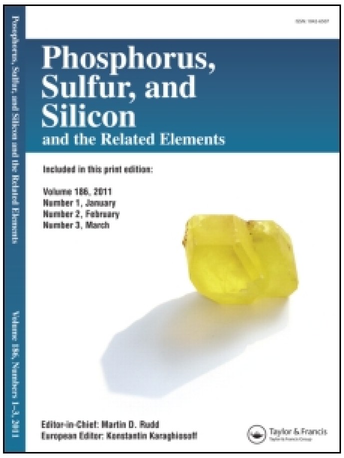

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SILICA GEL CATALYZED CONVERSION OF DIMETHYL 2-(5-BROMO-2-HYDROXYPHENYL)-3-(TRIPHENYLPHOSPHORANYLIDENE)BUTANEDIOATE TO METHYL 6-BROMO-2-OXO-2*H*-CHROMENE-4-CARBOXYLATE IN SOLVENT-FREE CONDITIONS

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Protonation of the highly reactive 1:1 intermediates, produced in the reaction between triphenylphosphine and dimethyl acetylenedicarboxylate, by 4-bromophenol leads to vinyltriphenylphosphonium salt, which undergoes aromatic electrophilic substitution reaction with conjugate base to produce dimethyl 2-(5-bromo-2-hydroxyphenyl)-3-(triphenylphosphoranylidene)butanedioate. Silica gel was found to catalyze conversion of dimethyl 2-(5-bromo-2-hydroxyphenyl)-3-(triphenylphosphoranylidene)butanedioate to methyl 6-bromo-2-oxo-2H-chromene-4-carboxylate in solvent-free conditions at 80°C in fairly high yield.

Keywords: 4-Bromophenol; chromene; dimethyl acetylenedicarboxylate; silica gel; vinyltriphenylphosphonium salt

Coumarins are very well known natural products and many such compounds exhibited high levels of biological activity.[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 generation of the phosphonium salts.[5–10] In this article, we report on the catalytic action of silica

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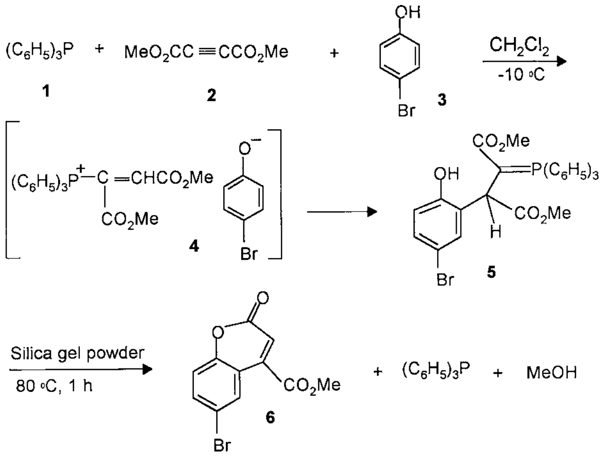
gel powder in the conversion of dimethyl 2-(5-bromo-2-hydroxyphenyl)-3-(triphenylphosphoranylidene)butanedioate to methyl 6-bromo-2-oxo-2*H*-chromene-4-carboxylate in solvent-free conditions at 80°C in fairly high yield[10–12] (Scheme 1).



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 to the aromatic ring at *ortho*-position relative to the strong activating group (Scheme 1). TLC indicated formation of ylide **5** in CH_2Cl_2. Silica gel powder was found to catalyze conversion of ylide 5 to methyl 6-bromo-2-oxo-2*H*-chromene-4-carboxylate (**6**) in solvent-free conditions at 80°C in fairly high yield[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 (**6**) at reflux temperature (CH_2Cl_2 as solvent) after 120 h.[13] We also have used $MgSO_4$, $Mg(HSO_4)_2$, ZnO, $ZnSO_4$, Al_2O_3, $Al_2(SO_4)_3$, $KAlSO_4$, $NaHSO_4$, $NaNO_2$, CuO, $Cu(NO_3)_2$ $CuSO_4$, $FeSO_4$, $Mn(NO_3)_2$, and MnO_2 powder instead of silica gel in this reaction, but no correspounding product **6** was observed, and in all cases decomposition were observed. The structure **6** was deduced from its IR, UV, ^1H NMR, ^{13}C NMR spectra, and mass spectrometry.

In summary, we have found that silica gel powder is able to catalyze conversion of ylide **5** to compound **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. UV spectra were recorded on a Shimadzu UV-2100 spectrophothometer. 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.

Procedure for the Preparation of Ylide 5 and Compound 6

To a magnetically stirred solution of triphenylphosphine **1** (0.524 g, 2 mmol) and 4-bromophenol **3** (0.346 g, 2 mmol) in CH_2Cl_2 (8 ml) was added dropwise a mixture of **2** (0.26 ml, 2 mmol) in CH_2Cl_2 (6 ml) at–10°C over 15 min. The mixture was allowed to warm up 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 product was obtained as white crystals (**6**). The characterization data of the compound (**6**) are given below.

Methyl 6-Bromo-2-oxo-2H-chromene-4-carboxylate (6)

White crystals, m.p. 115.7–115.9°C; Yield: 71.5%. UV (EtOH 95%) ($\lambda_{max/nm}$, log ε): 345, 4.029; 286, 4.363; 223, 4.786; 210, 4.789. IR (KBr) (ν_{max}, Cm^{-1}): 3032, 2975, 1709, 1241. ^{1}H NMR ($CDCl_3$) δ_H: 4.02 (3H, s, OCH_3), 7.01 (1H, s, vinylic), 7.46 (2 H, d, $^3J_{HH} = 8.8$ Hz, 2CH, arom.), 7.49 (1H, s, arom.). ^{13}C NMR ($CDCl_3$) δ_C: 53.41 (CH_3), 118.82, 120.73, 129.53 and 135.27 (4CH), 117.23 and 117.30 (2C), 140.91 (C—Br), 153.11 (C—O), 159.29 and 163.72 (2C=O, ester). MS (*m/z*, %): 284 ($M^+ + 2$, 70), 281 (M^+, 100), 254 (20), 226 (80); 223 (95); 192 (30); 178 (22); 167 (17); 148 (10).

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