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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 conditions¹⁵ 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 $\mathbf{1}^{11}$ to electron-poor (Z)-N-vinylimides $(\mathbf{2})^{10}$ in solvent-free conditions 15 at $95^{\circ}\mathrm{C}$ 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 $95^{\circ}\mathrm{C}$ (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 $(\mathbf{2a})$ even at reflux temperature (toluene as solvent) after 24 h. TLC indicated that the solution contained unreacted ylide $(\mathbf{1a})$

The structures **2a-d** were deduced from their ¹H NMR, and ¹³C 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 $\mathbf{1}^{11}$ to compounds $\mathbf{2}^{10}$ 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 ¹³C NMR spectra were measured with a BRUKER DRX-500 AVANCE spectrometer at 500 and 125 MHz respectively.

General Procedure for the Preparation of Compounds 2a-d

The powdered mixture of dry silica gel (2 g) and ylide $\mathbf{1}^{11}$ (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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