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NOTE

Silica Gel Powder Catalyzed Stereoselective Conversion of 2-(2-acetylphenoxy)-3-(triphenylphosphoranylidene)-butanedioates to Dialkyl (Z)-2-(2-Acetylphenoxy)-2-butenedioates in Solvent-free Conditions

ALI RAMAZANI*, MAHSHID RAHIMIFARD and ALI SOULDOZI
Chemistry Department, Zanjan University, P.O. Box 45195-313, Zanjan, Iran
E-mail: a-ramazani@mail.znu.ac.ir; aliramazani@yahoo.com

Protonation of the highly reactive 1 : 1 intermediates, produced in the reaction between triphenylphosphine and dialkyl acetylenedicarboxylates, by 1-(2-hydroxyphenyl)-1-ethanone leads to vinyltriphenylphosphonium salts, which undergo Michael addition reaction with conjugate base to produce dialkyl 2-(2-acetylphenoxy)-3-(triphenylphosphoranylidene) butanedioates. Silica gel powder was found to catalyze stereoselective conversion of dialkyl 2-(2-acetylphenoxy)-3-(triphenylphosphoranylidene)butanedioates to dialkyl (Z)-2-(2-acetylphenoxy)-2-butenedioates in solvent-free conditions at 100°C.

Key Words: 1-(2-Hydroxyphenyl)-1-ethanone, Silica gel, Michael addition, Vinyltriphenylphosphonium salt, Acetylenic esters.

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[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]. As previously reported a convenient, one-pot method for preparing stabilized phosphorus ylides utilizing *in situ* generation of the phosphonium salts[1, 3] is established. In this article, the catalytic role of silica gel powder in the stereoselective conversion of dialkyl 2-(2-acetylphenoxy)-3-(triphenylphosphoranylidene)butanedioates (**5**) to dialkyl (Z)-2-(2-acetylphenoxy)-2-butenedioates (**6**) in solvent-free conditions[6] at 100°C is reported (**Scheme-1**).

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.

General Procedure for the Preparation of Ylides 5 and Compounds 6a–b

To a magnetically stirred solution of triphenylphosphine **(1)** (1 mmol) and 1-(2-hydroxyphenyl)-1-ethanone **(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°C over 15 min. The mixture was allowed to warm up to room temperature. Silica gel powder (1.5 g) was added and the solvent was evaporated. Dry silica gel and the residue were heated for 2 h at 100°C 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 eluent. The solvent was removed under reduced pressure and products were obtained as colourless viscous oils **(6a–b)**. The characterization data of the compounds **(6a–b)** are given below.

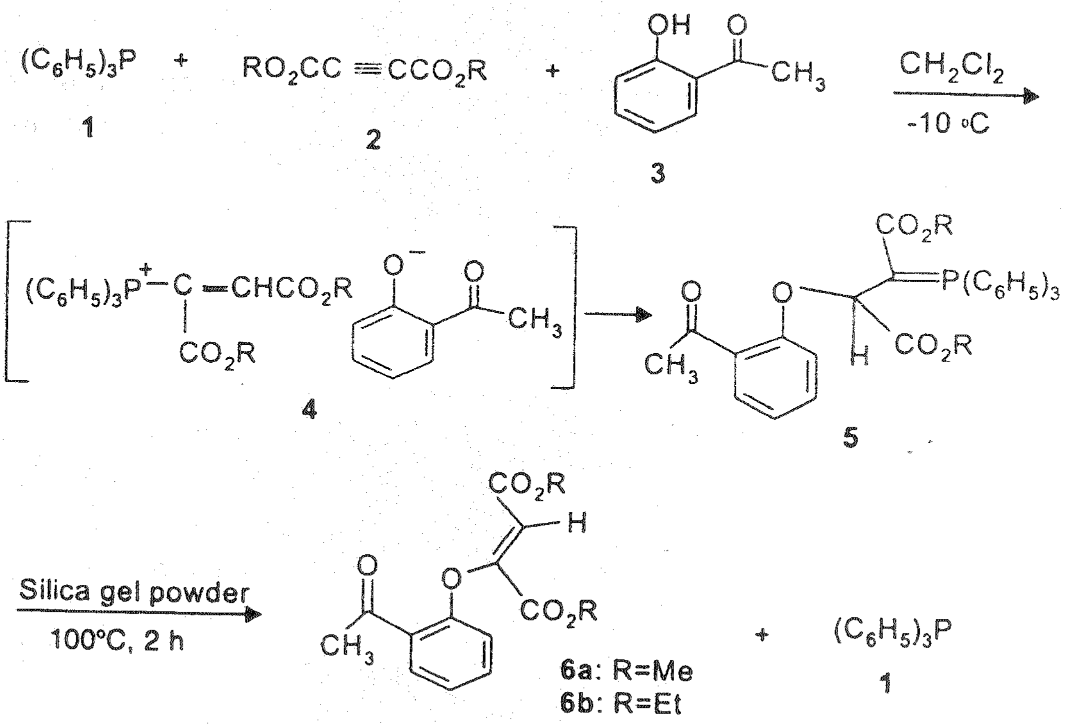
Dimethyl (Z)-2-(2-acetylphenoxy)-2-butenedioate (6a)

Colourless viscous oil; Yield: (18%) IR (neat) (ν_{max}, cm^{-1}): 3084, 3015, 2961, 2860, 1742, 1688 and 1603. ^1H NMR ($CDCl_3$) δ_H: 2.71 (3H, s, CH_3), 3.71 and 3.76 (6H, 2s, $2OCH_3$), 6.69 (1H, s, vinylic), 6.77 (1H, d, $^3J_{HH}$ = 8.2 Hz, arom.), 7.15 (1H, t, $^3J_{HH}$ = 7.5 Hz, arom.), 7.40 (1H, t, $^3J_{HH}$ = 7.8 Hz. arom.), 7.85 (1H, d, $^3J_{HH}$ = 7.8 Hz, arom.). ^{13}C NMR ($CDCl_3$) δ_C: 31.71 (CH_3), 52.11 and 53.24 ($2OCH_3$), 114.99 (=CH, vinylic), 115.93, 123.54, 128.52 and 130.88 (4CH, arom.), 133.49 and 148.85 (2C, arom.), 155.70 (OC=, vinylic), 162.22 and 163.52 (2C=O, ester), 198.44 (C=O, ketone).

Diethyl (Z)-2-(2-acetylphenoxy)-2-butenedioate (6b)

Colourless viscous oil; Yield: (14%). IR (neat) (ν_{max}, cm^{-1}): 3077, 2985, 2939, 1727 and 1681. ^1H NMR ($CDCl_3$) δ_H: 1.16 and 1.21 (6H, 2t, $^3J_{HH}$ = 7.1 Hz, $2CH_3$ of 2Et), 2.71 (3H, s, $COCH_3$), 4.15–4.25 (4H, m, $2OCH_2$ of 2Et), 6.68 (1H, s, vinylic), 6.79 (1H, d, $^3J_{HH}$ = 8.2 Hz, arom.), 7.14 (1H, t, $^3J_{HH}$ = 7.5 Hz, arom.), 7.40 (1H, t, $^3J_{HH}$ = 7.8 Hz, arom.), 7.80 (1H, d, $^3J_{HH}$ = 7.8 Hz, arom.). ^{13}C NMR ($CDCl_3$) δ_C: 13.85 and 14.03 ($2CH_3$ of 2Et), 31.80 (CH_3 of $COCH_3$), 61.16 and 62.56 ($2OCH_2$), 115.09 (=CH, vinylic), 116.17, 123.43, 128.44 and 130.83 (4CH, arom.), 133.48 and 149.91 (2C, arom.), 155.90 (OC=, vinylic), 161.75 and 163.22 (2C=O , ester), 198.44 (C=O, ketone).

The ylide **(5)** may result from initial addition of triphenylphosphine **(1)** to the acetylenic ester **(2)** and concomitant protonation of the 1 : 1 adduct by 1-(2-hydroxyphenyl)-1-ethanone leads to vinyltriphenylphosphonium salts **(4)** which undergo Michael addition reaction with conjugate base to produce dialkyl 2-(2-acetylphenoxy)-3-(triphenylphosphoranylidene)butanedioates **(5)**. TLC indicated formation of ylides **(5)** in CH_2Cl_2. Silica gel powder was found to catalyze stereoselective conversion of dialkyl 2-(2-acetylphenoxy)-3-(triphenylphosphoranylidene)butanedioates **(5)** to dialkyl (Z)-2-(2-acetylphenoxy)-2-butenedioates **(6)** in solvent-free conditions[6] at 100°C **(Scheme-1)**. TLC indicated that the reaction was completed after 2 h.



Scheme-1

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