



Iron-doped single walled carbon nanotubes as an efficient and reusable heterogeneous catalyst for the synthesis of organophosphorus compounds under solvent-free conditions



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ABSTRACT

Iron-doped single walled carbon nanotubes (Fe/SWCNTs) is an efficient, eco-friendly, and reusable heterogeneous catalyst for the synthesis of diversely decorated α -aminophosphonates via multicomponent reaction of amines, carbonyl compounds, and phosphorus compounds under solvent-free conditions. This methodology illustrates a very simple procedure, with wide applicability, extending the scope to aliphatic and aromatic amines and carbonyl compounds. It also enabled the development of one-pot synthesis of β -phosphonomalonates during the reaction of carbonyl compounds, malononitrile and phosphorus compounds. Excellent results were obtained in each case affording the corresponding organophosphorus adducts in good yields.

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1. Introduction

Organophosphorus compounds have been found a wide range of applications in the areas of industrial, agricultural, and medicinal chemistry owing to their biological and physical properties as well as their utility as synthetic intermediates.¹ In particular, compounds of tetracoordinated pentavalent phosphorus bearing heteroatomic substituents in the α - and β -position to the phosphorus atom have shown strong activities as antibiotics, anticancer drugs, antibacterial agents, antiviral agents, enzyme inhibitors, peptide mimetic, insecticides, herbicides, fungicides, as well as plant growth regulators.² They have also become important in the treatment of bone disorders and in medical decalcification.³ From their physical properties, phosphonates are used as fire retardants for materials.⁴ In this regard, the wide application of phosphonates has provoked the search for simple, efficient, and cost-effective procedures for the synthesis of such significant scaffolds in recent years.^{2,5}

A large number of useful transformations have been achieved during the past decades, in which dialkyl/trialkyl phosphites were

used as standard nucleophilic species for the construction of C–P bonds, in which various compounds can act as the acceptor, such as imines (ketimines),⁶ carbonyl groups,⁷ alkylidene malonates,⁸ α,β -unsaturated carbonyl compounds,⁹ nitroalkenes,¹⁰ and so on.

Recently, one-pot three-component Kabachnik–Fields synthesis of α -aminophosphonates starting from aldehydes, amines, and dialkyl/trialkyl phosphites have been reported using Lewis and Brønsted acid catalysts, heteropoly acids, heterogeneous catalysts, and nano catalysts.⁶ On the other hand, phospho-Michael addition, that is, the addition of a phosphorous nucleophile to an electron-deficient alkene has evoked remarkable attention by organic chemists. Synthesis of β -phosphonomalonates by this method is most commonly promoted by bases, Brønsted/Lewis acids, transition metals, and radical initiators, such as AIBN or microwaves.⁸

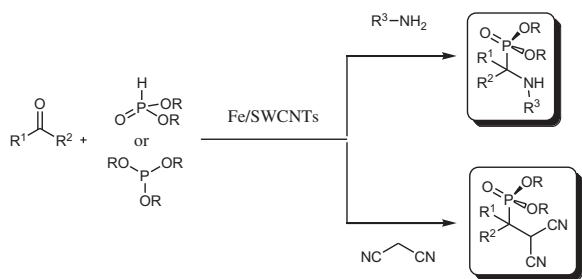
Although, some of these approaches are effective and for satisfactory synthesis of phosphonates, many of them cause reactor and plant corrosion problems, involve tedious separation procedures, require prolonged reaction times, and need use of toxic organic solvents and also are expensive. With regard to this, it is of great practical importance to develop a more efficient, convenient, and also an environmentally benign method using inexpensive and readily available reagents for the synthesis of these scaffolds.

Heterogeneous-reagent systems have many advantages, such as simple experimental procedures, mild reaction conditions, and the

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minimization of chemical wastes as compared to their liquid phase counterparts.¹¹ Catalysis is currently recognized as a potential field of application for carbon nanotubes (CNTs), and throughout the past decade the number of publications and patents on this subject has been increasing exponentially.¹²

As a part of our program aiming at developing efficient and environmentally friendly heterogeneous catalysts for organic synthesis, we have developed iron-doped single walled carbon nanotubes (Fe/SWCNTs) as an easily prepared, air stable, water tolerated, and recyclable catalyst in promoting acylation of alcohols, phenols, acids, and amines with acid chlorides or acid anhydrides under solvent-free conditions.¹³ In this paper, we report a practical, facile, and efficient method for the synthesis of α -aminophosphonates and β -phosphonomalonates via reaction of amines/malononitrile, carbonyl compounds and phosphorus compound, promoted by Fe/SWCNTs under solvent-free conditions (Scheme 1).



Scheme 1.

2. Results and discussion

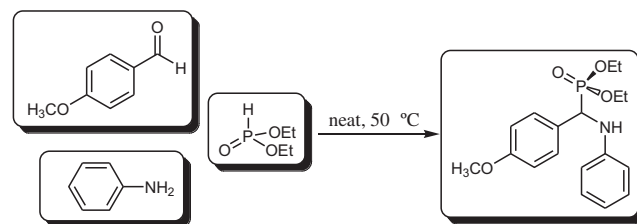
2.1. Optimization of reaction

In search for an effective catalyst, for our initial screening experiments, the implementation of three-component strategies to obtain α -aminophosphonates in the presence of different catalysts was allowed. 4-Methoxybenzaldehyde and aniline were selected as model substrates and treated with diethyl phosphite (Table 1). When reaction was carried out in the absence of catalyst, the product yield was 25% after 1 h (Table 1, entry 1). The reaction did not proceed well when single-walled CNTs (SWCNTs) and multi-walled CNTs (MWCNTs) were employed, (Table 1, entries 2 and 3), whereas the yield of product was higher in the case of SWCNTs. The use of TiO₂-doped MWCNTs, ZnO-doped MWCNTs, TiO₂-doped SWCNTs, and Nano SnO₂ did not provide desired product in acceptable yields (Table 1, entries 4–7). Although, Nano-Fe and Fe-doped MWCNTs could accelerate the reaction to produce the target compound diethyl (4-methoxybenzaldehyde) (phenylamino) methylphosphonate, they could not provide satisfactory yields (Table 1, entries 8 and 9). We observed an increase in the reaction yield using Fe/SWCNTs (2.4 mol%). The optimum amount of nanocatalyst loading in this one-pot and three component reaction, was found to be 5.0 mol%, (Table 1, entry 11). By lowering the catalyst loading to 2.4 mol%, the desired product was obtained in lower yield while increasing of the catalyst loading to 10.0 mol% has no significant effect on reaction rate and isolated yield of product (Table 1, entries 10–13).

In the next step, the effect of solvent and temperature were surveyed (Table 2, entries 1–7). It was found that the use of 5.0 mol% of Fe-doped SWCNTs resulted in 60% formation of the corresponding α -aminophosphonates in solvent-free conditions at 30 °C within 3 h (Table 2, entry 1). Increase in the reaction temperature to 50 °C led to formation of product in higher yield, in 1 h (Table 2, entry 2). By increasing the temperature range to 80 °C the yield and time of reaction did not change significantly (Table 2, entry 3). The

Table 1

Screening of different catalyst for the synthesis of diethyl (4-methoxybenzaldehyde) (phenylamino) methylphosphonate^a



Entry	Catalyst	Yield ^b (%)
1	— ^c	25
2	Pure SWCNTs ^d	40
3	Pure MWCNTs ^d	25
4	TiO ₂ /MWCNTs	35
5	ZnO/MWCNTs	35
6	TiO ₂ /SWCNTs	45
7	Nano SnO ₂	30
8	Nano-Fe	60
9	Fe/MWCNTs	55
10	Fe/SWCNTs	80
11	Fe/SWCNTs (5.0 mol%)	95
12	Fe/SWCNTs (7.0 mol%)	97
13	Fe/SWCNTs (10.0 mol%)	97

^a *p*-Methoxy-benzaldehyde (1.0 mmol), aniline (1.0 mmol) and diethyl phosphite (1.2 mmol), catalyst (2.4 mol%), solvent free, 50 °C, 1 h.

^b Determined by ¹H NMR analysis.

^c In the absence of catalyst.

^d 0.02 g was used.

Table 2

The dependence of yield on the solvent and temperature^a

Entry	Solvent	Temperature (°C)	Time (h)	Yield ^b (%)
1	—	30	3	60
2	—	50	1	95
3	—	80	0.8	98
4	H ₂ O	50	4	10
5	EtOH	50	4	55
6	CHCl ₃	50	4	45
7	Dioxane	50	4	60

^a Reaction conditions: *p*-methoxy-benzaldehyde (1.0 mmol), aniline (1.0 mmol), and diethyl phosphite (1.2 mmol) with 5.0 mol% of the catalyst.

^b Determined by ¹H NMR analysis.

reaction was sluggish in H₂O probably due to the poor solubility of both the catalyst and the substrates (Table 2, entry 4). Other solvents improved yield less than neat condition (Table 2, entries 5–7). The best rate was observed when the reaction was carried out under neat condition at 50 °C (Table 2, entry 2).

2.2. Characterization of Fe/SWCNTs

The recent studies have shown that, for the efficient use of CNT structural properties, particularly as catalyst in organic synthesis, CNT bundles should be activated.¹⁴ In this study, oxygen was used for purification and functionalization of CNT bundles at 500 °C for about 2 h. To characterize the functionalized CNTs, the same amounts of each CNT sample was mixed with about 100 equiv KBr powder. The FT-IR spectrum of CNT sample is shown in Fig. 1. According to the FT-IR spectrum, the strong peak at around 3440 cm⁻¹ is related to the O–H bond, whereas the peaks at ~1620 cm⁻¹ are related to the carbonyl groups. Based on the back titration analysis, the amount of functionalization is ~7.2% for CVD process.

To study the amount of Fe nanoparticles doped on the CNT bundles TGA was used. The TGA instrument was adapted to study the thermal stability as well as the purity of CNT bundles. The CNT samples were analyzed according to a temperature program with

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