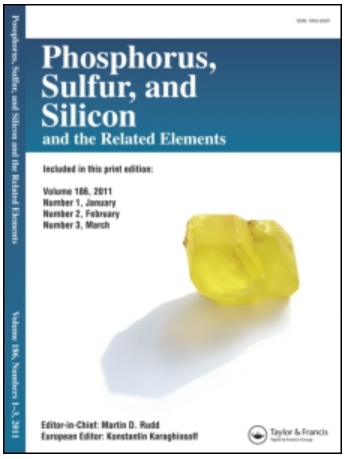

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

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To cite this Article Ramazani, Ali and Ahmadi, Ebrahim(2006) 'Microwave-Induced Conversion of Stabilized Phosphorus Ylides to Electron-Poor 2**H**-Cheromenes in the Presence of Silica Gel Powder in Solvent-Free Conditions', Phosphorus, Sulfur, and Silicon and the Related Elements, 181: 12, 2725 — 2729
To link to this Article: DOI: 10.1080/10426500600864395
URL: http://dx.doi.org/10.1080/10426500600864395

Phosphorus, Sulfur, and Silicon, 181:2725–2729, 2006

ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426500600864395

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Microwave-Induced Conversion of Stabilized Phosphorus Ylides to Electron-Poor 2*H*-Cheromenes in the Presence of Silica Gel Powder 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 cyclohexan-1,3-diones leads to vinyltriphenylphosphonium salts, which undergo a Michael addition reaction with a conjugate base to produce stabilized phosphorus ylides. Silica-gel powder was found to catalyze the conversion of the stabilized phosphorus ylides to corresponding electron-poor 2H-chromenes under solvent-free conditions under microwave irradiation (0.72 KW, 9 min) or thermal conditions (95°C, 45 min) in fairly good yields.

Keywords Acetylenic esters; cyclohexan-1,3-diones; 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 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.[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 the in situ generation of the phosphonium salts.[1,3] In this article, we report on the catalytic role of silica-gel powder in the conversion of stabilized phosphorus ylides to corresponding electron-poor 2*H*-chromenes under

Received April 6, 2006; accepted June 6, 2006.
This work was supported by the Sandoogh Hemayate as Pajuoheshgharane Keshvare Iran via the research project number N 84114.
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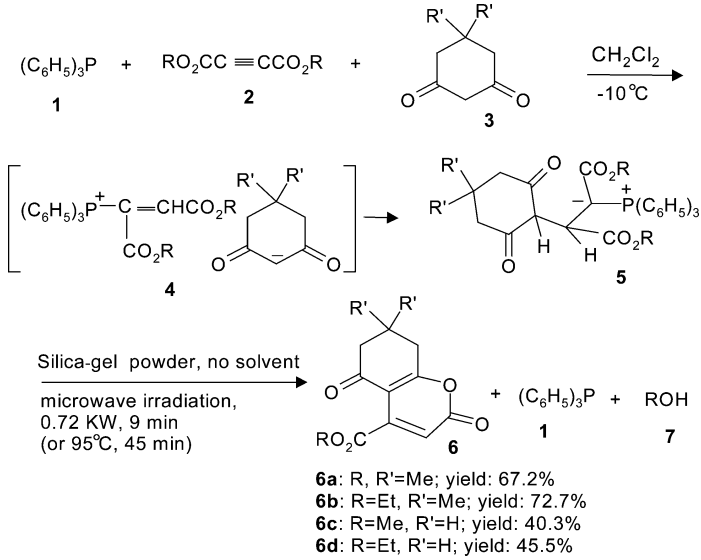
solvent-free conditions under microwave irradiation (0.72 KW, 9 min) or thermal conditions (95°C, 45 min) in fairly good yields (Scheme 1).



SCHEME 1

RESULTS AND DISCUSSION

The ylide (**5**) may result from an initial addition of triphenylphosphine **1** to the acetylenic ester **2**, and the concomitant protonation of the 1:1 adduct by cyclohexan-1,3-diones leads to vinyltriphenylphosphonium salts **4**, which undergo a Michael addition reaction with a conjugate base to produce stabilized phosphorus ylides (**5**). TLC indicated the formation of ylides **5** in CH_2Cl_2. Silica-gel powder was found to catalyze the conversion of stabilized phosphorus ylides (**5**) to corresponding electron-poor 2*H*-chromenes (**6**) in solvent-free conditions under microwave irradiation (0.72 KW, 9 min) or thermal conditions (95°C, 45 min) in fairly good yields. In the absence of silica-gel powder, the ylides **5** were not reacted under microwave irradiation or thermal conditions, and decomposition of the starting materials was observed.

CONCLUSION

In summary, we have found that silica-gel powder is able to catalyze the conversion of the ylides 5 to corresponding electron-poor 2*H*-chromenes (**6**) in solvent-free conditions[6,7] in fairly good yields (Scheme 1). Other aspects of this process are under investigation.

EXPERIMENTAL

Melting points were measured on an Electrothermal 9100 apparatus and are uncorrected. Elemental analyses were performed using a Heraeus CHN-O-rapid analyzer. 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. 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 5 and Compounds 6a–d

To a magnetically stirred solution of triphenylphosphine **1** (1 mmol) and **3** (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 powder and the residue were irradiated in a microwave oven for 9 min at microwave power 0.72 KW (or were heated under thermal conditions, 95°C, 45 min) 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 (**6a–d**) (Scheme 1). The characterization data of the compounds (**6a–d**) are given in the following section.

Methyl 7,7-Dimethyl-2,5-dioxo-5,6,7,8-tetrahydro-2*H*-chromene-4-carboxylate (6a)

White crystals, m.p. 92.7–94.2°C. Yield: 67.2%. UV(CH_2Cl_2) ($\lambda_{max\,/nm}$, $\log\varepsilon$): 213.0, 4.05; 263.0, 4.32. IR(KBr)(ν_{max}, cm^{-1}): 3084(CH, Vinyl); 2968(CH, Aliphatic); 1773, 1740 and 1680(C=O, Carbonyl). ^{1}H NMR ($CDCl_3$) δ_H: 1.15($2CH_3$, s, $C(CH_3)_2$); 2.43($1CH_2$, s, 1 alpha –C=C); 2.74($1CH_2$, s, 1 alpha –COC=C); 3.92($1CH_3$, s, OCH_3); 6.17(1H, s, ethylene). ^{13}C NMR ($CDCl_3$) δ_C: 28.24($2CH_3$, Aliphatic, $C(CH_3)_2$); 32.55(1C, Aliphatic, $C(CH_3)_2$); 42.15($1CH_2$, Aliphatic, 1 alpha –C=C); 50.63($1CH_2$, 1 alpha –COC=C); 53.20($1CH_3$, Aliphatic, OCH_3); 111.43, 145.70 and 159.1(3C, ethylene); 111.91(1CH, ethylene); 165.85, 174.04 and 192.41(3C, Carbonyl). MS(m/z, %) 249.5(M^+, 39); 194.2(100); 166.1(23); 92.9(3). Found: C, 62.95; H, 5.79. $C_{13}H_{14}O_5$ requires C, 62.40; H, 5.64%.

Ethyl 7,7-Dimethyl-2,5-dioxo-5,6,7,8-tetrahydro-2*H*-chromene-4-carboxylate (6b)

Viscous colorless oil. Yield: 72.66% UV(CH_2Cl_2)($\lambda_{max/nm}$, log ε): 212.0, 3.16; 264, 4.36.^{1}H NMR ($CDCl_3$) δ_H: 1.16(2CH_3, s, C(CH_3)$_2$); 1.37(1CH_3, t,$^3J_{HH}$ = 7.15, CH_3CH_2O); 2.44 (1CH_2, s, 1 alpha —C=C); 2.75(1CH_2, s, 1 alpha —COC=C); 4.40(1CH_2, q,$^3J_{HH}$ = 7.15, CH_3CH_2O); 6.18(1H, s, ethylene).^{13}C NMR ($CDCl_3$) δ_C: 14.09(1CH_3, Aliphatic, CH_3CH_2O); 28.27(2CH_3, Aliphatic, C(CH_3)$_2$); 32.59(1C, Aliphatic, C(CH_3)$_2$); 42.16(1CH_2, Aliphatic, 1 alpha —C=C); 50.67(1CH_2, 1 alpha —COC=C); 62.65(1CH_2, Aliphatic, CH_3CH_2O); 111.47, 146.08 and 159.22(3C, ethylene), 111.82(1CH, ethylene); 165.42, 174.00 and 192.41(3C, Carbonyl). Found: C, 63.89; H, 5.97. $C_{14}H_{16}O_5$ requires C, 63.63; H, 6.10%.

Methyl 2,5-Dioxo-5,6,7,8-tetrahydro-2*H*-chromene-4-carboxylate (6c)

White crystals; m.p. 96.3–97.1°C. Yield: 40.25%. UV(CH_2Cl_2) ($\lambda_{max/nm}$, log ε): 213.0, 3.56; 264.0, 4.73.^{1}H NMR ($CDCl_3$) δ_H: 2.18(1CH_2, m, $^3J_{HH}$ = 6.24, 6.68 Hz); 2.57(1CH_2, t,$^3J_{HH}$ = 6.68 Hz, 1 alpha —C=C); 2.87(1CH_2, t,$^3J_{HH}$ = 6.24 Hz, 1 alpha —COC=C); 3.92 (1CH_3, s, OCH_3); 6.18(1H, s, ethylene).^{13}C NMR ($CDCl_3$) δ_C: 19.67(1CH_2, Aliphatic, 2 alpha —CH_2); 28.53(1CH_2, Aliphatic, 1 alpha —C=C); 36.59(1CH_2, Aliphatic, 1 alpha —COC=C); 53.20(1CH_3, Aliphatic, OCH_3); 112.14(1CH, ethylene); 112.42, 145.95 and 158.72(3C, ethylene); 165.89, 175.44 and 192.42(3C, Carbonyl). Found: C, 60.01; H, 4.68. $C_{11}H_{10}O_5$ requires C, 59.46; H, 4.54%.

Ethyl 2,5-Dioxo-5,6,7,8-tetrahydro-2*H*-chromene-4-carboxylate (6d)

Viscous colorless oil. Yield: 45.5%. UV(CH_2Cl_2)($\lambda_{max/nm}$, log ε): 211.0, 3.54; 246.0, 4.54.^{1}H NMR ($CDCl_3$)δ_H: 1.37(1CH_3, t,$^3J_{HH}$ = 7.16, CH_3CH_2O); 2.20(1CH_2, m, $^3J_{HH}$ = 6.25, 6.68 Hz, 2 alpha —CH_2); 2.57(1CH_2, t,$^3J_{HH}$ = 6.68 Hz, 1 alpha —C=C); 2.88 (1CH_2, t,$^3J_{HH}$ = 6.25 Hz, 1 alpha —COC=C); 4.40(1CH_2, q, CH_3CH_2O); 6.18(1H, s, ethylene).^{13}C NMR ($CDCl_3$)δ_C: 13.91(1CH_3, CH_3CH_2O); 19.87(1CH_2, Aliphatic, 2 alpha —CH_2); 28.54(1CH_2, Aliphatic, 1 alpha —C=C); 36.62(1CH_2, Aliphatic, 1 alpha —COC=C); 62.62(1CH_2, Aliphatic, CH_3CH_2O); 112.08(1CH, ethylene); 112.45, 146.34 and 158.84(3C, ethylene); 165.44, 175.39 and 192.38(3C, Carbonyl). Found: C, 63.89; H, 5.97. $C_{12}H_{12}O_5$ requires C, 61.06; H, 5.12%.

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