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Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713618290>

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To cite this Article Ramazani, Ali , Rahimifard, Mahshid and Souldozi, Ali(2007) 'Silica-Gel Catalyzed Stereoselective Conversion of Stabilized Phosphorus Ylides to Dialkyl (*Z*)-2-(2-Methoxycarbonyl-phenoxy)-2-butenedioates in Solvent-Free Conditions', Phosphorus, Sulfur, and Silicon and the Related Elements, 182: 1, 1 — 5

To link to this Article: DOI: 10.1080/10426500600961571

URL: <http://dx.doi.org/10.1080/10426500600961571>

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Silica-Gel Catalyzed Stereoselective Conversion of Stabilized Phosphorus Ylides to Dialkyl (Z)-2-(2-Methoxycarbonyl-phenoxy)-2-butenedioates 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 methyl salicylate leads to vinyltriphenylphosphonium salts, which undergo a Michael addition reaction with a conjugate base to produce dialkyl 2-(2-methoxycarbonyl-phenoxy)-3-(triphenylphosphoranylidene)butanedioates. Silica-gel powder was found to catalyze the stereoselective conversion of dialkyl 2-(2-methoxycarbonyl-phenoxy)-3-(triphenylphosphoranylidene)butanedioates to dialkyl (Z)-2-(2-methoxycarbonyl-phenoxy)-2-butenedioates in solvent-free conditions under microwave (0.5 KW, 3 min) and thermal (90°C, 90 min) conditions.

Keywords Acetylenic esters; methyl salicylate; Michael addition; microwave irradiation; silica gel; vinyltriphenylphosphonium salt

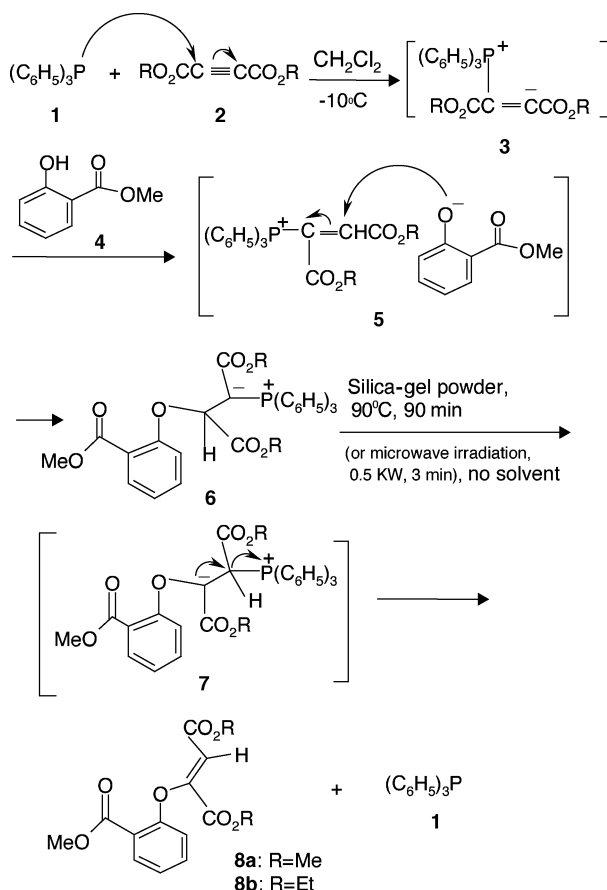
INTRODUCTION

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 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

Received December 30, 2005; accepted March 13, 2006.

This work was supported by the Sandoogh Hemayat as Pajuooheshgharane Keshvare Iran via the research project number N 84114.

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SCHEME 1

established a convenient, one-pot method for preparing stabilized phosphorus ylides utilizing in situ generation of phosphonium salts.^{1,3} In this article, we report on the catalytic role of silica-gel powder in the stereoselective conversion of dialkyl 2-(2-methoxycarbonylphenoxy)-3-(triphenylphosphoranylidene)butanedioates to dialkyl (*Z*)-2-(2-methoxycarbonylphenoxy)-2-butenedioates in solvent-free conditions under microwave (0.5 KW, 3 min) and thermal (90°C, 90 min) conditions (Scheme 1).

RESULTS AND DISCUSSION

Ylide (**6**) may result from an initial addition of triphenylphosphine **1** to the acetylenic ester **2** and concomitant protonation of the 1:1

adduct **3** by methyl salisylate **4**, which leads to vinyltriphenylphosphonium salts **5**, which undergo a Michael addition reaction with a conjugate base to produce dialkyl 2-(2-methoxycarbonyl-phenoxy)-3-(triphenylphosphoranylidene)butanedioates (**6**). TLC indicated the formation of ylides **6** in CH_2Cl_2 . Silica-gel powder was found to catalyze the stereoselective conversion of dialkyl 2-(2-methoxycarbonyl-phenoxy)-3-(triphenylphosphoranylidene)butanedioates (**6**) (In order to characterize these ylides, we tried to isolate them in pure form, but because of the inclusion of solvents molecules in the among of stabilized ylides molecules, the efforts were unsuccessful, and in each case highly viscous oil or impure powder was obtained.) to dialkyl (*Z*)-2-(2-methoxycarbonyl-phenoxy)-2-butenedioates (**8**) and triphenylphosphine (**1**) [This compound was detected via TLC and also was isolated via column chromatography. The number of mmoles of recovered triphenylphosphine (**1**) is approximately equal with the number of mmoles of products **8** in each cases.] in solvent-free conditions under microwave (0.5 KW, 3 min) and thermal (90°C, 90 min) conditions. The conversion of **6** to **8** may be passed via intermediate **7**. In this conversion the silica-gel surface may act as a general acid–base catalyst. We have also used MgO , MgSO_4 , Al_2O_3 , $\text{Al}_2(\text{SO}_4)_3$, $\text{KAl}(\text{SO}_4)_2$, NaH_2PO_4 , Na_2HPO_4 , Na_3PO_4 , KH_2PO_4 , K_3PO_4 , NaHCO_3 , and NaSO_4 in this reaction, but no product was observed, and in all cases decomposition (conversion to highly polar and black color materials that was checked via TLC) was observed. In the absence of the silica-gel powder, the ylide **5** did not react under microwave irradiation at 0.5 KW after 3 min or under thermal (90°C, 90 min) conditions, and decomposition (conversion to highly polar and black color materials that was checked via TLC) of the starting materials was observed.

CONCLUSION

In summary, we have found that silica-gel powder is able to catalyze the stereoselective conversion of ylides **6** to compounds **8** in solvent-free conditions⁶ (Scheme 1). The solvent-free nature and new chemistry of the present procedure makes it an interesting alternative to previous reports.^{7–10} 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. Mass spectra were recorded

on a Finnigan-Matt 8430 mass spectrometer operating at an ionization potential of 70 eV.

General Procedure for the Preparation of Ylides **6** and Compounds **8a–b**

To a magnetically stirred solution of triphenylphosphine **1** (0.262 g, 1 mmol) and methyl salisylate **4** (0.152 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 **8a**, 31%; yield for **8b**, 28%) for 90 min at 90°C (or irradiated in a microwave oven for 3 min at 0.5 KW; yield for **8a**, 35%; yield for **8b**, 29%) 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 colorless viscous oils (**8a–b**). The characterization data of the compounds (**8a–b**) is given in the following section.

Dimethyl (Z)-2-(2-methoxycarbonyl-phenoxy)-2-butenedioate (8a)

Colorless viscous oil. IR(neat) (ν_{max} , cm^{-1}): 3084, 2930, 2860, 1742, 1657 and 1611. ^1H NMR (CDCl_3) δ_{H} : 3.68, 3.74 and 3.90 (9H, 3s, 3OCH_3), 6.61 (1H, s, vinylic), 6.86 (1H, d, $^3J_{\text{HH}} = 8.2$ Hz, arom), 7.13 (1H, t, $^3J_{\text{HH}} = 7.6$ Hz, arom), 7.42 (1H, t, $^3J_{\text{HH}} = 7.8$ Hz, arom), 7.91 (1H, d, $^3J_{\text{HH}} = 7.8$ Hz, arom). ^{13}C NMR (CDCl_3) δ_{C} : 51.98, 52.19 and 53.10 (3OCH_3), 114.39 ($=\text{CH}$, vinylic), 116.69, 121.02, 123.27 and 132.07 (4CH, arom), 133.36 and 149.67 (2C, arom), 155.94 ($\text{OC}=\text{}$, vinylic), 162.32 and 163.77 and 165.63 ($3\text{C}=\text{O}$, ester). MS(m/z): 294 (M^+), 263; 235; 176; 77.

Diethyl (Z)-2-(2-methoxycarbonyl-phenoxy)-2-butenedioate (8b)

Colorless viscous oil; IR(neat) (ν_{max} , cm^{-1}): 3084, 2930, 2860, 1734, 1657 and 1611. ^1H NMR (CDCl_3) δ_{H} : 1.16 and 1.20 (6H, 2t, $^3J_{\text{HH}} = 7.2$ Hz, 2CH_3 of 2Et), 3.90 (3H, s, OCH_3); 4.15–4.24 (4H, m, 2OCH_2 of 2Et), 6.61 (1H, s, vinylic), 6.87 (1H, d, $^3J_{\text{HH}} = 8.2$ Hz, arom), 7.13 (1H, t, $^3J_{\text{HH}} = 7.6$ Hz, arom), 7.40 (1H, t, $^3J_{\text{HH}} = 7.8$ Hz, arom), 7.91 (1H, d, $^3J_{\text{HH}} = 7.8$ Hz, arom). ^{13}C NMR (CDCl_3) δ_{C} : 13.83 and 13.98 (2CH_3 of 2Et), 52.13 (OCH_3); 60.94 and 60.29 (2OCH_2), 114.87 ($=\text{CH}$, vinylic), 116.64, 121.05, 123.08 and 132.02 (4CH, arom), 133.25 and 149.70 (2C,

arom), 156.06 (OC=, vinylic), 161.82, 163.44 and 165.71 (2C=O, ester). MS(m/z): 322 (M⁺), 277; 249; 77.

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