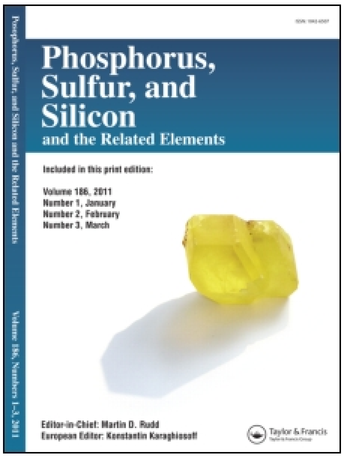

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Protonation of the highly reactive 1:1 intermediates, produced in a reaction between triphenylphosphine and dialkyl acetylenedicarboxylates, by 4-fluorophenol leads to vinyltriphenylphosphonium salts, which undergo a Michael addition reaction with a conjugate base to produce dialkyl 2-(4-fluoro-phenoxy)-3-(triphenylphosphoranylidene)butanedioates. Dipotassium hydrogen phosphate powder was found to catalyze the conversion of dialkyl 2-(4-fluoro-phenoxy)-3-(triphenylphosphoranylidene)butanedioates to dialkyl 2-(4-fluoro-phenoxy)-2-butenedioates in solvent-free conditions under microwave (0.5 KW, 3 min) and thermal (90°C, 60 min) conditions.

Keywords 4-fluorophenol; dipotassium hydrogen phosphate; Michael addition; acetylenic esters; vinyltriphenylphosphonium salt; microwave irradiation

INTRODUCTION

β-additions of nucleophiles to the vinyl group of vinylic phosphonium salts leading to the formation of new alkylidenephosphoranes have attracted much attention as a very convenient and synthetically useful method in organic synthesis.[1–3] Organophosphorus compounds have been extensively used in organic synthesis.[2] Silica gel as an additive promotes 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

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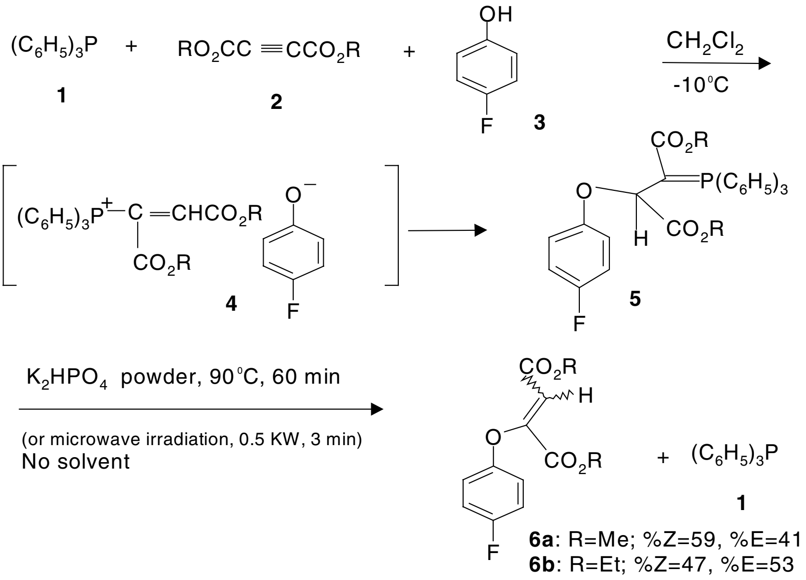

SCHEME 1

ylides utilizing in situ generation of phosphonium salts.[1,3] In this article, we report on the catalytic role of dipotassium hydrogen phosphate powder in the conversion of dialkyl 2-(4-fluoro-phenoxy)-3-(triphenylphosphoranylidene)butanedioates to dialkyl 2-(4-fluoro-phenoxy)-2-butenedioates in solvent-free conditions under microwave (0.5 KW, 3 min) and thermal (90°C, 60 min) conditions. (Scheme 1).

RESULTS AND DISCUSSION

The ylide (**5**) may result from an initial addition of triphenylphosphine **1** to acetylenic ester **2**, and the concomitant protonation of the 1:1 adduct by 4-fluorophenol leads to vinyltriphenylphosphonium salts **4**, which undergo a Michael addition reaction with a conjugate base to produce dialkyl 2-(4-fluoro-phenoxy)-3-(triphenylphosphoranylidene)butanedioates (**5**). TLC indicated formation of ylides **5** in CH_2Cl_2. Dipotassium hydrogen phosphate powder was found to catalyze the conversion of dialkyl 2-(4-fluoro-phenoxy)-3-(triphenylphosphoranylidene)butanedioates (**5**) to dialkyl 2-(4-fluoro-phenoxy)-2-butenedioates (**6**) in solvent-free conditions under microwave (0.5 KW, 3 min) and thermal (90°C, 60 min.) conditions. We have also used SiO_2, MgO, $MgSO_4$, NaH_2PO_4, Na_2HPO_4, $NaHCO_3$,

$NaHSO_4KH_2PO_4$, $CuSO_4$, and K_2CO_3 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 K_2HPO_4 powder, powdered ylide **5** was not reacted under microwave irradiation at microwave power 0.5 KW after 3 min or under thermal (90°C, 60 min) conditions, and decomposition of the starting materials was observed. Previously, other phenols (such as 4-bromophenol, 1-naphthol, and 2-naphthol) were used in a similar reaction, but in the all cases coumarins were observed.[1] High electronegativity of the fluorine atom may be a factor in the reaction.

CONCLUSION

In summary, we have found that K_2HPO_4 powder is able to catalyze stereoselective conversion of ylides **5** to compounds **6** in solvent-free conditions[6,7] (Scheme 1). Other aspects of this process are under investigation.

EXPERIMENTAL

Commerical-oven Butane M245 was used for microwave irradiation. IR spectra were recorded on a Shimadzu IR-460 spectrometer. Elemental analyses were performed using a Heraeus CHN-O-Rapid analyzer. ^1H, ^{19}F, and ^{13}C NMR spectra were measured with a BRUKER DRX-500 AVANCE spectrometer at 500, 470.6, and 125 MHz, respectively.

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 4-fluorophenol **3** (0.112 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**, 42%; yield for **6b**, 29%) for 90 min at 60°C (or irradiated in a microwave oven for 3 min at microwave power 0.5 KW; yield for **6a**, 40.5%; yield for **6b**, 27%) 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 new compounds (**6a–b**) follow.

Dimethyl 2-(4-fluoro-phenoxy)-2-butenedioate (6a)

Viscous yellow oil. IR(neat) (ν_{max}, cm^{-1}): 3084, 3015, 2961, 2853, 1734, and 1649. Found: C, 56.98; H, 4.69. $C_{12}H_{11}FO_5$ requires C, 56.70; H, 4.36%. ^{1}H NMR (CDCl$_3$) for *Z* isomer, δ_H: 3.73, and 3.75 (6H, 2s, 2OCH$_3$), 6.59 (1H, s, vinylic), 6.95 (2H, m, arom.), 7.10 (2H, d, $^3J_{HH} = 6.5$ Hz, arom.), 7.10 (2H, d, $^3J_{HH} = 6.5$ Hz, arom.). ^{13}C NMR (CDCl$_3$) for *Z* isomer, δ_C: 52.01 and 53.02 (2OCH$_3$), 115.06 (=CH, vinylic), 116.15 (1C, d, $^1J_{CF} = 23.5$ Hz, C—F), 117.53 (2C, d, $^2J_{CF} = 8.4$ Hz, C3 and C5), 149.86 (C2 and C6), 152.53 (C1, arom.), 159.76 (OC=, vinylic), 162.45 and 163.81 (2C=O, ester). ^{19}F NMR (CDCl$_3$) for *Z* isomer, δ_F: −120.54 (1F, s, CF). ^{1}H NMR (CDCl$_3$) for *E* isomer, δ_H: 3.68 and 3.93 (6H, 2s, 2OCH$_3$), 5.12 (1H, s, vinylic), 6.95 (2H, m, arom.), 7.10 (2H, d, $^3J_{HH} =$ 6.5 Hz, arom.), 7.10 (2H, d, $^3J_{HH} = 6.5$ Hz, arom.). ^{13}C NMR (CDCl$_3$) for *E* isomer, δ_C: 51.78 and 53.11 (2OCH$_3$), 98.99 (=CH, vinylic), 116.93 (1C, d, $^1J_{CF} = 23.5$ Hz, C—F), 122.40 (2C, d, $^2J_{CF} = 8.4$ Hz, C3 and C5), 149.74 (C2 and C6), 157.84 (C1, arom.), 159.48 (OC =, vinylic), 163.12 and 165.74 (2C=O, ester). ^{19}F NMR (CDCl$_3$) for *E* isomer, δ_F: −115.84 (1F, s, CF).

Diethyl-2-(4-fluoro-phenoxy)-2-butenedioate (6b)

Viscous yellow oil; IR(neat) (ν_{max}, cm^{-1}): 3077, 2985, 2939, 2908, 1727 and 1643. Found: C, 59.85; H, 5.62. $C_{12}H_{11}FO_5$ requires C, 59.57; H, 5.36%. ^{1}H NMR (CDCl$_3$) for *Z* isomer, δ_H: 1.18–1.24 (6H, m, 2CH$_3$ of 2Et), 4.15–4.24 (4H, m, 2OCH$_2$ of 2Et), 6.60 (1H, s, vinylic), 6.96 (2H, m, C3 and C5, arom.), 7.09 (2H, d, $^3J_{HH} = 6.2$ Hz, C2 and C6, arom.). ^{13}C NMR (CDCl$_3$) for *Z* isomer, δ_C: 14.02 and 14.04 (2CH$_3$ of 2Et), 60.67 and 62.45 (2OCH$_2$), 115.31 (=CH, vinylic), 116.12 (1C, d, $^1J_{CF} = 23.5$ Hz, C—F), 117.43 (2C, d, $^2J_{CF} = 8.6$ Hz, C3 and C5), 149.89 (C2 and C6), 150.00 (C1, arom.), 159.71 (OC=, vinylic), 162.70 and 163.34 (2C=O, ester). ^{19}F NMR (CDCl$_3$) for *Z* isomer, δ_F: −120.85 (1F, s, CF).

^{1}H NMR (CDCl$_3$) for *E* isomer, δ_H: 1.23 and 1.37 (6H, 2t, $^3J_{HH} =$ 7.2 Hz, 2CH$_3$ of 2Et), 4.17 (2H, m, OCH$_2$), 4.38 (2H, q, $^3J_{HH} = 7.1$ Hz, OCH$_2$); 5.11 (1H, s, vinylic), 6.96 (2H, m, C3 and C5, arom.), 7.09 (2H, d, $^3J_{HH} = 6.2$ Hz, C2 and C6, arom.). ^{13}C NMR (CDCl$_3$) for *E* isomer, δ_C: 13.85 and 14.10 (2CH$_3$ of 2Et), 61.04 and 62.31 (2OCH$_2$), 99.37 (=CH, vinylic), 116.78 (1C, d, $^1J_{CF} = 23.6$ Hz, C—F), 122.47 (2C, d, $^2J_{CF} =$ 8.7 Hz, C3 and C5), 149.55 (C2 and C6), 152.66 (C1, arom.), 159.46

(OC=, vinylic), 162.55 and 165.23 (2C=O, ester). ^{19}F NMR ($CDCl_3$) for *E* isomer, δ_F: -116.24 (1F, s, CF).

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