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Ali Ramazani ^a & Mahshid Rahimifard ^a ^a Chemistry Department, Zanjan University, Zanjan, Iran Published online: 01 Feb 2007.

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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

Ali Ramazani Mahshid Rahimifard Chemistry Department, Zanjan University, Zanjan, Iran

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)-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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Address correspondence to Ali Ramazani, Zanjan University, Chemistry Department, PO Box 45195-313, Zanjan, Iran. E-mail: aliramazani@gmail.com

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 CH₂Cl₂. 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)-2butenedioates (6) in solvent-free conditions under microwave (0.5 KW, $3 \min$) and thermal (90°C, 60 min) conditions. We have also used MgO, NaH₂PO₄, Na₂HPO₄, Na₃PO₄, KH₂PO₄, K₂HPO₄, K₃PO₄, and K₂CO₃ 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 solventfree conditions⁶ (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. ¹H and ¹³C 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 $-10^{\circ}C$ 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 ¹H 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. ¹H NMR (CDCl₃) for Z isomer, δ_{H} : 3.72, and 3.78 (6H, 2s,

20CH₃), 6.74 (1H, s, vinylic), 6.98 (1H, d, ${}^{3}J_{\rm HH} = 8.2$ Hz, arom.), 7.21 (1H, t, ${}^{3}J_{\rm HH} = 7.8$ Hz, arom.), 7.51 (1H, t, ${}^{3}J_{\rm HH} = 7.9$ Hz, arom.), 7.99 (1H, d, ${}^{3}J_{\rm HH} = 8.1$ Hz, arom.). 13 C NMR (CDCl₃) for Z isomer, $\delta_{\rm C}$: 52.26 and 53.39 (20CH₃), 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).

¹H NMR (CDCl₃) for *E* isomer, $\delta_{\rm H}$: 3.71, and 3.92 (6H, 2s, 2OCH₃), 5.26 (1H, s, vinylic), 7.32 (1H, d, ³ $J_{\rm HH}$ = 8.2 Hz, arom.), 7.44 (1H, t, ³ $J_{\rm HH}$ = 7.8 Hz, arom.), 7.69 (1H, t, ³ $J_{\rm HH}$ = 7.5 Hz, arom.), 8.07 (1H, d, ³ $J_{\rm HH}$ = 8.1 Hz, arom.). ¹³C NMR (CDCl₃) for *E* isomer, $\delta_{\rm C}$:52.05 and 53.30 (2OCH₃), 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. ¹H NMR (CDCl₃) $\delta_{\rm H}$: 1.14–1.24 (6H, m, 2CH₃ of 2Et), 4.15–4.24 (4H, m, 2OCH₂ of 2Et), 6.74 (1H, s, vinylic), 6.98 (1H, d, ³ $J_{\rm HH} = 8.3$ Hz, arom.), 7.19 (1H, t, ³ $J_{\rm HH} = 7.8$ Hz, arom.), 7.50 (1H, t, ³ $J_{\rm HH} = 7.9$ Hz, arom.), 7.98 (1H, d, ³ $J_{\rm HH} = 8.2$ Hz, arom.). ¹³C NMR (CDCl₃) $\delta_{\rm C}$: 13.88 and 13.99 (2CH₃ of 2Et), 61.37 and 62.74 (2OCH₂), 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 = 0, ester).

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