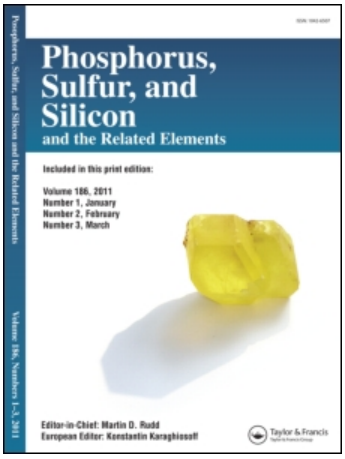

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Stereoselective Conversion of Stabilized Phosphorus Ylides to Dialkyl 2-(2-Nitro-phenoxy)-2-butenedioates in the Presense of Silica Gel in Solvent-Free Conditions

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

Keywords 2-nitrophenol; acetylenic esters; Michael addition; microwave irradiation; silica gel; vinyltriphenylphosphonium salt

INTRODUCTION

Organophosphorus compounds have been extensively used in organic synthesis.[1,2] 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] 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

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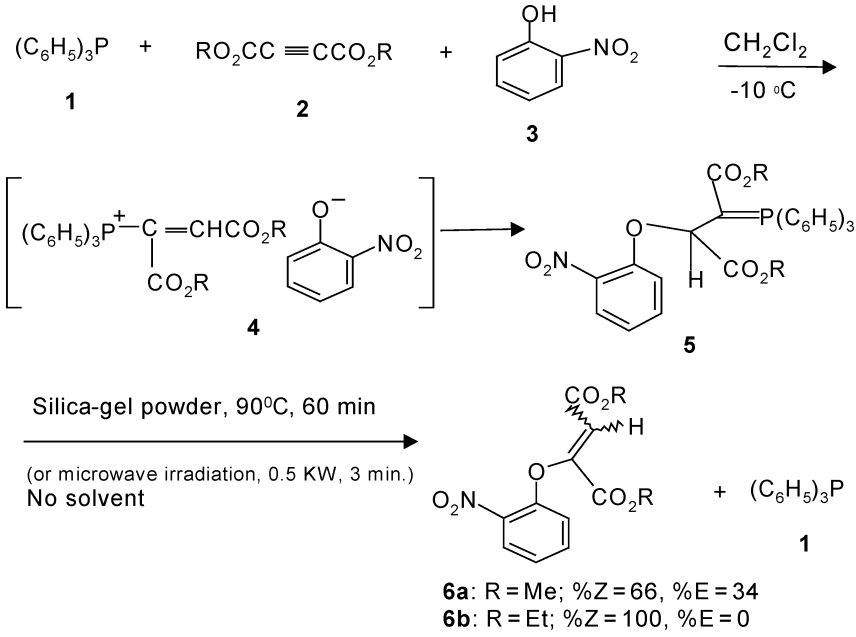
on the catalytic role of silica-gel powder in the stereoselective conversion of dialkyl 2-(2-nitro-phenoxy)-3-(triphenylphosphoranylidene)-butanedioates to dialkyl 2-(2-nitro-phenoxy)-2-butenedioates in solvent-free conditions under microwave (0.5 KW, 3 min) and thermal (90°C, 60 min) conditions Scheme 1.



SCHEME 1

RESULTS AND DISCUSSION

The ylide (**5**) may result from an initial addition of triphenylphosphine **1** to the acetylenic ester **2** and concomitant protonation of the 1:1 adduct by 2-nitrophenol, which leads to vinyltriphenylphosphonium salts **4**, which undergo a Michael addition reaction with a conjugate base to produce dialkyl 2-(2-nitro-phenoxy)-3-(triphenylphosphoranylidene)butanedioates (**5**). TLC indicated the formation of ylides **5** in CH_2Cl_2. Silica-gel powder was found to catalyze the stereoselective conversion of dialkyl 2-(2-nitro-phenoxy)-3-(triphenylphosphoranylidene)butanedioates (**5**) to dialkyl 2-(2-nitro-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 MgO, NaH_2PO_4, Na_2HPO_4, Na_3PO_4, KH_2PO_4, K_2HPO_4, K_3PO_4, and K_2CO_3

in this reaction, but no product was observed, and in all cases, decomposition was observed. In the absence of silica-gel powder, the 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 were observed.

CONCLUSION

In conclusion, we have found that silica gel powder is able to catalyze the stereoselective conversion of ylides **5** to compounds **6**[7] in solvent-free conditions[6] (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. ^{1}H 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 2-nitrophenol **3** (0.139 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. Silica-gel powder (1.5 g) was added, and the solvent was evaporated. Dry silica gel and the residue were heated (yield for **6a**, 37.3%; yield for **6b**, 31.5%) for 90 min at 60°C (or irradiated in a microwave oven for 3 min at a microwave power of 0.5 KW; yield for **6a**, 36%; yield for **6b**, 33%) 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 aneluent. The solvent was removed under reduced pressure, and products were obtained as colorless viscous 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 the compounds (**6a–b**) are given below.

Dimethyl 2-(2-nitro-phenoxy)-2-butenedioate (6a)

Viscous yellow oil. IR(neat) (ν_{max}, cm^{-1}): 3092, 2961, 2860, 1742, 1665 and 1611. ^{1}H NMR ($CDCl_3$) for *Z* isomer, δ_H: 3.72, and 3.78 (6H, 2s,

$2OCH_3$), 6.74 (1H, s, vinylic), 6.98 (1H, d, $^3J_{HH} = 8.2$ Hz, arom.), 7.21 (1H, t, $^3J_{HH} = 7.8$ Hz, arom.), 7.51 (1H, t, $^3J_{HH} = 7.9$ Hz, arom.), 7.99 (1H, d, $^3J_{HH} = 8.1$ Hz, arom.). ^{13}C NMR ($CDCl_3$) for *Z* isomer, δ_C: 52.26 and 53.39 ($2OCH_3$), 116.65 (=CH, vinylic), 117.62, 123.50, 126.07 and 134.18 (4CH, arom.), 139.96 and 148.49 (2C, arom.), 149.90 (OC =, vinylic), 161.67 and 163.26 (2C = O, ester).

^{1}H NMR ($CDCl_3$) for *E* isomer, δ_H: 3.71, and 3.92 (6H, 2s, $2OCH_3$), 5.26 (1H, s, vinylic), 7.32 (1H, d, $^3J_{HH} = 8.2$ Hz, arom.), 7.44 (1H, t, $^3J_{HH} = 7.8$ Hz, arom.), 7.69 (1H, t, $^3J_{HH} = 7.5$ Hz, arom.), 8.07 (1H, d, $^3J_{HH} = 8.1$ Hz, arom.). ^{13}C NMR ($CDCl_3$) for *E* isomer, δ_C:52.05 and 53.30 ($2OCH_3$), 102.10 (=CH, vinylic), 126.99, 123.76, 126.29 and 134.99 (4CH, arom.), 141.76 and 146.05 (2C, arom.), 158.21 (OC =, vinylic), 162.19 and 165.03 (2C = O, ester).

Diethyl (Z)-2-(2-nitro-phenoxy)-2-butenedioate (6b)

Viscous yellow oil; IR(neat) (ν_{max}, cm^{-1}): 3085, 2923, 2854, 1727, 1658 and 1596. ^{1}H NMR ($CDCl_3$) δ_H: 1.14–1.24 (6H, m, $2CH_3$ of 2Et), 4.15–4.24 (4H, m, $2OCH_2$ of 2Et), 6.74 (1H, s, vinylic), 6.98 (1H, d, $^3J_{HH} = 8.3$ Hz, arom.), 7.19 (1H, t, $^3J_{HH} = 7.8$ Hz, arom.), 7.50 (1H, t, $^3J_{HH} = 7.9$ Hz, arom.), 7.98 (1H, d, $^3J_{HH} = 8.2$ Hz, arom.). ^{13}C NMR ($CDCl_3$) δ_C: 13.88 and 13.99 ($2CH_3$ of 2Et), 61.37 and 62.74 ($2OCH_2$), 117.14 (=CH, vinylic), 117.62, 123.35, 126.03 and 134.12 (4CH, arom.), 139.98 and 148.46 (2C, arom.), 150.07 (OC =, vinylic), 161.20 and 162.97 (2C = O, ester).

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