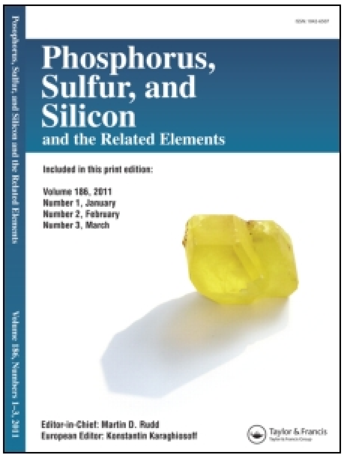

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Protonation of highly reactive 1:1 intermediates, produced in the reaction between triphenylphosphine and dialkyl acetylenedicarboxylates, by phenols leads to vinyltriphenylphosphonium salts, which undergo Michael addition reaction with a conjugate base to produce corresponding stabilized phosphorus ylides. Dipotassium hydrogen phosphate powder was found to catalyze the conversion of stabilized phosphorus ylides to electron-poor O*-vinyl ethers in solvent-free conditions under microwave (0.6 KW, 3 min) and thermal (100 °C, 60 min) conditions. Relative population of* E *and* Z *isomers of electron-poor* O*-vinyl ethers was determined via their* ^{1}*H NMR spectra.*

Keywords Acetylenic esters; dipotassium hydrogen phosphate; electron-poor *O*-vinyl ether; 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 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

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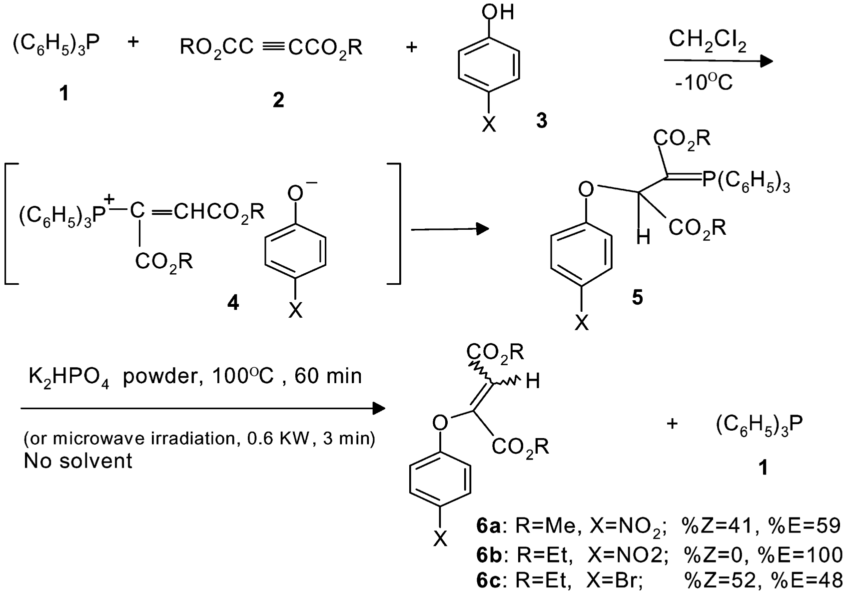
method for preparing stabilized phosphorus ylides utilizing in situ generation of the phosphonium salts.[1,3] In this article, we report on the catalytic role of dipotassium hydrogen phosphate powder in the conversion of stabilized phosphorus ylides to electron-poor *O*-vinyl ethers in solvent-free conditions under microwave (0.6 KW, 3 min) and thermal (100°C, 60 min) conditions (Scheme 1).



SCHEME 1

RESULTS AND DISCUSSION

Ylide (**5**) may result from an initial addition of triphenylphosphine **1** to acetylenic ester **2**, and concomitant protonation of 1:1 adduct by phenols **3** leads to vinyltriphenylphosphonium salts **4**, which undergo Michael addition reaction with a conjugate base to produce corresponding stabilized phosphorus ylides (**5**). TLC indicated the formation of ylides **5** in CH_2Cl_2. Dipotassium hydrogen phosphate powder was found to catalyze the conversion of stabilized phosphorus ylides (**5**) to electron-poor *O*-vinyl ethers (**6**) in solvent-free conditions[6,7] under microwave (0.6 KW, 3 min) and thermal (100°C, 60 min) conditions. Relative population of *E* and *Z* isomers of electron-poor *O*-vinyl ethers (**6**) were determined via their ^1H NMR spectra (See Experimental section). We have also used K_2HPO_4 in this reaction at r.t. in solvent-free conditions but the yield of products **6a** and **6b** were very low, and only in the case of **6c** the reaction was completed in 60 min. In the absence of 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 (100°C, 60 min) conditions, and decomposition of the starting materials was observed. Previously, other phenols (such as 1-naphthol and 2-naphthol) were used in a similar reaction but in all cases coumarins were observed.[7] It seems that in the present work, poor electron density on the aromatic ring is an important factor in the conduction of the reaction to form of electron-poor *O*-vinyl ethers (**6**) instead of coumarins.[7]

CONCLUSION

In summary, we have found that dipotassium hydrogen phosphate 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 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 Ylides 5 and Compounds 6a–c

To a magnetically stirred solution of triphenylphosphine **1** (0.262 g, 1 mmol) and phenol **3** (1 mmol) in CH_2Cl_2 (3 mL) was added dropwise a mixture of **2** (1 mmol) in CH_2Cl_2 (4 mL) at −10°C over 15 min. The mixture was allowed to warm up to r.t. Dipotassium hydrogen phosphate powder (1.0 g) was added, and the solvent was evaporated. Dry dipotassium hydrogen phosphate and the residue were heated (yield for **6a**, 42%; yield for **6b**, 39%; yield for **6c**, 68%) for 60 min at 100°C (or irradiated in a microwave oven for 3 min at microwave power 0.6 KW; yield for **6a**, 40%; yield for **6b**, 41%; yield for **6c**, 65%) 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 the eluent. The solvent was removed under reduced pressure, and products were obtained as viscous yellow oils (**6a–c**). Relative population of *E* and Z isomers were determined via their ^{1}H NMR spectra (Scheme 1). The characterization data of the new compounds (**6a–c**) follow.

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

Viscous yellow oil. IR(neat) (ν_{max}, cm^{-1}): 3092, 2961, 2860, 1734 and 1649. Found: 51.36; H, 3.86; N, 4.87. $C_{12}H_{11}NO_7$ requires C, 51.25; H, 3.94; N, 4.98%. ^{1}H NMR (CDCl$_3$) for Z isomer, δ_H: 3.73, and 3.81 (6H, 2s, 2OCH$_3$), 6.80 (1H, s, vinylic), 7.04 (2H, d, $^3J_{HH} = 9.1$ Hz, arom.), 8.23 (2H, d, $^3J_{HH} = 9.1$ Hz, arom.). ^{13}C NMR (CDCl$_3$) for Z isomer, δ_C: 52.32 and 53.43 (2OCH$_3$), 115.63 (=CH, vinylic), 117.52, 125.96, 145.14, and 161.50 (4 C, arom.), 156.40 (O—C=), 161.79 and 163.23 (2C=O, ester).

^{1}H NMR (CDCl$_3$) for E isomer, δ_H: 3.75, and 3.89 (6H, 2s, 2OCH$_3$), 5.54 (1H, s, vinylic), 7.26 (2H, d, $^3J_{HH} = 9.0$ Hz, arom.), 8.30 (2H, d, $^3J_{HH} = 9.0$ Hz, arom.). ^{13}C NMR (CDCl$_3$) for E isomer, δ_C: 52.22 and 53.31 (2OCH$_3$), 116.08 (=CH, vinylic), 120.27, 126.12, 148.37 and 161.35 (4 C, arom.), 158.58 (O—C=), 162.2 and 164.97 (2C=O, ester).

Diethyl (E)-2-(4-Nitro-phenoxy)-2-butenedioate (6b)

Viscous yellow oil. IR(neat) (ν_{max}, cm^{-1}): 3155, 2962, 2931, 1720 and 1643. Found: 54.47; H, 4.78; N, 4.61. $C_{14}H_{15}NO_7$ requires C, 54.37; H, 4.89; N, 4.53%. ^{1}H NMR (CDCl$_3$), δ_H: 1.27 and 1.32 (6H, 2t, $^3J_{HH} = 7.1$ Hz, 2CH$_3$ of 2Et); 4.21 and 4.33 (4H, 2q, $^3J_{HH} = 7.1$ Hz, 2 OCH$_2$ of 2Et); 5.53 (1H, s, vinylic), 7.26 (2H, d, $^3J_{HH} = 9.0$ Hz, arom.), 8.29 (2H, d, $^3J_{HH} = 9.0$ Hz, arom.). ^{13}C NMR (CDCl$_3$), δ_C: 13.83 and 14.07 (2CH$_3$ of 2Et), 61.21 and 62.69 (2OCH$_2$), 106.13 (=CH, vinylic), 120.25, 126.05, 145.02 and 158.78 (4 C, arom.), 156.18 (O—C=), 161.73 and 164.41 (2C=O, ester).

Diethyl 2-(4-Bromo-phenoxy)-2-butenedioate (6c)

Viscous yellow oil; IR(neat) (ν_{max}, cm^{-1}): 2923, 2854, 1720 and 1643. Found: C, 49.12; H, 4.32; $C_{14}H_{15}BrO_5$ requires C, 49.00; H, 4.41%. ^{1}H NMR (CDCl$_3$) for Z isomer, δ_H: 1.19–1.23 (6H, m, 2CH$_3$ of 2Et), 4.14–4.23 (4H, m, 2OCH$_2$ of 2Et), 6.63 (1H, s, vinylic), 6.86 (2H, d, $^3J_{HH} = 8.8$ Hz, arom.), 7.43 (2H, d, $^3J_{HH} = 8.8$ Hz, arom.). ^{13}C NMR (CDCl$_3$) for Z isomer, δ_C: 13.92 and 14.05 (2CH$_3$ of 2Et), 61.10 and 62.44 (2OCH$_2$), 116.05 (=CH, vinylic), 115.84, 117.96, 132.51 and 152.22 (4 C, arom.), 155.87 (O—C=), 162.50 and 163.23 (2 C=O, ester).

^{1}H NMR (CDCl$_3$) for E isomer, δ_H: 1.19–1.23 (3 H, m, CH$_3$ of Et), 1.37 (3 H, t, $^3J_{HH} = 7.1$ Hz, CH$_3$ of Et) 4.20 (2H, m, OCH$_2$ of Et), 4.38 (2 H, q, ${}^3J_{HH} = 7.1$ Hz, OCH_2 of Et); 5.17 (1H, s, vinylic), 7.03 (2H, d, ${}^3J_{HH} =$ 8.7 Hz, arom.), 7.52 (2H, d, ${}^3J = 8.7$ Hz, arom.). ${}^{13}C$ NMR ($CDCl_3$) for E isomer, δ_C: 13.87 and 14.11 (2 CH_3 of 2 Et), 60.77 and 62.52 (2 OCH_2), 100.25 (=CH, vinylic), 117.23, 122.65, 133.27 and 149.14 (4 C, arom.), 160.04 (O—C=), 162.58 and 165.13 (2 C=O, ester).

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