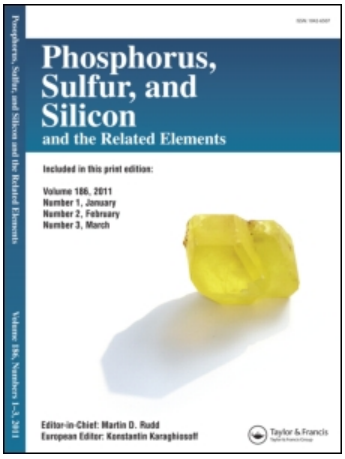

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Silica Gel Catalyzed Stereoselective Conversion of Dialkyl 2-(Imido- N -YL)-3-(triphenylphosphoranylidene)-butanedioates to Electron-Poor (Z)- N -Vinylimides in Solvent-Free Conditions

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SILICA GEL CATALYZED STEREOSELECTIVE CONVERSION OF DIALKYL 2-(IMIDO-*N*-YL)-3-(TRIPHENYLPHOSPHORANYLIDENE)-BUTANEDIOATES TO ELECTRON-POOR (*Z*)-*N*-VINYLIMIDES IN SOLVENT-FREE CONDITIONS

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*Silica gel was found to catalyze the stereoselective conversion of dialkyl 2-(imido-*N*-yl)-3-(triphenylphosphoranylidene)butanedioates to electron-poor (*Z*)-*N*-vinylimides in solvent-free conditions at 95°C in high coversions.*

Keywords: Catalyst; phosphorus ylide; silica gel; solvent-free conditions; (*Z*)-*N*-vinylimide

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.[1–11] 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.[12,13] In the past we have established a convenient, one-pot method for preparing stabilized phosphorus ylides utilizing in situ generation of the phosphonium salts.[1–11] In this article, we report on the catalytic action of silica gel powder in the stereoselective conversion of dialkyl 2-(imido-*N*-yl)-3-(triphenylphosphoranylidene)butanedioates (**1**)[11] to electron-poor (*Z*)-*N*-vinylimides (**2**)[10] in solvent-free conditions[15] at 95°C with high coversions (Scheme 1).

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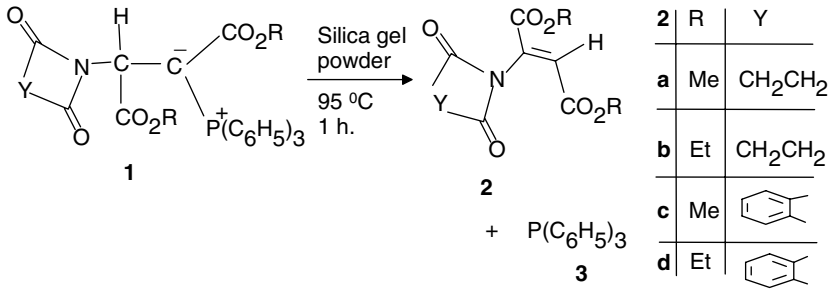

SCHEME 1

RESULTS AND DISCUSSION

Silica gel powder was found to catalyze stereoselective conversion of ylides **1**[11] to electron-poor (*Z*)-*N*-vinylimides (**2**)[10] in solvent-free conditions[15] at 95°C with high coversions (Scheme 1).[10–13] TLC indicated that the reaction was completed after 1 h. The reaction proceeds smoothly and cleanly under solvent-free conditions[15] at 95°C (in all cases the reaction works efficiently with high coversions) and no side reactions were observed. In the absence of silica gel powder, this reaction did not afford the corresponding compounds (**2a**) even at reflux temperature (toluene as solvent) after 24 h. TLC indicated that the solution contained unreacted ylide **1a**.[11]

The structures **2a–d** were deduced from their ^{1}H NMR, and ^{13}C NMR spectra and also via x-ray single crystal (for **2c**) structure determination.[14]

In summary, we have found that silica gel powder is able to catalyze stereoselective conversion of ylides **1**[11] to compounds **2**[10] 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. 1H and ^{13}C NMR spectra were measured with a BRUKER DRX-500 AVANCE spectrometer at 500 and125 MHz respectively.

General Procedure for the Preparation of Compounds 2a–d

The powdered mixture of dry silica gel (2 g) and ylide **1**[11] (1 mmol) were heated for 1 h at 95°C and then placed over a column of silica gel

(12 g). The column chromatography was washed using ethyl acetate-light petroleum ether (1:9) as eluent. The solvent was removed under reduced pressure and the products (**2a–d**) were obtained. The characterization data of the compounds (**2a–d**) are given in our previous report.[10]

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