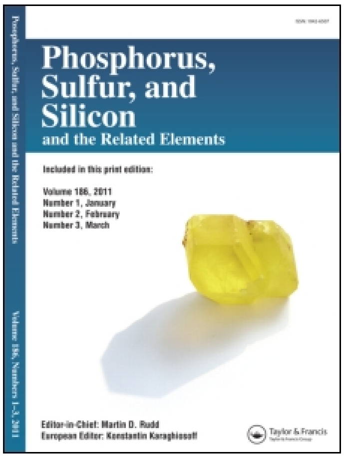

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Ali Ramazani[a]; Ali Souldozi[a]
[a] Zanjan University, Zanjan, Iran

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SILICA GEL CATALYZED CONVERSION OF DIALKYL 2-(1-HYDROXY-2-NAPHTHYL)-3-(TRIPHENYLPHOSPHORANYLIDENE)-BUTANEDIOATES TO ALKYL 2-OXO-2*H*-BENZO[*h*]CHROMENE-4-CARBOXYLATES IN SOLVENT-FREE CONDITIONS

Ali Ramazani and Ali Souldozi
Zanjan University, Zanjan, Iran

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Protonation of the highly reactive 1:1 intermediates, produced in the reaction between triphenylphosphine and dialkyl acetylenedicarboxylates, by 1-hydroxynaphthalene leads to vinyltriphenylphosphonium salts, which undergo aromatic electrophilic substitution reaction with conjugate base to produce dialkyl 2-(1-hydroxy-2-naphthyl)-3-(triphenylphosphanylidene)butanedioates. Silica gel was found to catalyze conversion of dialkyl 2-(1-hydroxy-2-naphthyl)-3-(triphenylphosphanylidene)butanedioates to alkyl 2-oxo-2H-benzo-[h*]chromene-4-carboxylates in solvent-free conditions at 80°C in fairly good yields.*

Keywords: Acetylenic esters; chromene; 1-hydroxynaphthalene; silica gel; vinyltriphenylphosphonium salt

While chromene skeleton compounds have been long studied in recent years they have attracted a greater growing interest, some having been found to possess properties of considerable pharmacological or industrial significance.[1] They are used as anticoagulants, additives in food and cosmetics, and in the preparation of insecticides, optical brighteners, and dispersed fluorescent and laser dyes.[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.[3,4] In the past we have established a convenient, one-pot method for preparing stabilized phosphorus ylides utilizing in situ

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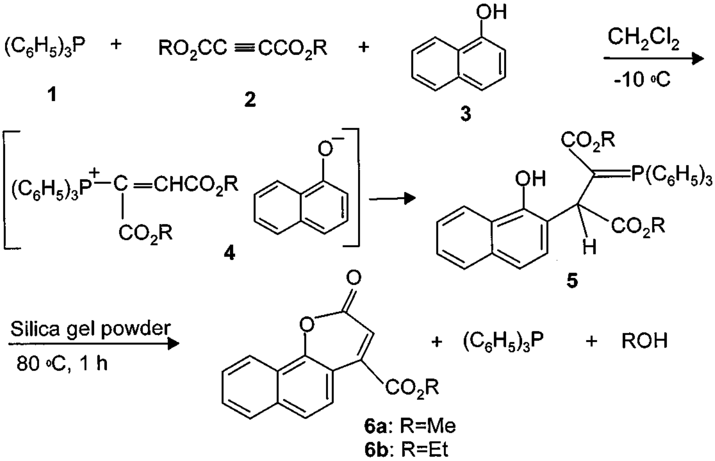
Address correspondence to Ali Ramazani, Chemistry Department, Zanjan University, PO Box 45195-313, Zanjan, Iran. E-mail: a-ramazani@mail.znu.ac.ir

generation of the phosphonium salts.[5–10] In this article, we report on the catalytic activity of silica gel powder in the conversion of dialkyl 2-(1-hydroxy-2-naphthyl)-3-(triphenylphosphoranylidene)butanedioates to alkyl 2-oxo-2*H*-benzo[*h*]chromene-4-carboxylates in solvent-free conditions at 80°C in fairly good yields[10,12] (Scheme 1).



SCHEME 1

RESULTS AND DISCUSSION

The ylide (**5**) may result from initial addition of triphenylphosphine **1** to the acetylenic ester **2** and concomitant protonation of the 1:1 adduct, followed by the electrophilic attack of the vinyltriphenylphosphonium cation on the aromatic ring at *ortho* β-position relative to the strong activating group (Scheme 1). TLC indicated formation of ylides **5** in CH_2Cl_2.

Silica gel powder was found to catalyze conversion of ylides **5** to alkyl 2-oxo-2*H*-benzo[*h*]chromene-4-carboxylates (**6**) in solvent-free conditions at 80°C in fairly good yields[10–12] (Scheme 1). TLC indicated that the reaction was completed after 1 h. In the absence of silica gel powder, this reaction was completed (**6a**) at reflux temperature (CH_2Cl_2 as solvent) after 120 h.[13] The structures of **6a–b** were deduced from their ^1H NMR and ^{13}C NMR spectra and via x-ray single crystal (for **6a**) structure determination.[14]

In summary, we have found that silica gel powder is able to catalyze conversion of ylides **5** to compounds **6** in solvent-free conditions. Other aspects of this process are under investigation.

EXPERIMENTAL

Melting points were measured on an Electrothermal 9100 apparatus and are uncorrected. ^{1}H 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–b

To a magnetically stirred solution of triphenylphosphine **1** (0.524 g, 2 mmol) and 1-hydroxynaphthalene **3** (0.288 g, 2 mmol) in CH_2Cl_2 (9 ml) was added dropwise a mixture of **2** (2 mmol) in CH_2Cl_2 (8 ml) at 10°C over 15 min. The mixture was allowed to warm to room temperature. Silica gel powder (3 g) was added and the solvent was evaporated. Dry silica gel and the residue were heated for 1 h at 80°C and then placed over a column of silica gel (12 g). The column chromatography was washed using ethyl acetate-light petroleum ether (1:10) as eluent. The solvent was removed under reduced pressure and the products were obtained as reddish crystals (**6a–b**). The characterization data of the compounds (**6a–b**) are given below.

Methyl 2-Oxo-2H-benzo[h]chromene-1-carboxylate (6a)

Orange crystals, m.p. 162.0–162.2°C; Yield: 84%. ^{1}H NMR ($CDCl_3$) δ_H: 4.05 (3H, s, OCH_3), 7.00 (1H, s, vinylic), 7.6 7.7 (2H, m, 2CH, arom.), 7.69 (1H, d, $^3J_{HH} = 9.0$ Hz, arom.), 7.86 (1H, d, $^3J_{HH} = 7.5$ Hz, arom.), 8.17 (1H, d, $^3J_{HH} = 9.0$ Hz, arom.), 8.53 (1H, d, $^3J_{HH} = 8.7$ Hz). ^{13}C NMR ($CDCl_3$) δ_C: 53.27 (CH_3), 111.54, 123.01, 134.92, and 143.39 (4C), 118.30, 121.81, 122.60, 124.60, 127.29, 127.67, and 129.25 (47 CH), 151.87 160.09 and 164.57 (2C = O, ester).

Ethyl 2-Oxo-2H-benzo[h]chromene-4-carboxylate (6b)

Orange crystals, m.p. 145.2–145.5°C; Yield: 82%. ^{1}H NMR ($CDCl_3$) δ_H: 1.43 (3H, t, $^3J_{HH} = 7.1$ Hz, CH_3 of Et); 4.50 (2H, q, $^3J_{HH} = 7.1$ Hz, OCH_2 of Et); 7.00 (1H, s, vinylic), 7.6 7.7 (2H, m, 2CH, arom.), 7.70 (1H, d, $^3J_{HH} = 8.9$ Hz, arom.), 7.87 (1H, d, $^3J_{HH} = 7.6$ Hz, arom.), 8.18 (1H, d, $^3J_{HH} = 8.9$ Hz, arom.), 8.54 (1H, d, $^3J_{HH} = 7.7$ Hz). ^{13}C NMR ($CDCl_3$) δ_C: 14.17 (CH_3 of Et); 62.61 (OCH_2); 111.64, 123.04, 134.91, and 143.78 (4C), 118.08, 121.83, 122.61, 124.57, 127.27, 127.66, and 129.21 (7CH), 151.87, 160.20, and 164.12 (2C = O, ester).

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