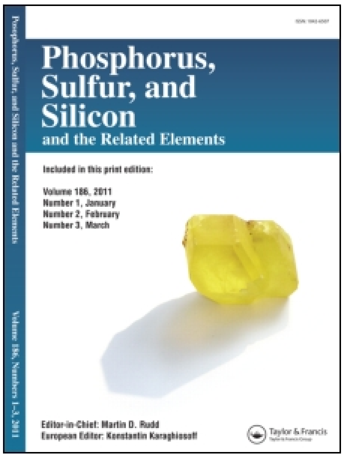

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A Facile and Clean Procedure for Preparation of α-Aminophosphonates via a Rotary Evaporator Equipped with Circulating Water Vacuum Pumps

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A FACILE AND CLEAN PROCEDURE FOR PREPARATION OF α-AMINOPHOSPHONATES VIA A ROTARY EVAPORATOR EQUIPPED WITH CIRCULATING WATER VACUUM PUMPS

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RE-CWVP (rotary evaporator equipped with a circulating water vacuum pump)–assisted synthesis is reported as an extremely efficient, facile, and clean procedure for the preparation of α-aminophosphonates in organic synthesis and industrial processes. The title α-aminophosphonates are obtained in good to satisfactory yields by the method and characterized by means of IR, ^{1}H NMR, ^{31}P NMR, ^{13}C NMR, and mass spectrometry.

Keywords α-Aminophosphonates; clean synthesis; flame retardants; Mannich-type reaction

INTRODUCTION

In the 1970s, Pyrovatex CP (N-hydroxymethyl-3-(dimethoxy-phosphoryl)propanamide) was successfully applied as a durable flame retardant to modify pure cotton fabric.[1] But it is a fatal defect that formaldehyde is easily released during industrial processes and use.[2] On 15 June 2004, a panel of the World Health Organization from 10 countries announced in its conclusions that formaldehyde poses a greater hazard than previously thought.[3] They noted that the chemical is “carcinogenic to humans.” Thus, to a large extent, its application is restricted for some uses.[2,4] In addition, the processes for the synthesis of industrially important flame retardants require the use of many harmful organic solvents, chemicals, and catalysts,[5] and many of these processes consist of a number of steps that are neither environmental friendly nor economical. Therefore, we attempted to develop alternative flame retardants for cotton fabrics that are synthesized by a Mannich-type reaction, as shown in Scheme 1.

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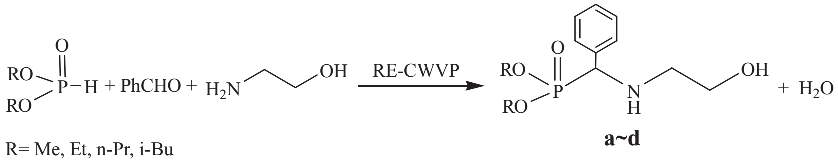

Scheme 1 Synthetic route of α-aminophosphonates containing a hydroxyl group.

Generally, transformations of the Mannich-type reaction could be fulfilled under the catalysis of Brönsted[6] or Lewis acids such as BF_3/Et_2O,[7] $ZnCl_2$,[8] $MgBr_2$,[8] or $SnCl_4$.[6] However, these methods have limitations, as many imines are hygroscopic and are not sufficiently stable for isolation. The first one-pot synthesis of α-aminophosphonates has been achieved by the reaction of phosphite with imines in the presence of lanthanide triflate[9] as the catalyst in organic solvent, and has been generated in situ from aldehydes and amines. Subsequently, one-pot variations in organic solvents have been improved.[10–18] Recently, it was reported that solvent-free transformations of phosphites to α-aminophosphonates could be accomplished in the presence of acidic catalysts[19] using microwave-assisted methods.[20] All of the above preparation procedures are uneconomical, however, because they are require a certain amount of catalyst, whether or not an organic solvent is needed.

In this article we report a clean and facile procedure for the solvent-free and catalyst-free preparation of α-aminophosphonates containing an active hydroxyl group by rotary evaporator equipped with a circulating water vacuum pump (RE-CWVP) as a preparation tool.

RESULTS AND DISCUSSION

The preparation of the compounds **a** and **b** have been reported previously,[20,21] but complete spectroscopic data for them have not yet appeared. Therefore, in this article, we shall not only supplement their spectroscopic data but also report a cleaner and more facile preparation procedure compared with the previous synthetic methods.

Experimental Principle

A reverse reaction can occur if the water released by a Mannich-type reaction is not separated from the reaction system. For that reason, we employ circulating water vacuum pumps (CWVP) that can continuously suck water out of the vessel through the valve of a circulating water vacuum pump equipment to shift the equilibrium to the right, namely, to shift the equilibrium to the target product.

In order to further reduce the effect of the solvent pollution on CWVP, the ethanol is cooled by low-temperature cooling liquid circulating pumps and then carried in the cooling circulating system for rotary evaporator.

Effects of the Factors on Synthesis of α-Aminophosphonates

Taking the compound **a** as an example below, we discuss carefully the influence of the three factors, i.e., the reaction temperature, the reaction time, and RE-CWVP on preparation of α-aminophosphonates.

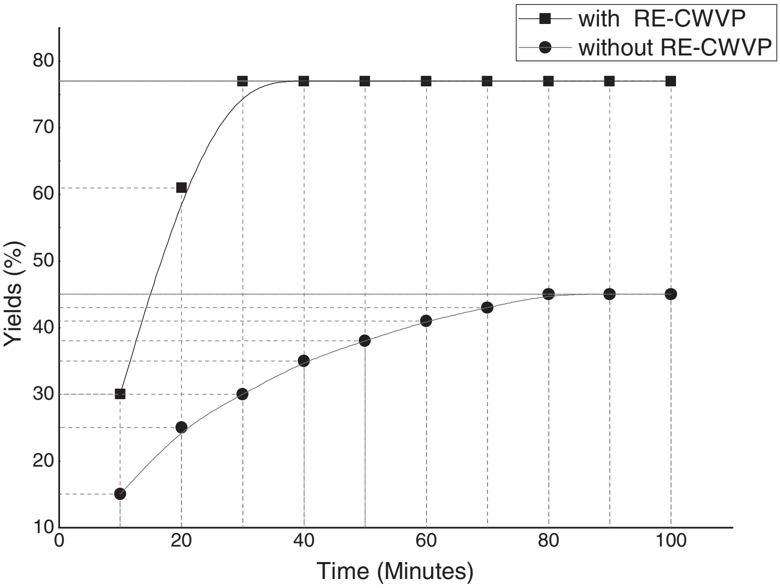

Figure 1 Both yields of different reaction time for the compound **a** with and without RE-CWVP (solvent-free, temperature at 70°C).

When the reaction temperature reaches 75°C, the viscous solvent changes quickly into a white solid within a few minutes. The mixture was checked by TLC to observe five new spots and recorded by ESI-MS. When the reaction occurs at 65°C, the yield of the compound **a** is about 60% in 2 h. However when the temperature rises to 70°C, a satisfactory yield (77%) is obtained in a short time (30 min). Prolonged time at that temperature keeps its yield almost constant (shown in Figure 1). Therefore, the optimal conditions should be at 70°C for 30 min.

Compared with an experiment without using RE-CWVP under the same conditions. (Figure 1), the yield of the compound **a** is only 30% at 30 min. However, it is approximately 40% for a prolonged time (60 min), which demonstrates that RE-CWVP is an extremely efficient and facile device for the preparation of α-aminophosphonates containing an active hydroxyl group.

Hence the one-pot synthesis for α-aminophosphonates containing an active hydroxyl group has optimized reaction conditions of 30 min at 70°C under solvent-free and catalyst-free conditions for benzaldehyde, monoethanolamine, and dialkyl phosphite operated by RE-CWVP.

CONCLUSION

The common RE-CWVP is an extremely efficient, facile, and clean reaction device for the preparation of α-aminophosphonates containing an active hydroxyl group, which displays not only environmentally friendly methods and economy, but also a convenient operation. The corresponding α-aminophosphonates are obtained under solvent-free and catalyst-free conditions in satisfactory yields. Title compounds are characterized by IR, ^{1}H NMR, ^{31}P NMR, ^{13}C NMR, and mass spectrometry.

EXPERIMENTAL

All chemicals and materials were of analytical grade, and all solutions were freshly dried by standard methods.

^{1}H NMR spectra and ^{13}C NMR were obtained on a Bruker Advance DMX 400 MHz instrument using TMS as internal standard in $CDCl_3$. ^{31}P NMR spectra were obtained on a Bruker Advance DMX 400 spectrometer at 162 MHz, and the chemical shifts values were referenced to 85% H_3PO_4 as an external reference. Chemical shifts were reported in δ ppm. FT-IR spectra were recorded on a Nicolet Avatar spectrophotometer. Mass spectra were recorded on a Bruker Esquire 3000 ion trap mass spectrometer. RE-52AA-type rotary evaporator equipped with circulating water vacuum pumps was purchased from Shanghai Yarong Biochemical Instrument Factory, China. DLSB-4/10-type low-temperature cooling liquid circulating pump was produced by Gongyi Yingyu Instrument Factory, China.

General Procedure

At a temperature of 70°C (water bath temperature) and vacuum of 0.09 MPa, a mixture of benzaldehyde (5 mmol), monoethanolamine (5 mmol), and dialkyl phosphite (5.25 mmol) was rotated and heated by rotary evaporator for 30 min (checked by TLC). After the reaction was complete, the mixture was isolated by gel chromatography with ethyl acetate:alcohol (3:1) as the eluent to afford the target products as colorless viscous liquids. All products were characterized by NMR, IR, and mass spectral data, and the complete spectroscopic data are given below.

Compound a: Yield: 77%. ^{1}H NMR: 7.32~7.43 (m, 5H, C_6H_5), 4.07 (d, 1H, CH, $^2J_{PH} = 20.5$ Hz), 3.76(d, 3H, CH_3, $^2J_{PH} = 8.3$ Hz), 3.53 (d, 3H, CH_3, $^2J_{PH} = 8.3$ Hz), 3.55~3.74 (m, 2H, CH_2OH), 2.63~2.79 (m, 2H, CH_2N), 2.11 (br, 2H); ^{31}P NMR: 25.71; ^{13}C NMR: 135.58, 128.69, 128.35, 128.18, 61.50, 59.38, 53.59, 49.41; IR(KBr)(cm^{-1}): 3200~3500, 3028, 2954, 2852, 1637, 1603, 1455, 1400, 1242, 1055; ESI-MS: *m/z* 259.8 $[M+H]^+$.

Compound b: Yield: 80%. ^{1}H NMR: 7.31~7.43 (m, 5H, C_6H_5), 4.10 (d, 1H, CH, $^2J_{PH} = 20.5$ Hz), 4.12 (m, 2H, CH_2O), 3.64 (m, 2H, CH_2O), 3.76~3.97 (m, 2H, CH_2OH), 2.65~2.77 (m, 2H, CH_2N), 2.09 (br, 2H), 1.31 (t, 3H, CH_3, $^3J = 7.3$ Hz), 1.14 (t, 3H, CH_3, $^3J = 7.3$ Hz); ^{31}P NMR: 23.44; ^{13}C NMR: 135.87, 128.55, 128.41, 128.02, 62.87, 61.10, 59.66, 49.44, 16.35; IR(KBr)(cm^{-1}): 3200~3500, 3030, 2985, 2932, 1638, 1493, 1454, 1397, 1238, 1053, 1026; ESI-MS: *m/z* 287.9 $[M+H]^+$.

Compound c: Yield: 81%. ^{1}H NMR: 7.30~7.43 (m, 5H, C_6H_5), 4.05 (d, 1H, CH, $^2J_{PH} = 20.5$ Hz), 4.00 (m, 2H, CH_2O), 3.65~3.84 (m, 2H, CH_2OH), 3.60 (m, 2H, CH_2O), 2.67~2.77 (m, 2H, CH_2N), 1.67 (m, 2H, CH_2CH_3), 1.50 (m, 2H, CH_2CH_3), 2.06 (br, 2H), 0.93 (t, 6H, CH_3, $^3J = 7.3$ Hz), 0.81 (t, 3H, CH_3, $^3J = 7.3$ Hz); ^{31}P NMR: 23.29; ^{13}C NMR: 135.98, 128.52, 128.41, 128.00, 68.30, 60.05, 59.61, 49.43, 23.84, 9.94; IR(KBr)(cm^{-1}): 3200~3500, 3030, 2969, 1636, 1460, 1399, 1237, 1061, 1001; ESI-MS: *m/z* 316.0 $[M+H]^+$.

Compound d: Yield: 83%. ^{1}H NMR: 7.34~7.41 (m, 5H, C_6H_5), 4.05 (d, 1H, CH, $^2J_{PH} = 20.5$ Hz), 3.81 (m, 2H, CH_2O), 3.46~3.80 (m, 2H, CH_2OH), 3.42 (m, 2H, CH_2O), 2.65~2.79 (m, 2H, CH_2N), 2.06 (br, 2H), 1.92 (s, H, CH), 1.75 (s, H, CH), 0.91 (s, 12H, CH_3); ^{31}P NMR: 23.02; ^{13}C NMR: 135.07, 128.48, 128.40, 127.94, 69.63, 60.03, 59.62, 49.49, 29.18, 18.65; IR(KBr)(cm^{-1}): 3200~3500, 2962, 2868, 1650, 1593, 1470, 1401, 1240, 1045, 1013; ESI-MS: *m/z* 344.0 $[M+H]^+$.

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