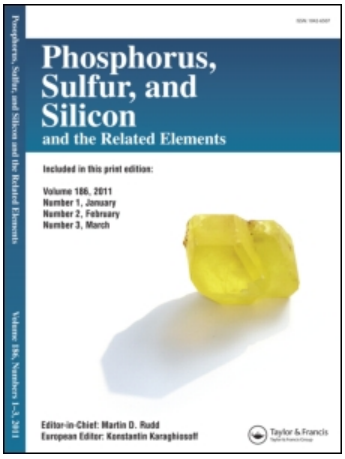

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*Potassium dihydrogen phosphate powder and sodium dihydrogen phosphate powder were found to catalyze stereoselective conversion of dialkyl 2-(imido-*N*-yl)-3-(triphenylphosphoranylidene)butanedioates to electron-poor (*Z*)-*N*-vinylimides in solvent-free conditions under microwave irradiation in 5–6 minutes in high conversions.*

Keywords Microwave irradiation; phosphorus ylide; potassium dihydrogen phosphate; sodium dihydrogen phosphate; solvent-free conditions; (*Z*)-*N*-vinylimide

INTRODUCTION

β-Additions of nucleophiles to the vinyl group of vinylic phosphonium salts leading to the formation of new alkylidenephosphoranes has attracted much attention as a very convenient and synthetically useful method in organic synthesis.[1–11] In the past we have established a convenient, one-pot method for preparing stabilized phosphorus ylides utilizing *in situ* generation of the phosphonium salts.[1–11] In this article, we report on the catalytic rule of Potassium-dihydrogen-phosphate powder and sodium-dihydrogen-phosphate

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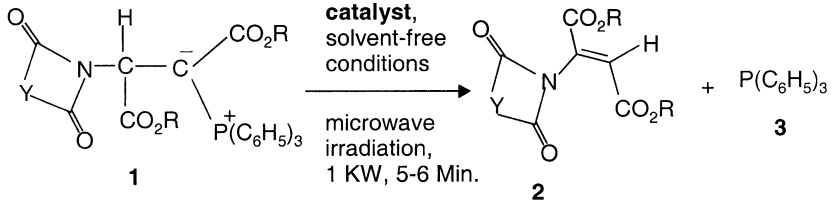

previous report.[10]

SCHEME 1

powder in the stereoselective conversion of dialkyl 2-(imido-*N*-yl)-3-(triphenylphosphoranylidene)butanedioates (**1**)[11] to electron-poor (*Z*)-*N*-vinylimides (**2**)[10] in solvent-free conditions[12] under microwave irradiation in 5–6 minutes in high conversions (Scheme 1).

RESULTS AND DISCUSSION

Potassium-dihydrogen-phosphate powder and sodium-dihydrogen-phosphate powder were found to catalyze stereoselective conversion of dialkyl 2-(imido-*N*-yl)-3-(triphenylphosphoranylidene)butanedioates (**1**) to electron-poor (*Z*)-*N*-vinylimides (**2**) in solvent-free conditions under microwave irradiation in 5–6 minutes at microwave power 1 KW in high conversions (Scheme 1).[10–11] TLC indicated that the reactions were completed after 5 minutes in the presence of sodium dihydrogen phosphate and 6 minutes in the presence of potassium-dihydrogen phosphate. The reaction proceeds smoothly and cleanly under solvent-free conditions[12] and no side reactions were observed. In the absence of potassium-dihydrogen-phosphate powder and sodium-dihydrogen-phosphate powder, this reaction did not afford the corresponding compounds (**2a**) even at reflux temperature (toluene as solvent) after 24 h. TLC indicated that the solution contained unreacted ylide **1a**.[11] In the absence of the microwave irradiation the reactions were not completed in the presence of sodium-dihydrogen phosphate and potassium-dihydrogen phosphate at 95°C after 1 h. We have also used Na_3PO_4, Na_2HPO_4, K_3PO_4, and K_2HPO_4 in this reaction under thermal (95°C, 1 h) and microwave (1 KW, 6 minutes) conditions but in all cases the reactions were not completed, and TLC indicated that the reaction mixture contained unreacted ylide **1** and (*Z*)-*N*-vinylimide

2. In the absence of the NaH_2PO_4 powder or KH_2PO_4 powder, the conversion of powdered ylide **1** to (*Z*)-*N*-vinylimide **2** was not observed under thermal (95°C, 1 h) and microwave (1 KW, 6 minutes) conditions, and decomposition of the starting material was observed. The structures of **2a–d** were deduced from their ^{1}H NMR, and ^{13}C NMR spectra. The full characterization data of the compounds (**2a–d**) are given in our previous report.[10]

In summary, we have found that NaH_2PO_4 powder and KH_2PO_4 powder are able to catalyze stereoselective conversion of ylides **1**[11] to compounds **2**[10] in solvent-free conditions under microwave heating. Other aspects of this process are under investigation.

EXPERIMENTAL

Commercial-oven Butane M245 was used for microwave irradiation. Melting points were measured on an Electrothermal 9100 apparatus and are uncorrected. ^{1}H and ^{13}C NMR spectra were measured with a BRUKER DRX-500 AVANCE spectrometer at 500 and 125 MHz, respectively.

General Procedure for the Preparation of Compounds 2a–d

The powdered mixture of dry NaH_2PO_4 powder (or KH_2PO_4 powder) (2 g) and ylide **1**[11] (1 mmol) were irradiated in the microwave oven at microwave power 1 KW (100%) for 5 minutes (NaH_2PO_4) and 6 minutes (KH_2PO_4), and then placed over a column of silica gel (10 g). The column chromatography was washed using ethyl acetate-light petroleum ether (1:9) as eluent. The solvent was removed under reduced pressure and products (**2a–d**) were obtained. The characterization data of the compounds (**2a–d**) are given in our previous report.[10]

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