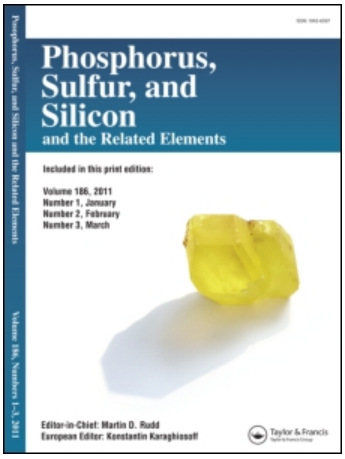

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*Protonation of the highly reactive 1:1 intermediates, which are produced in the reaction between triphenylphosphine and dialkyl acetylenedicarboxylates, by 3,5-dimethylpyrazol leads to vinyltriphenylphosphonium salts, which undergo a Michael addition reaction with a conjugate base to produce dialkyl 2-(3,5-dimethyl-1*H*-pyrazol-1-yl)-3-(triphenylphosphoranylidene)butanedioates. Dipotassium hydrogen phosphate powder was found to catalyze the stereoselective conversion of dialkyl 2-(3,5-dimethyl-1*H*-pyrazol-1-yl)-3-(triphenylphosphoranylidene) butanedioates to dialkyl 2-(3,5-dimethyl-1*H*-pyrazol-1-yl)-2-butenedioates in solvent-free conditions under microwave (0.6 KW, 3 min) and thermal (90°C, 60 min) conditions.*

Keywords 3,5-dimethylpyrazol; acetylenic esters; dipotassium hydrogen phosphate; Michael addition; microwave irradiation; vinyltriphenylphosphonium salt

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.[1–3] Organophosphorus compounds have

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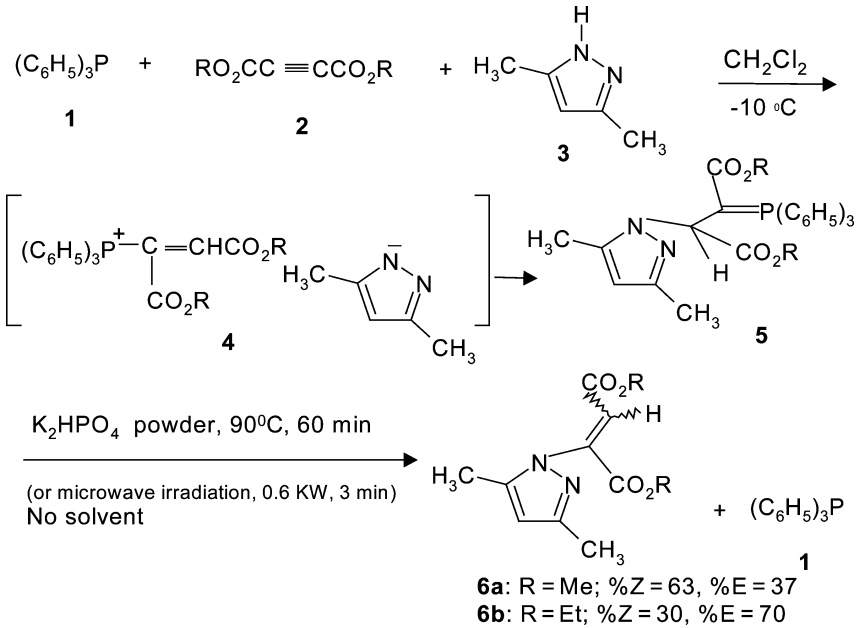
been extensively used in organic synthesis.[2] Silica gel as an additive promotes the Wittig reactions of phosphorus ylides with aldehydes, including sterically hindered aldehydes, to increase the rate and yields of alkenes.[4,5] In the past we have established a convenient, one-pot method for preparing stabilized phosphorus ylides utilizing in situ generation of the phosphonium salts.[1,3] In this article, we report on the catalytic role of dipotassium hydrogen phosphate powder in the stereoselective conversion of dialkyl 2-(3,5-dimethyl-1*H*-pyrazol-1-yl)-3-(triphenylphosphoranylidene)butanedioates to dialkyl 2-(3,5-dimethyl-1*H*-pyrazol-1-yl)-2-butenedioates in solvent-free conditions under microwave (0.6 KW, 3 min) and thermal (90°C, 60 min) conditions (Scheme 1).



SCHEME 1

RESULTS AND DISCUSSION

The ylide (**5**) may result from an initial addition of triphenylphosphine **1** to the acetylenic ester **2**, and the concomitant protonation of the 1:1 adduct by 3,5-dimethylpyrazol leads to vinyltriphenylphosphonium salts **4**, which undergo a Michael addition reaction with conjugate a base to produce dialkyl 2-(3,5-dimethyl-1*H*-pyrazol-1-yl)-3-(triphenylphosphoranylidene)butanedioates (**5**). TLC

indicated the formation of ylides **5** in CH_2Cl_2. Dipotassium hydrogen phosphate powder was found to catalyze the stereoselective conversion of dialkyl 2-(3,5-dimethyl-1*H*-pyrazol-1-yl)-3-(triphenylphosphoranylidene)butanedioates (**5**) to dialkyl 2-(3,5-dimethyl-1*H*-pyrazol-1-yl)-2-butenedioates (**6**) in solvent-free conditions under microwave (0.6 KW, 3 min) and thermal (90°C, 60 min) conditions. We have also used MgO, $MgSO_4$, Al_2O_3, $Al_2(SO_4)_3$, NaH_2PO_4, Na_2HPO_4, Na_3PO_4, and KH_2PO_4 in this reaction, but the yield of product was very low, and in all cases decomposition and several products were observed. In the absence of the K_2HPO_4 powder, the powdered ylide **5** was not reacted under microwave irradiation at microwave power 0.6 KW after 3 min or under thermal (90°C, 60 min) conditions, and decomposition of the starting materials was observed.

CONCLUSION

In conclusion, we have found that K_2HPO_4 powder is able to catalyze the stereoselective conversion of dialkyl 2-(3,5-dimethyl-1*H*-pyrazol-1-yl)-3-(triphenylphosphoranylidene)butanedioates to dialkyl 2-(3,5-dimethyl-1*H*-pyrazol-1-yl)-2-butenedioates in solvent-free conditions[6] under microwave (0.6 KW, 3 min) and thermal (90°C, 60 min) conditions. Other aspects of this process are under investigation.

EXPERIMENTAL

Commercial oven Butane M245 was used for microwave irradiation. IR spectra were recorded on a Shimadzu IR-460 spectrometer. ^1H and ^{13}C NMR spectra were measured with a Bruker DRX-500 Avance spectrometer at 500 and 125 MHz, respectively.

The General Procedure for the Preparation of Ylides 5 and Compounds 6a–b

To a magnetically stirred solution of triphenylphosphine **1** (0.262 g, 1 mmol) and 3, 5-dimethylpyrazol **3** (0.096 g, 1 mmol) in CH_2Cl_2 (4 mL) was added dropwise a mixture of **2** (1 mmol) in CH_2Cl_2 (3 mL) at −10°C over 15 min. The mixture was allowed to warm up to r.t. Dipotassium hydrogen phosphate powder (1.5 g) was added, and the solvent was evaporated. Dry dipotassium hydrogen phosphate and the residue were heated (yield for **6a**, 31%; yield for **6b**, 30%) for 90 min at 60°C (or irradiated in a microwave oven for 3 min. at microwave power 0.6 KW; yield for **6a**, 32%; yield for **6b**, 32%) and then placed over a column of silica gel powder (12 g). The column chromatography was washed using

ethyl acetate-light petroleum ether (1:10) as an eluent. The solvent was removed under reduced pressure, and products were obtained as viscous yellow oils (**6a–b**). The relative population of *E* and *Z* isomers were determined via their ^{1}H NMR spectra (Scheme 1) The characterization data of compounds (**6a–b**) is given below.

Dimethyl 2-(3,5-dimethyl-1H-pyrazol-1-yl)-2-butenedioate (6a)

Solidified colorless oil. IR (CCl_4) (ν_{max}, cm^{-1}): 2954 and 2931(C–H); 1743 (C=O, ester). ^{1}H NMR ($CDCl_3$) for Z-isomer (63%), δ_H : 2.12 and 2.24 (6 H, 2 s, 2 CH_3, pyrazole ring), 3.67 and 3.84 (6 H, 2 s, 2 OCH_3), 5.95 (1 H, s, CH=, pyrazole ring), 7.09 (1 H, s, CH=). ^{13}C NMR ($CDCl_3$) for Z-isomer, δ_C : 11.09 and 13.51 (2 CH_3 of pyrazole ring); 52.24 and 53.35 (2 OCH_3); 106.47 (CH= of pyrazole ring), 127.65 (CH=); 141.62, 148.85 and 150.33 (3 C), 163.17 and 163.22 (2C=O of esters).

^{1}H NMR ($CDCl_3$) for E-isomer (37%), δ_H : 2.18 and 2.43 (6 H, 2 s, 2 CH_3, pyrazole ring), 3.55 and 3.76 (6 H, 2 s, 2 OCH_3), 5.80 (1 H, s, CH=, pyrazole ring), 5.89 (1 H, s, CH=).

^{13}C NMR ($CDCl_3$) for E-isomer, δ_C : 10.97 and 13.66 (2 CH_3 of pyrazole ring); 52.61 and 52.90 (2 OCH_3); 105.73 (CH= of pyrazole ring), 128.41 (CH=); 141.23, 141.35 and 149.16 (3 C), 167.08 and 168.05 (2C=O of esters).

Diethyl-2-(3,5-dimethyl-1H-pyrazol-1-yl)-2-butenedioate (6b)

Solidified colorless oil. IR (CCl_4)(ν_{max}, cm^{-1}): 2977 and 2931(C–H); 1736 (C=O, ester). ^{1}H NMR ($CDCl_3$) for Z-isomer (30%), δ_H : 1.15 and 1.22 (6 H, 2 t, $^3J_{HH} = 7.1$ Hz, 2 CH_3 of 2 Et), 2.13 and 2.23 (6 H, 2 s, 2 CH_3, pyrazole ring), 4.11 and 4.22 (4 H, 2 q, $^3J_{HH} = 7.1$ Hz, 2 OCH_2 of 2 Et), 5.93 (1 H, s, CH=, pyrazole ring), 7.08 (1 H, s, CH=). ^{13}C NMR ($CDCl_3$) for Z-isomer, δ_C : 11.09 and 13.49 (2 CH_3 of pyrazole ring); 13.81 and 13.89 (2 CH_3 of 2 Et); 61.34 and 62.58 (2 OCH_2); 106.32 (CH= of pyrazole ring), 130.00 (CH=); 141.48, 148.69, and 150.04 (3 C), 162.65 and 163.00 (2C=O of esters).

^{1}H NMR ($CDCl_3$) for E-isomer (70%), δ_H : 1.05 and 1.31 (6 H, 2 t, $^3J_{HH} = 7.1$ Hz, 2 CH_3 of 2 Et), 2.19 and 2.42 (6 H, 2 s, 2 CH_3, pyrazole ring), 4.01 and 4.31 (4 H, 2 q, $^3J_{HH} = 7.1$ Hz, 2 OCH_2 of 2 Et), 5.79 (1 H, s, CH=, pyrazole ring), 5.89 (1 H, s, CH=). ^{13}C NMR ($CDCl_3$) for E-isomer, δ_C : 11.00 and 13.63 (2 CH_3 of pyrazole ring); 13.74 and 14.00 (2 CH_3 of 2 Et); 58.69 and 61.53 (2 OCH_2); 105.62 (CH= of pyrazole ring), 128.22 (CH=); 141.12, 141.32 and 148.91 (3 C), 166.68 and 167.53 (2C=O of esters).

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