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### Synthesis of $\alpha$ -Aminophosphonates Using Polystyrene Supported Al(OTf)<sub>3</sub> as a Heterogeneous Catalyst

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A mild and efficient method has been devised for the preparation of  $\alpha$ -aminophosphonates from three component condensation of an aldehyde, an amine, and diethyl phosphite in the presence of catalytic amounts of cross-linked polystyrene supported aluminium triflate (Ps-Al(OTf)<sub>3</sub>) under solvent-free conditions in good to excellent yields. The catalyst is stable (as a bench top catalyst) and can be easily recovered and reused without appreciable change in its efficiency.

Keywords  $\alpha$ -aminophosphonates, aldehydes, aluminium triflate, amines, diethyl phosphate

#### INTRODUCTION

 $\alpha$ -Aminophosphonates as a kind of natural amino acid analogues have been the focus of attention in recent years because of a wide range of applications in the areas of industrial, biological, and medical chemistry.<sup>[1-3]</sup> Their potential as plant growth regulators,<sup>[4]</sup> herbicidals,<sup>[5]</sup> antibiotics,<sup>[6]</sup> enzyme inhibitors,<sup>[7]</sup> HIV protease,<sup>[8]</sup> anti-thrombotic agents,<sup>[9]</sup> and inhibitors of UDH-galactopyranose mutase<sup>[10]</sup> is well documented. Three component condensation of an aldehyde, an amine, and a phosphite is the most convenient method for the preparation of these compounds. For this purpose several types of catalysts such as ZrCl<sub>4</sub>,<sup>[11]</sup> AlCl<sub>3</sub>,<sup>[12]</sup> LiClO<sub>4</sub>,<sup>[13]</sup> SiO<sub>2</sub>- $NH_4HCO_3$ ,<sup>[14]</sup> Al(OTf)<sub>3</sub>,<sup>[15]</sup> ionic liquid [bmim]Cl-AlCl<sub>3</sub>,<sup>[16]</sup> Mg(ClO<sub>4</sub>)<sub>2</sub>,<sup>[17]</sup> TiCl<sub>4</sub>,<sup>[18]</sup> Al<sub>2</sub>O<sub>3</sub>-SbCl<sub>3</sub>,<sup>[19]</sup> ZrOCl<sub>2</sub>.8H<sub>2</sub>O,<sup>[20]</sup>  $TiO_2$ ,<sup>[21]</sup> amberlyst-15,<sup>[22]</sup> [Cu(3,4-tmtppa)](MeSO<sub>4</sub>)<sub>4</sub>,<sup>[23]</sup> sulfamic acid,<sup>[24]</sup> FeCl<sub>3</sub>,<sup>[25]</sup> sodium dodecyl sulfate,<sup>[26]</sup> mesoporous aluminosilicate nanocage,<sup>[27]</sup> and  $H_3BO_3^{[28]}$  have been used. A large number of these catalysts suffer from their own drawbacks such as generation of environmentally perilous waste material, tedious work-up, long reaction times, the use of malodorous trialkyl phosphite as the phosphorus nu-

$$\begin{array}{c} R^{1}CHO + R^{2}NH_{2} & \xrightarrow{H - P(OEt)_{2}} & \xrightarrow{R^{2}HN} & \xrightarrow{H} R^{1}(OEt)_{2} \\ R^{1}, R^{2}: Alkyl \text{ or } Aryl \end{array}$$

SCH. 1.

cleophile, unsatisfactory yields, complicated operations, and the use of moisture-sensitive, expensive, hazardous, difficult to handle or unreusable catalysts. Sometimes, a part of mentioned catalysts do not work well with electron deficient amines and/or secondary amines. On the other hand, the formation of  $\alpha$ -hydroxyphosphonate or a product of its rearrangement frequently accompanies the formation of  $\alpha$ -aminophosphonates. However, the developments in this area demand further searches for better catalysts that could be superior to the existing ones with regard to toxicity, handling, selectivity, and recyclability.

In a continuation of our ongoing program to develop environmentally benign methods using heterogeneous catalysts,<sup>[29,30]</sup> we reported Ps-Al(OTf)<sub>3</sub> as a new polymeric Lewis acid catalyst for dithioacetalization of carbonyl compounds and transdithioacetalization of acetals.<sup>[31]</sup> Along this line, we now wish to report that Ps-Al(OTf)<sub>3</sub> is also an effective and highly chemoselective heterogeneous catalyst for the synthesis of  $\alpha$ aminophosphonates under solvent-free conditions (Scheme 1).

#### **EXPERIMENTAL**

#### **Material and Techniques**

Chemicals were either prepared in our laboratory or were purchased from Merck and Fluka. Polystyrene (8% divinylbenzene, prepared via suspension polymerization, polyvinylpyrrolidone 90 K as suspension agent, grain size range: 0.25–0.6 mm) was obtained from Iran Polymer and Petrochemical Institute. IR spectra were run on a Shimadzu model 8300 FT-IR spectrophotometer. <sup>1</sup>H NMR spectra were recorded on a Bruker DPX-300 (300 MHz) spectrometer using CDCl<sub>3</sub> as solvent and TMS as the internal standard. Capacity of the catalyst was determined by gravimetric method and atomic absorption technique using a Philips atomic absorption instrument. Melting points were determined on a Fisher-Jones melting-point apparatus and are

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uncorrected. Reaction monitoring and purity determination of the products were accomplished by GLC or TLC on silica-gel polygram SILG/UV<sub>254</sub> plates.

#### Preparation of Ps-Al(OTf)<sub>3</sub><sup>[31]</sup>

In a two necked round bottomed flask (100 mL) equipped with a reflux condenser, a solution of Ps-AlCl<sub>3</sub><sup>[30]</sup> (3 g, 8% DVB) in Freon-113 (50 mL) was prepared. To the stirred solution was added dropwise 5 mL of triflic acid over a period of 2 h, while mentioning a gentle reflux. The mixture was then refluxed for 12 h. The polymer beads were filtered and washed with CH<sub>2</sub>Cl<sub>2</sub> (50 mL) and then with Et<sub>2</sub>O (50 mL) and dried in a vacuum oven overnight to give Ps-Al(OTf)<sub>3</sub>. The loading of Al(OTf)<sub>3</sub> determined was 0.41 mmol/g.

#### Typical Procedure for α-Aminophosphonate Synthesis

To a stirred solution of benzaldehyde (1 mmol), aniline (1 mmol), and Ps-Al(OTf)<sub>3</sub> (0.1 mmol) was added diethyl phosphite (1.2 mmol). The reaction mixture was stirred magnetically at room temperature. After completion of the reaction (monitored by TLC) the catalyst was filtered off and washed with CH<sub>2</sub>Cl<sub>2</sub> (2 × 10 mL). Then, the filtrate was washed with H<sub>2</sub>O (2 × 10 mL) and the organic layer was separated, dried (Na<sub>2</sub>SO<sub>4</sub>), and concentrated on a rotary evaporator under reduced pressure to give the crude product. Whenever required, the products were purified by column chromatography (silica gel) using *n*-hexane-EtOAc as eluent so as to afford the pure product. The spent catalyst from different experiments was washed with Et<sub>2</sub>O, dried, and used again.

#### **RESULTS AND DISCUSSION**

Ps-Al(OTf)<sub>3</sub> was prepared by the exchange reaction between cross-linked polystyrene supported aluminium chloride (Ps-AlCl<sub>3</sub>) and triffic acid in Freon-113 under reflux conditions. To exploit a simple and suitable condition for three component condensation of aldehydes, amines, and diethyl phosphite using Ps-Al(OTf)<sub>3</sub> as a catalyst, initially, we tried to convert 4-methoxybenzaldehyde (1 mmol) to its corresponding  $\alpha$ aminophosphonate with aniline (1 mmol) and diethyl phosphite (1.2 mmol) using different catalytic amounts of Ps-Al(OTf)<sub>3</sub> in the presence of various solvents and also under solvent-free conditions at different reaction temperatures. The best yield of the corresponding  $\alpha$ -aminophosphonate was obtained in the presence of 10 mol% of Ps-Al(OTf)<sub>3</sub> under solvent-free conditions at room temperature. Therefore, we employed the above conditions for conversion of various aldehydes to the corresponding  $\alpha$ -aminophosphonates (Table 1). Both electron-deficient and electron-releasing benzaldehydes react efficiently with aniline to give the corresponding  $\alpha$ -aminophosphonates (entries 1–8). Naphthalene-2-carbaldehyde also gave the corresponding product in high yield (entry 9). In addition, this method is even effective with aliphatic aldehydes, which normally produce low yields (entry 10). Acid sensitive substrates such as cinnamaldehyde and furan-2-carbaldehyde gave the corresponding  $\alpha$ -aminophosphonates without any decomposition, conjugate

TABLE 1 Ps-Al(OTf)<sub>3</sub> catalyzed synthesis of α-aminophosphonate derivatives

| Entry | Aldehyde   | Amine                               | Time (h) | Yield (%) <sup>a,b</sup> |
|-------|------------|-------------------------------------|----------|--------------------------|
| 1     | Сно        | NH <sub>2</sub>                     | 0.9      | 92 <sup>[26]</sup>       |
| 2     | ме-СНО     | NH <sub>2</sub>                     | 1        | 93 <sup>[21]</sup>       |
| 3     | мео-       |                                     | 1.1      | 93 <sup>[26]</sup>       |
| 4     | но-Д-сно   |                                     | 1.3      | 92 <sup>[21]</sup>       |
| 5     | 02N-СНО    | NH <sub>2</sub>                     | 0.7      | 95 <sup>[21]</sup>       |
| 6     | СІ         | NH <sub>2</sub>                     | 1.1      | 91 <sup>[23]</sup>       |
| 7     | сі-        | NH <sub>2</sub>                     | 0.9      | 91 <sup>[26]</sup>       |
| 8     | СНО        | NH <sub>2</sub>                     | 1        | 90 <sup>[21]</sup>       |
| 9     | CI         | NH <sub>2</sub>                     | 1.2      | 91 <sup>[15]</sup>       |
| 10    | CH0        | NH <sub>2</sub>                     | 1.5      | 91 <sup>[23]</sup>       |
| 11    | Ph         | NH <sub>2</sub>                     | 1.5      | 83 <sup>[26]</sup>       |
| 12    | СНО        | NH <sub>2</sub>                     | 1.3      | 91 <sup>[26]</sup>       |
| 13    | COMe       | NH <sub>2</sub>                     | 2        | 83 <sup>c,[16]</sup>     |
| 14    | <b></b> 0  | NH <sub>2</sub>                     | 2        | 89 <sup>c,[15]</sup>     |
| 15    | СНО        | MeO-NH2                             | 0.7      | 93 <sup>[11]</sup>       |
| 16    | СНО        | Me-NH <sub>2</sub>                  | 0.8      | 91 <sup>[15]</sup>       |
| 17    | СНО        | Cl-                                 | 1.8      | 82 <sup>[23]</sup>       |
| 18    | <b>СНО</b> | CI<br>NH <sub>2</sub>               | 2        | 84 <sup>[15]</sup>       |
| 19    | МеО-       | O <sub>2</sub> N-                   | 2.2      | 86 <sup>[21]</sup>       |
| 20    | <u> </u>   | O <sub>2</sub> N<br>NH <sub>2</sub> | 2.3      | 82 <sup>[15]</sup>       |
| 21    | Сно        | Ph NH-                              | 1.1      | 95 <sup>[15]</sup>       |
| 22    | Сно        | NH NH                               | 1.3      | 91 <sup>[21]</sup>       |
| 23    | Сно        | NH NH                               | 1.5      | 90 <sup>[17]</sup>       |
| 24    | Сно        | (Et) <sub>2</sub> NH                | 1.7      | 90 <sup>[16]</sup>       |
| 25    | Сно        | PhMeNH                              | 1.5      | 90 <sup>[25]</sup>       |

<sup>a</sup>Ratio of catalyst:carbonyl compound:amine:diethyl phosphite is 0.1:1:1:1.2.

<sup>b</sup>Isolated yields. All products are known compounds and were identified by comparison of their physical and spectral data with those of the authentic samples.

<sup>c</sup>The reaction was carried out at 40°C.



SCH. 2.

addition to the  $\alpha$ ,  $\beta$ -unsaturated carbonyl group or generation of polymeric by-products under the present reaction conditions (entries 11,12). Ketones also afforded the corresponding phosphates in relatively good yields (entries 13,14). In order to test the generality of the protocol, we have reacted different substituted anilines and primary aliphatic amines with benzaldehyde and diethyl phosphite (entries 15-22). As it is evident from the results, the presence of electron-withdrawing substituents on the aromatic ring in substituted anilines increases the reaction times and decreases the yields (entries 17-20). Also, the coupling reaction of secondary amines like piperidine, diethylamine, and N-methylaniline with benzaldehyde and diethyl phosphite in the presence of Ps-Al(OTf)<sub>3</sub> at ambient temperatures resulted in the formation of tertiary  $\alpha$ -aminophosphonate in high yields (entries 23–25). It is noteworthy that no competitive side reactions such as the formation of  $\alpha$ -hydroxyphosphonates were observed in these transformations.

To find out whether the reaction takes place in the solid matrix of Ps-Al(OTf)<sub>3</sub> or whether Al(OTf)<sub>3</sub> simply released in the reaction medium is responsible for the coupling reaction, Ps-Al(OTf)<sub>3</sub> was added to benzaldehyde and the mixture was stirred at room temperature for 2 h. Then, the catalyst was filtered off and the filtrate was analyzed for its aluminium content, which showed a negligible release of Al(OTf)<sub>3</sub>. The filtrate was found to be inactive for the coupling reaction of benzaldehyde, aniline, and diethyl phosphite. These observations indicate that Ps-Al(OTf)<sub>3</sub> is stable under the reaction conditions and there is no leaching of acid moieties during reactions.

It is important to note that Ps-Al(OTf)<sub>3</sub> shows a higher catalytic activity than Ps-AlCl<sub>3</sub> in the coupling reaction of aldehydes, amines, and diethyl phosphite (Scheme 2).

| PhCHO<br>(1 mmol)<br>Ps- | PhNH <sub>2</sub> (<br>HPO(OEt)<br>-Al(OTf) <sub>3</sub> (0 | 1mmol)<br>) <sub>2</sub> (1.2 mi<br>).1 mmol | mol)<br>) / rt / 0.9 | PhHN<br>9 h H | $\times^{P(OE}_{Ph}$ | (t) <sub>2</sub> |
|--------------------------|---|--|----------------------|---------------|----------------------|------------------|
| Use <sup>a</sup>         | 1   | 2  | 3                    | 4             | 5                    |                  |
| Yield (%)                | 92  | 92   | 91                   | 90            | 90                   |                  |

<sup>a</sup>Recovered catalyst was used successively (Use 2,3,...).

SCH. 3.

In order to know whether  $Ps-Al(OTf)_3$  could be reused to catalyze the coupling reaction of aldehydes, amines, and diethyl

 TABLE 2

 Comparison of the efficiencies of a number of different

 reported catalysts with that of Ps-Al(OTf)<sub>3</sub> in condensation of

 aniline and 4-methoxybenzaldehyde with diethyl phosphite

| Entry | Cat./Solv./Temp.   | Time (h) | Yield (%)                 |
|-------|--|----------|---------------------------|
| 1     | ZrCl <sub>4</sub> /MeCN/rt                                 | 5        | <b>90</b> <sup>[11]</sup> |
| 2     | Al(OTf) <sub>3</sub> /neat/80°C                            | 3        | 90 <sup>[15]</sup>        |
| 3     | ionic liquid   | 2        | 95 <sup>[16]</sup>        |
|       | [bmim]Cl-AlCl <sub>3</sub> /neat/rt <sup>a</sup>           |          |                           |
| 4     | Mg(ClO <sub>4</sub> ) <sub>2</sub> /neat/rt                | 5 min    | 95 <sup>[17]</sup>        |
| 5     | Al <sub>2</sub> O <sub>3</sub> -SbCl <sub>3</sub> /MeCN/rt | 3.5      | 92 <sup>[19]</sup>        |
| 6     | ZrOCl <sub>2</sub> .8H <sub>2</sub> O/neat/rt <sup>a</sup> | 5 min    | 95 <sup>[20]</sup>        |
| 7     | TiO <sub>2</sub> /neat/50°C                                | 2.5      | 98 <sup>[21]</sup>        |
| 8     | [Cu(3,4-tmtppa)](MeSO <sub>4</sub> ) <sub>4</sub> /        | 3        | 90 <sup>23</sup>          |
|       | $H_2O/80^{\circ}C$   |          |                           |
| 9     | sulfamic acid/neat/rt                                      | 2        | 87 <sup>[24]</sup>        |
| 10    | FeCl <sub>3</sub> /THF/60°C                                | 0.75     | 92 <sup>[25]</sup>        |
| 11    | sodium dodecyl   | 30 min   | 98 <sup>[26]</sup>        |
|       | sulfate/H <sub>2</sub> O/50°C                              |          |                           |
| 12    | AlKIT-5 <sup>b</sup> /MeCN/80°C                            | 4        | 90 <sup>[27]</sup>        |
| 13    | Ps-Al(OTf) <sub>3</sub> /neat/rt                           | 1.1      | 93                        |

<sup>a</sup>With benzaldehyde

<sup>b</sup>Mesoporous aluminosilicate nanocage catalyst

phosphite, a sample of the solid catalyst was recovered by filtration after the reaction and it was then reused in an identical reaction of benzaldehyde with aniline and diethyl phosphite. As is shown in Scheme 3, the efficiency of the recycled catalyst did not change appreciably after five cycles.

A comparison of the present protocol, using  $Ps-Al(OTf)_3$ , with selected previously known protocols is collected in Table 2. As it is seen in addition to having the general advantages attributed to the solid catalysts,  $Ps-Al(OTf)_3$  has a good efficiency compared to many of those reported catalysts in the condensation of aniline and 4-methoxybenzaldehyde with diethyl phosphite.

#### CONCLUSION

In summary, three component coupling reaction of aldehydes, amines, and diethyl phosphite using Ps-Al(OTf)<sub>3</sub> has been achieved. This catalyst has comparable activity with Al(OTf)<sub>3</sub>, but it has added advantages that involve its ability to be recycled, non-toxicity, non-corrosiveness, ease of handling, high chemoselectivity, and environmental compatibility. High yields, green and mild reaction conditions, facile work-up, and short reaction times are other notable features of this protocol.

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