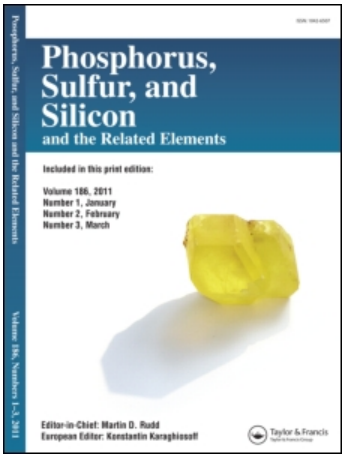

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Silica-Gel Catalyzed Stereoselective Conversion of Dialkyl 2-(Imido-*N*-YL)-3- (triphenylstibanylidene)succinates to Electron-Poor (*Z*)-*N*-Vinylimides in Solvent-Free Conditions

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

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*Protonation of the highly reactive 1:1 intermediates, produced in the reaction between triphenylstibine and dialkyl acetylenedicarboxylates, by imides (phthalimide and succinimide) leads to vinyltriphenylstibinium salts, which undergo a Michael addition reaction with a conjugate base to produce dialkyl 2-(imido-*N*-yl)-3-(triphenylstibanylidene)succinates. Silica gel was found to catalyze the stereoselective conversion of dialkyl 2-(imido-*N*-yl)-3-(triphenylstibanylidene)succinates to electron-poor (*Z*)-*N*-vinylimides in solvent-free conditions at 97°C in high conversions.*

Keywords Stibine ylide; silica gel; (*Z*)-*N*-vinylimide; solvent-free conditions; catalyst

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 extensively used 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 utilizing *in situ* generation of the phosphonium salts.[1] In this article, we report on the catalytic role of silica gel powder in the stereoselective conversion of dialkyl 2-(imido-*N*-yl)-3-(triphenylstibanylidene)succinates (**6**)[5]

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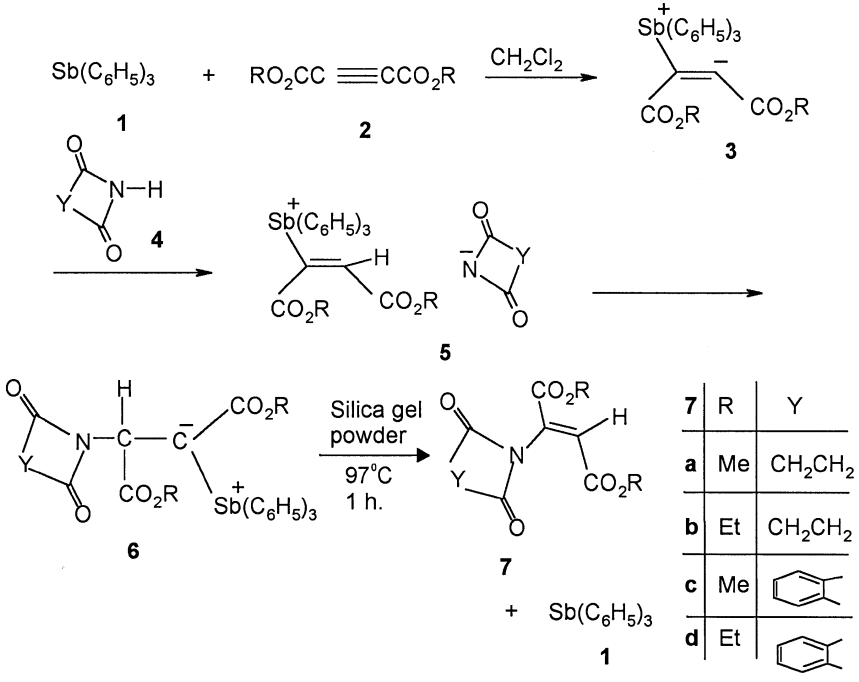
to electron-poor (*Z*)-*N*-vinylimides (**7**)[6] in solvent-free conditions[7] at 97°C with high conversions (Scheme 1).

RESULTS AND DISCUSSION

Protonation of the highly reactive 1:1 intermediates **3**, produced in the reaction between triphenylstibine **1** and dialkyl acetylenedicarboxylates **2**, by imides **4** (phthalimide and succinimide) leads to vinyltriphenylstibinium salts **5**, which undergo a Michael addition reaction with a conjugate base to produce dialkyl 2-(imido-*N*-yl)-3-(triphenylstibanylidene)succinates **6**. Silica gel powder was found to catalyze stereoselective conversion of ylides **6**[5] to electron-poor (*Z*)-*N*-vinylimides (**7**)[6] in solvent-free conditions[7] at 95°C with high conversions (Scheme 1).[3–6] TLC indicated that the reaction was completed after 1 h. The reaction proceeds smoothly and cleanly under solvent-free conditions[7] at 97°C (in all cases the reaction works efficiently with high conversions) and no side reactions were observed. The structures **7a–d** were deduced from their ^{1}H NMR, and ^{13}C NMR spectra and also



SCHEME 1

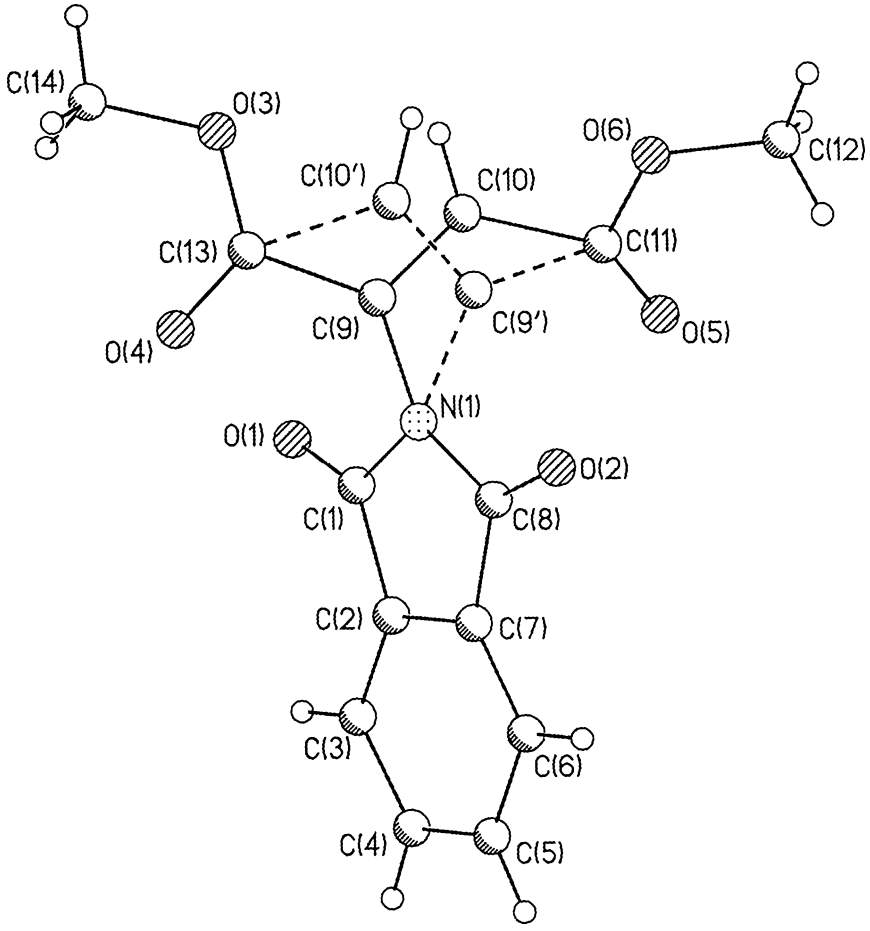


FIGURE 1 Molecular structure of **7c**.

via X-ray single crystal (for **7c**) structure determination (Figure 1 and Figure 2).[8]

In summary, we have found that silica gel powder is able to catalyze stereoselective conversion of ylides **6**[5] to compounds **7**[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. ^{1}H and ^{13}C NMR spectra were measured with

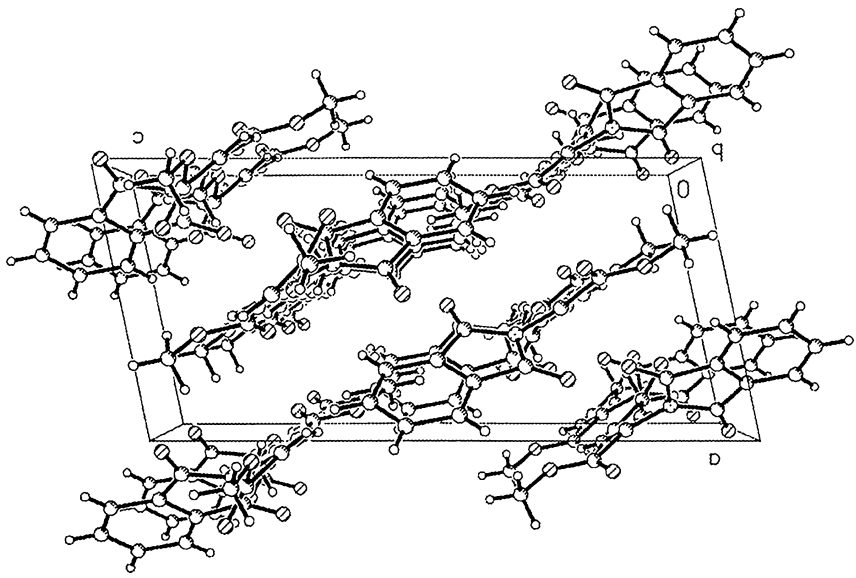


FIGURE 2 Unit cell crystal structure of **7c**.

a BRUKER DRX-500 AVANCE spectrometer at 500 and 125 MHz, respectively.

General Procedure for the Preparation of Compounds 7a–d

To a magnetically stirred solution of triphenylstibine **1** (1 mmol) and imide **4** (1 mmol) in CH_2Cl_2(5 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 g) was added and the solvent was evaporated. Dry silica gel and the residue were heated for 1 h at 97°C and then placed over a column of silica gel (5 g). The column chromatography was washed using ethyl acetate-light petroleum ether (1:9) as eluent. The solvent was removed under reduced pressure and products (**7a–d**) were obtained. The characterization data of the compounds (**7a–d**) are given in our previous report.[6]

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