28 (s), 122.57 (s), 123.35 (s), 129.79 (s), 130.03 (s), 133.83 (s), 137.77 (s), 146.66 (s), 148.88 (s), 149.26 (s). IR (KBr): cm^{-1} 3270, 3085, 2990, 1620, 1530, 1355, 1235, 1025, 985, 965, 750. Major mass peaks (CI–MS): m/e 409 (M^+), 273, 272 (base peak), 255, 238, 226, 179, 138, 111, 82, 76. Anal. calcd. for $C_{17}H_{20}O_7N_3P$ (409.334): C 49.88%; H 4.92%; N 10.26%; found: C 50.01%, H 5.08%, N 10.22%.

10d: yield 77%. Yellow crystals (Et_2O-pet. ether, 60–80°) mp 114°. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.16 (t, J 7.04 Hz, 3H), 1.31 (t, J 7.04 Hz, 3H), 3.75–3.79 (m, 1H), 3.98–4.01 (m, 1H), 4.12–4.20 (m, 2H), 4.76 (d, $^1J_{PH}$ 24.3 Hz, 1H), 5.49 (bs, 1H), 6.83–6.86 (dd, J 1.97 and 8.07 Hz, 1H), 7.22–7.43 (m, 6H), 7.51–7.54 (dd, J 1.49 and 8.01 Hz, 1H). ^{13}C NMR (proton decoupled, $CDCl_3$, 75.4 MHz): 16.24 (d, $^3J_{PC}$ 5.5 Hz), 16.44 (d, $^3J_{PC}$ 5.6 Hz), 55.30 (d, $^1J_{PC}$ 151.85 Hz), 63.5 (d, $^2J_{PC}$ 6.86 Hz), 63.7 (d, $^2J_{PC}$ 6.9 Hz), 107.9 (s), 113.18 (s), 119.42 (s), 129.07 (s), 129.19 (s), 129.84 (s), 133.57 (s), 134.27 (s), 147.1 (d, J_{PC} 14.5 Hz), 149.25 (s). IR (KBr): cm^{-1} 3280, 3080, 2990, 1640, 1590, 1530, 1490, 1350, 1230, 1020. Major mass peaks: m/e 261 (base peak), 215, 152, 76, 65, 50. Anal. calcd. for $C_{17}H_{20}O_5N_2ClP$ (398.78): C 51.20%; H 5.05%; N 7.02%; found: C 51.43%; H 5.17%; N 7.02%.

11d: yield 83%. Light yellow crystals (EtOAc, pet. ether, 60–80°), mp 131°. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.31 (t, J 7.01 Hz, 3H), 1.64 (t, J 7.01 Hz, 3H), 3.70–3.81 (m, 1H), 3.94–4.04 (m, 1H), 4.08–4.17 (m, 2H), 4.78 (d, $^1J_{PH}$ 23.98 Hz, 1H), 5.8 (bs, 1H), 6.56 (d, J 9.06 Hz, 2H), 7.33 (d, J 8.42 Hz, 2H), 7.39 (d, J 7.7 Hz, 2H), 8.01 (d, J 9.03 Hz, 2H). ^{13}C NMR (proton decoupled, $CDCl_3$, 75.4 MHz): δ 16.23 (d, $^3J_{PC}$ 4.65 Hz), 16.43 (d, $^3J_{PC}$ 4.8 Hz), 55.0 (d, $^1J_{PC}$ 151.47 Hz), 63.55 (d, $^2J_{PC}$ 6.48 Hz), 63.9 (d, $^2J_{PC}$ 6.10 Hz), 112.47 (s), 126.09 (s), 129.0 (d, J_{PC} 4.52 Hz), 129.1 (s), 133.26 (s), 134.46 (s), 139.32 (s), 151.5 (d, J_{PC} 13.1 Hz). Major mass peaks: m/e 227 (base peak), 210, 181, 152, 76, 50. IR (KBr): cm^{-1} 3280, 3050, 2980, 1590, 1500, 1480. Anal. calcd. for $C_{17}H_{20}O_5N_2ClP$ (398.782): C 51.20%; H 5.05%; N 7.02%; found: C 51.41%; H 5.13%; N 7.03%.

14d: yield 80%. Yellow crystals (EtOAc-pet. ether), mp 152°. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.13 (t, J 7.04 Hz, 3H), 1.30 (t, J 7.05 Hz, 3H), 3.65–3.68 (m, 1H), 3.78 (s, 3H), 3.90–3.96 (m, 1H), 4.10–4.17 (m, 2H), 4.73 (d, $^1J_{PH}$ 23.59 Hz, 1H), 6.88 (d, J 8.42 Hz, 3H), 7.21 (t, J 8.13 Hz, 1H), 7.37–7.43 (m, 3H), 7.49–7.52 (dd, J 1.83 and 7.84 Hz, 1H). ^{13}C NMR (proton decoupled, $CDCl_3$, 75.4 MHz): δ 16.27 (d, $^3J_{PC}$ 5.0 Hz), 16.44 (d, $^3J_{PC}$ 5.07 Hz), 55.15 (d, $^1J_{PC}$ 153.31 Hz), 55.25 (s), 63.22 (d, $^2J_{PC}$ 6.22 Hz), 63.64 (d, $^2J_{PC}$ 6.49 Hz), 107.86 (s), 112.90 (s), 114.29 (s), 119.64 (s), 126.50 (s), 129.0 (d, J_{PC} 4.75 Hz), 129.7 (s), 147.30 (d, J_{PC} 15.08 Hz), 149.21 (s), 159.6 (s). Major mass peaks (CI–MS): m/e 394 (M^+), 257 (base peak), 240, 211, 167, 149, 121, 103, 76, 65. IR (KBr): cm^{-1} 3280, 3100, 2980, 1620, 1610, 1580, 1530, 1510. Anal. calcd. for $C_{18}H_{23}O_6N_2P$ (394.363): C 54.82%; H 5.88%; N 7.10%; found: C 55.17%; H 5.84%; N 7.18%.

15d: yield 92%. Light yellow crystals (EtOAc-pet. ether), mp 115°. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.12 (t, J 7.04 Hz, 3H), 1.30 (t, J 7.04 Hz, 3H), 3.60–3.68 (m, 1H), 3.79 (s, 3H), 3.86–3.99 (m, 1H), 4.06–4.17 (m, 2H), 4.74 (d, $^1J_{PH}$ 23.45 Hz, 1H), 5.55 (bs, 1H), 6.56 (d, J 9.10 Hz, 2H), 6.89 (d, J 8.50 Hz, 2H), 7.34 (d, J 8.49 Hz, 2H), 8.02 (d, J 9.09 Hz, 2H). ^{13}C NMR (proton decoupled, $CDCl_3$, 75 MHz): δ 16.19 (d, $^3J_{PC}$ 5.55 Hz), 16.38 (d, $^3J_{PC}$ 5.62 Hz), 54.78 (d, $^1J_{PC}$ 152.47 Hz), 55.21 (s), 63.20 (d, $^2J_{PC}$ 7.20 Hz), 63.75 (d, $^2J_{PC}$ 6.97 Hz), 112.35 (s), 114.26 (d, J 2.1 Hz), 125.99 (s), 126.22 (d, J_{PC} 2.8 Hz), 128.88 (d, J_{PC} 5.4 Hz), 138.82 (s), 151.9 (d, J_{PC} 13.65 Hz), 159.64 (s). IR (KBr): cm^{-1} 3280, 3060, 2980, 1590, 1540, 1500, 1330, 1310, 1290, 1230, 1110, 1040, 1010. Anal. calcd. for $C_{18}H_{23}O_6N_2P$ (394.36): C 54.82%; H 5.87%; N 7.10%; found: C 54.94%; H 6.06%; N 7.16%.

17d: yield 88%. Dark yellow crystals (pet. ether), mp 118–119°. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.08 (d, J 7.61 Hz, 3H), 1.10 (d, J 7.13 Hz, 3H), 1.17 (t, J 7.05 Hz, 3H), 1.30 (t, J 7.05 Hz, 3H), 2.25–2.34 (m, 1H), 3.65–3.73 (m, 1H), 4.00–4.15 (m, 4H), 4.32–4.37 (dd, J 3.71 and $^1J_{PH}$ 13.35 Hz, 1H), 6.93–6.96 (dd, J 1.94 and 8.12 Hz, 1H), 7.28 (t, J 8.13 Hz, 1H), 7.49–7.54 (m, 2H). ^{13}C NMR (proton decoupled, 75.4 MHz): δ 16.49 (s), 17.95 (d, $^3J_{PC}$ 4.35 Hz), 20.64 (s), 20.81 (s), 29.79 (d, $^2J_{PC}$ 5.11 Hz), 56.05 (d, $^1J_{PH}$ 152.9 Hz), 62.15 (d, $^2J_{PC}$ 7.22 Hz), 62.65 (d, $^2J_{PC}$ 7.11 Hz), 106.85 (s), 112.47 (s), 119.15 (s), 129.87 (s), 148.67 (s), 149.42 (s). IR (KBr): cm^{-1} 3320, 2980, 1625, 1590, 1530, 1352, 1290, 1230, 1060, 1050, 1025, 960, 895, 825. Anal.

calcd. for $C_{14}H_{23}N_2O_5P$ (330.319): C 50.91%; H 7.02%; N 8.48%; found: C 50.90%; H 7.31%; N 8.09%.

3. Results and discussion

At the outset, the reaction was standardized with benzaldehyde, aniline and diethylphosphite using 5 mol% $In(OTf)_3$ as the catalyst in the presence of magnesium sulphate as internal desiccant in various solvents, such as, tetrahydrofuran, dichloroethane and acetonitrile under nitrogen. The reactions did not proceed well in the absence of magnesium sulphate, and best yield was obtained in tetrahydrofuran. Under the optimized condition, the reaction of *m*- and *p*-nitroanilines with a variety of aromatic aldehydes such as benzaldehyde (entries 2 and 3) and its derivatives containing electron withdrawing group (entry 6) or donating group (entries 10, 11, 14 and 15) or with aliphatic aldehydes, such as, iso-butyraldehyde (entry 17) or decanal (entry 19) and diethylphosphite furnished the corresponding α-amino phosphonates in very high to excellent yields (79–99%, Table 2). For generalization of this method, we also screened aniline (entries 5, 7–9, 12, 16 and 20) or *p*-methoxyaniline (entry 13) or benzylamine (entries 4, 18, 19 and 21) in reaction with different aldehydes (aromatic and aliphatic) or ketone and diethylphosphite (Table 2). The yields of α-amino phosphonates from diethylphosphite and in situ generated imines from aniline or benzylamine and benzaldehyde were very high to excellent (entries 1 and 4, Table 2); that from *m*-nitrobenzaldehyde and aniline was quite satisfactory (entry 5). The yields of the products from the reactions of imines generated from aniline and *m*-hydroxy- or *p*-chlorobenzaldehyde with diethylphosphite were also excellent (entries 8 and 9, Table 2). The reaction of aniline with *p*-nitrobenzaldehyde and phosphite was, however, sluggish (entry 7). Although, the yields of the desired aminophosphonate from *iso*-butyraldehyde, *m*-nitroaniline and diethylphosphite was excellent (entry 17, Table 2), those from *iso*-butyraldehyde or decanal, benzylamine and diethylphosphite were only moderately satisfactory or poor (entries 18 and 19, respectively, Table 2). Moreover, the aliphatic aldehydes required longer reaction time compared to that of their aromatic counterparts. The reaction of cyclohexanone with benzylamine and diethylphosphite led to the desired α-aminophosphonate in very good yield (entry 21), although, that with aniline and phosphite was moderate (entry 20, Table 2).

4. Conclusion

Thus, we have shown the efficacy of $In(OTf)_3$ as a catalyst in a simple one-pot synthesis of α-amino phosphonates incorporating nitro substituted anilines. The method is equally effective for other amino phosphonates derived from various carbonyl substrates and amines.

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