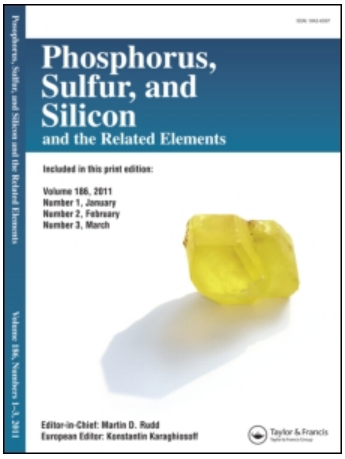

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Microwave-Induced Stereoselective Conversion of Dialkyl 2-(1,1,3-Trioxo-1,3-dihydro-2*H*-1,2-Benzisothiazol-2-yl)-3-(triphenylphosphoranylidene)succinates to Dialkyl 2-(1,1,3-Trioxo-1,3-dihydro-2*H*-1,2-benzisothiazol-2-yl)-2-butendioates in the Presence 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 saccharin leads to vinyltriphenylphosphonium salts, which undergo an addition reaction with a counter anion in CH_2Cl_2 at r.t. to produce the corresponding stabilized phosphorus ylides. Silica-gel powder was found to catalyze the stereoselective conversion of the stabilized phosphorus ylides to the corresponding electron-poor N*-vinylated isothiazoles in solvent-free conditions under thermal and microwave irradiation in fairly good yields.*

Keywords Microwave; phosphorus ylide; saccharin; silica gel; solvent-free conditions

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] Organophosphorus compounds have been used extensively in organic synthesis as useful reagents as well as ligands of a number of transition metal catalysts.[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

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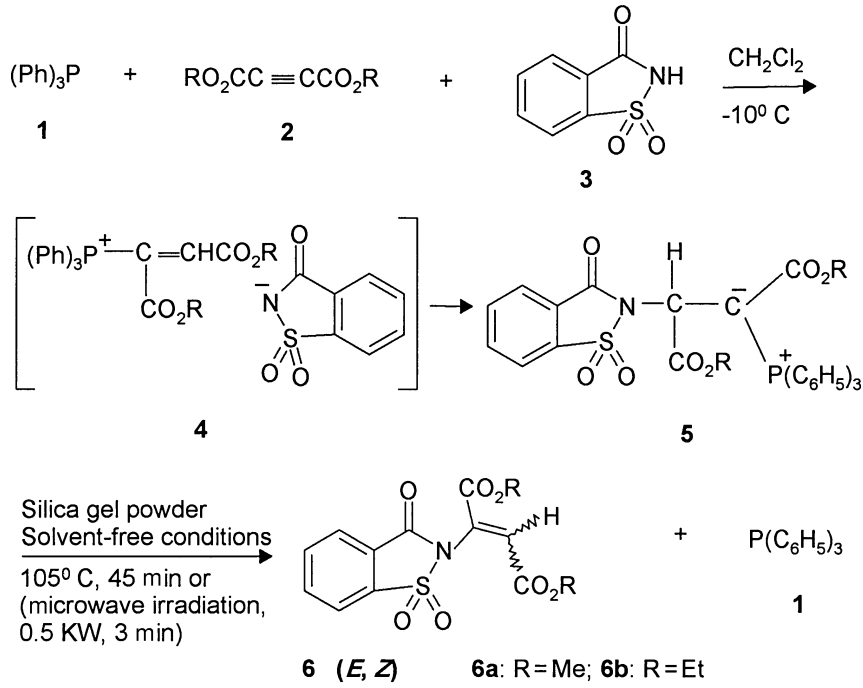
utilizing the in situ generation of the phosphonium salts.[5] In this article, we report on catalytic role of silica-gel powder in the stereoselective conversion of dialkyl 2-(1,1,3-trioxo-1,3-dihydro-2*H*-1,2-benzisothiazol-2-yl)-3-(triphenylphosphoranylidene)succinates (**5**) to dialkyl 2-(1,1,3-trioxo-1,3-dihydro-2*H*-1,2-benzisothiazol-2-yl)-2-butendioates (**6**) in solvent-free conditions[6] under thermal and microwave irradiation in fairly good yields (Scheme 1).



SCHEME 1

RESULTS AND DISCUSSION

Reactions are known in which an α,β-unsaturated carbonyl compound is produced from phosphonium salts.[5] Thus, compounds **6** may result from an initial addition of triphenylphosphine **1** to the acetylenic ester **2** and concomitant protonation of the 1:1 adduct by the saccharin (**3**) to form the corresponding triphenylphosphonium salts **4**. A conjugate addition of the saccharin (**3**) anion to the vinyltriphenylphosphonium cation **4** leads to the formation of the stabilized phosphorus ylide **5**.

Silica-gel powder was found to catalyze the stereoselective conversion of the stabilized phosphorus ylides **5** to the corresponding electron-poor *N*-vinylated isothiazoles **6** in solvent-free conditions under thermal and microwave irradiation in fairly good yields (Scheme 1). TLC indicated that the reaction was completed after 45 min at 105°C (3 min at microwave power 0.5 KW). The reaction proceeded smoothly and cleanly under solvent-free conditions[6] (in all cases the reaction worked efficiently with high coversions) and no side reactions were observed. We also have used $KHSO_4$, $MgSO_4$, Al_2O_3, MgO, ZnO, K_2HPO_4, KH_2PO_4, $NaHCO_3$, and $MnSO_4$ in this reaction, but the yields of the correspounding products **6** in cases of MgO, $MgSO_4$, K_2HPO_4, and KH_2PO_4 were low, and in the others cases, no products were observed; in all cases, decomposition was observed. In the absence of the silica-gel powder, the reactions were not completed at reflux temperature (toluene as solvent) after 24 h and decomposition of the starting materials and product were observed. The structures **6a–b** were deduced from their IR, ^{1}H NMR, and ^{13}C NMR spectra.

In summary, we have found that silica-gel powder is able to catalyze stereoselective conversion of ylide **5** compound **6** in solvent-free conditions (Scheme 1). Other aspects of this process are under investigation.

EXPERIMENTAL

Commerical-oven Butane M245 was used for microwave irradiation. Melting points were measured on an Electrothermal 9100 apparatus and are uncorrected. IR spectra were recorded on a Shimadzu IR-460 spectromer. ^{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 saccharin **3** (1 mmol) in CH_2Cl_2, 6 mL was added dropwise a mixture of **2** (1 mmol) in CH_2Cl_2 (4 mL) at −10°C over 15 min. The mixture was allowed to warm up to r.t. Silica-gel power (2 g) was added and the solvent was evaporated. Dry silica gel and the residue were heated for 45 min at 105°C (or irradiated at microwave power 0.5 KW for 3 min) and then placed over a column of silica gel (10 g). The column chromatography was washed using ethyl acetate-light petroleum ether (1:9) as an eluent. The solvent was removed under reduced pressure and products **(6a–b)** were obtained. The following are the characterization data of the compounds (**6a–b**).

Dimethyl 2-(1,1,3-Trioxo-1,3-dihydro-2H-1,2-benzisothiazol-2-yl)-2-butendioates (6a)

White crystals, m.p. 130–137°C; Yield: 47%. IR (KBr) (ν_{max}, Cm^{-1}): 3085, 2923, 2854, 1751,1727, and 1635. ^1H NMR ($CDCl_3$), *Z*-isomer: 51%, *E*-isomer: 49%, δ_H for Z-isomer: 3.74 and 3.90 (6 H, 2 s, 2 OCH_3); 7.47 (1 H, s CH=), 7.8–8.2 (4 H, m, arom.). δ_H for *E*-isomer: 3.84 and 3.90 (6 H, 2 s, 2 OCH_3); 6.74 (1 H, s, CH=), 7.8–8.2 (4 H, m, arom.). ^{13}C NMR ($CDCl_3$) δ_c for *Z*-isomer: 53.55 and 53.45 (2 OCH_3); 121.12 (CH=); 137.89 (N-C=), 121.36, 125.85, 128.40, and 134.61 (4 CH, arom.), 125.93 and 135.23 (2 C, arom.), 161.35 and 162.53 (2C=O of esters); 157.18 (C=O, imide). δ_C for *E*-isomer: 52.70 and 53.74 (2 OCH_3); 135.83 (CH=); 138.46 (N-C=), 121.47, 126.87, 131.18, and 134.95 (4 CH, arom.), 126.03 and 135.27 (2C, arom.), 161.80 and 163.75 (2C=O of esters); 158.15 (C=O, imide).

Diethyl 2-(1,1,3-Trioxo-1,3-dihydro-2H-1,2-benzisothiazol-2-yl)-2-butendioates (6b)

Viscous colorless oil; Yield: 40%. IR (CCl_4) (ν_{max}, Cm^{-1}): 3084, 2937, 2868, 1742, and 1641. ^1H NMR ($CDCl_3$), Z-isomer: 69.5%, *E*-isomer: 30.5%, δ_H for Z-isomer: 1.15 (3H, t, $^3J_{HH} = 7.1$ Hz, CH_3 of Et); 1.33 (3H, t, $^3J_{HH} = 7.1$ Hz, CH_3 of Et), 4.17 (2 H, q, $^3J_{HH} = 7.1$ Hz, OCH_2 of Et); 4.34 (2H, q, $^3J_{HH} = 7.1$ Hz, OCH_2 of Et); 7.45 (1 H, s, CH=), 7.8–8.2 (4 H, m, arom.). δ_H for *E*-isomer: 1.25 (3H, t, $^3J_{HH} = 7.1$ Hz, CH_3 of Et); 1.34 (3H, t, $^3J_{HH} = 7.1$ Hz, CH_3 of Et), 4.29 (2 H, q, $^3J_{HH} = 7.1$ Hz, OCH_2 of Et); 4.35 (2 H, q, $^3J_{HH} = 7.1$ Hz, OCH_2 of Et); 6.73 (1 H, s, CH=), 7.8–8.2 (4 H, m, arom.). ^{13}C NMR ($CDCl_3$), δ_C for Z-isomer: 13.75 and 13.99 (2 CH_3 of 2 Et); 61.90 and 63.14 (2 OCH_2); 121.31 (CH=); 138.48 (N-C=), 122.25, 125.83, 134.57, and 135.24 (4 CH, arom.), 128.40 and 135.49 (2 C, arom.), 161.32 and 162.14 (2C=O of esters); 158.16 (C=O, imide). δ_C for *E*-isomer: 13.75 and 14.04 (2 CH_3 of 2 Et); 61.74 and 62.85 (2 OCH_2); 121.45 (CH=); 137.94 (N-C=), 125.91, 125.95, 134.91, and 135.77 (4 CH, arom.), 126.91 and 135.49 (2 C, arom.), 160.77 and 163.29 (2C=O of esters); 157.27 (C=O, imide).

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