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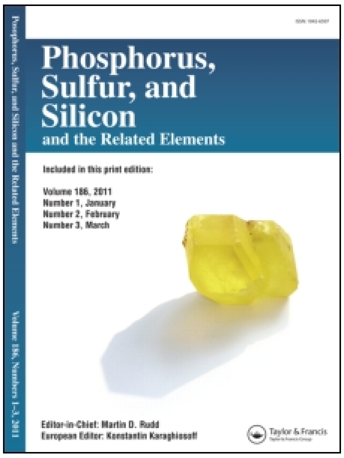

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Dipotassium-Hydrogen-Phosphate-Powder-Catalyzed Stereoselective C-Vinylation of Diphenylacetonitril

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Dipotassium-Hydrogen-Phosphate-Powder-Catalyzed Stereoselective C-Vinylation of Diphenylacetonitril

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*Protonation of the highly reactive 1:1 intermediates, produced in the reaction between triphenylphosphine and dialkyl acetylenedicarboxylates by diphenylacetonitril, leads to the vinyltriphenylphosphonium salts, which undergo a Michael addition reaction with a conjugate base to produce the corresponding stabilized phosphorus ylides. Dipotassium hydrogen phosphate powder was found to catalyze the conversion of the stabilized phosphorus ylides to dialkyl(*Z*)-2-[cyano (diphenyl)methyl]-2-butenedioates under thermal and microwave conditions in a solventless system.*

Keywords Acetylenic esters; diphenylacetonitril; dipotassium hydrogen phosphate; triphenylphosphine; vinyltriphenylphosphonium salt

INTRODUCTION

The β-addition of nucleophiles to the vinylic group of vinylic phosphonium salt leading to the formation of new alkylidene phosphoran has attracted much attention as a very convenient and synthetically useful method in organic synthesis.[1–5] In recent years, we have established a convenient, one-pot method for preparation of the phosphonium salt.[1] In this article, we report the facial one-pot stereoselective synthesis of dialkyl(*Z*)-2[cyano(diphenyl)methyl]-2-butenedioates in fairly high yields under thermal and microwave conditions in a solvent less system (Scheme 1).

RESULTS AND DISCUSSION

The ylide **5** may result from the initial addition of triphenylphosphine **1** to the acetylenic ester **2** and concomitant protonation of the 1:1 adduct,

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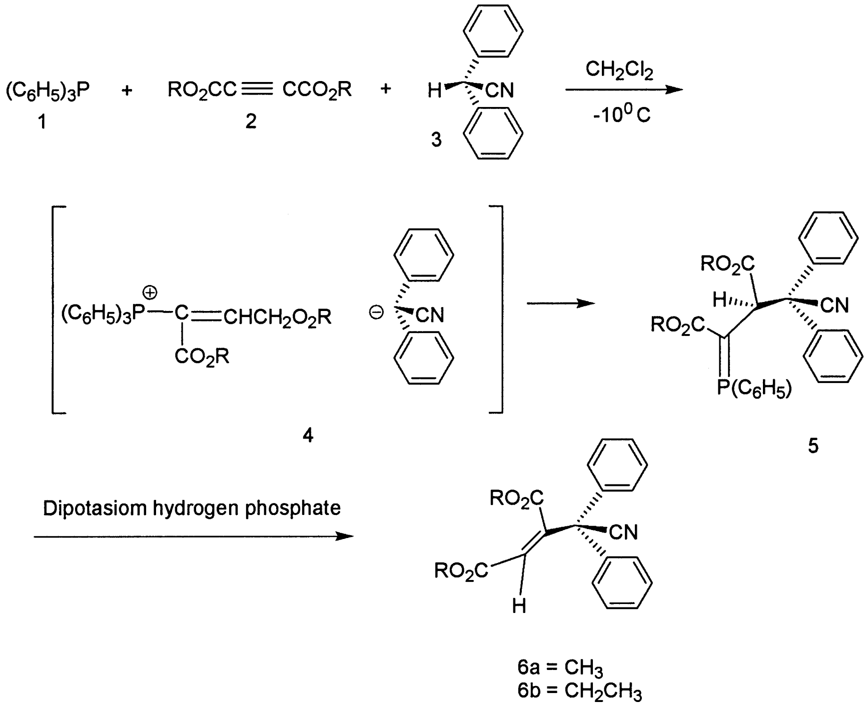
followed by the electrophilic attack of the vinyltriphenylphosphonium cation to the carbanion **4** (Scheme 1). TLC indicated the formation of ylides **5** in CH_2Cl_2.



SCHEME 1

Dipotassium hydrogen phosphate powder was found to catalyze the conversion of the stabilized phosphorus ylides **5** to dialkyl(*Z*)-2-[cyano(diphenyl)methyl]-2-butenedioates **6** under thermal and microwave conditions in a solventless system. TLC indicated that the reaction was completed in the solid phase (dipotassium hydrogen phosphate) under microwave irradiation at a microwave power of 0.4 KW after 3 min and thermally at 90°C after 45 min. We also have used $MgSO_4$, $Mg(HSO_4)_2$, ZnO, $ZnSO_4$, Al_2O_3, $Al_2(SO_4)_3$, $NaHSO_4$, $NaNO_2$, CuO, $Cu(NO_3)_2$, $CuSO_4$, $FeSO_4$, $Mn(NO_3)_2$, MnO, and SiO_2 powder instead of K_2HPO_4 in this reaction, but no corresponding products were observed and in all cases decomposition was observed. The structures of the products were deduced from their melting points, IR, ^1H NMR, and ^{13}C NMR spectra. In summary, we have found that dipotassium hydrogen phosphate powder is able to catalyze the conversion of the stabilized phosphorus ylides **5** to dialkyl(*Z*)-2-[cyano(diphenyl) methyl]-2-butenedioates **6** under thermal and microwave conditions in solvent-less system (Scheme 1) . Other aspects of this process are under investigation.

EXPERIMENTAL

Commerical-oven butane M245 was used for microwave irradiation. IR spectra were recorded on Shimadzo IR-460 spectrometer. 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 250.0 and 62.5, MHz respectively.

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

To a magnetically stirred solution of triphenylphosphine **1** (0.524 g, 2 mmol) and diphenylacetonitril **3** (0.3865 g, 2 mmol) in CH_2Cl_2, 8 mL was added dropwise a mixture of **2** (2 mmol) in CH_2Cl_2 (6 mL) at −10°C over 15 min. The mixture was allowed to warm to room temperature. Dipotassium hydrogen phosphate powder (2 g) was added and the solvent was evaporated. Dry dipotassium hydrogen phosphate and the residue were heated for 45 min at 90°C (or irradiated at microwave power 0.4 KW for 3 min) and then placed over a column of silica gel (10 g). The column chromatography was washed with ethyl acetate-light petroleum ether (2:10) as eluent. The solvent was removed under reduced pressure and the products were obtained as white crystals (**6a–b**). The characterization data of the compounds (**6a–b**) are given below.

Dimethyl(*Z*)-2[Cyano(diphenyl)methyl]-2-butenedioate (6a)

White crystals, m.p. 109.3°C; Yield: 71.31%. IR(KBr) ($\nu_{\max}$, cm^{-1}): 3069.02, 2961.02, 2229.33, 1742.22, 1657.37, 1271.67, 770.26, and 708.55. ^1H NMR ($CDCl_3$) δ_H: 3.62 and 3.77 (6H, s, OCH_3); 6.00 (1H, s, vinylic); 7.4–7.5 (10H, m, arom.). ^{13}C NMR ($CDCl_3$) δ_C: 52.47 and 52.73 (2 CH_3); 56.03 (C) 120.14 (CN); 128.27, 128.46, 128.51, 128.75, and 128.96 (10CH, arom); 132.53 (2C, arom); 136.59 (CH, vinylic); 146.32 (C, vinylic); 165.33 and 165.47 (2C=O, ester). Based on the NMR spectra, the amount of the dimethyl(*E*)-2[cyano(diphenyl)methyl]-2-butenedioate is fairly low (less than 10%).

Diethyl(*Z*)-2[Cyano(diphenyl)methyl]-2-butenedioate (6b)

White crystals, m.p. 100.1°C; Yield: 69.72%. IR(KBr) ($\nu_{\max}$, cm^{-1}): 3068.72, 2961.52, 2229.31, 1742.22, 1657.31, 1271.70, 770.30, and

708.60. ^{1}H NMR (CDCl$_3$) δ_H: 1.05 (3H, t, $^{3}J_{HH} = 7.1$ Hz, CH$_3$ of Et); 1.28 (3H, t,$^{3}J_{HH} = 7.1$ Hz, CH$_3$ of Et); 4.04 (2 H, q, $^{3}J_{HH} = 7.1$ Hz, OCH$_2$ of Et); 4.23 (2H, q, $^{3}J_{HH} = 7.1$ Hz, OCH$_2$ of Et); 6.00 (1H, s, vinylic); 7.4–7.5 (10H, m, arom.). ^{13}C NMR (CDCl$_3$) δ_C: 13.51 and 14.01 (2CH$_3$ of Et); 55.97 (C); 61.58 and 62.03 (2 OCH$_2$); 120.27 (CN); 128.21, 128,37, 128.68, and 128.91 (10 CH); 132.59 (2C); 136.63 (CH, vinylic); 145.64 (C, vinylic); 164.40 and 164.77 (2C=O , ester). Based on the NMR spectra, the amount of the diethyl(*E*)-2[cyano(diphenyl)methyl]-2-butenedioate is very low (less than 4%).

REFERENCES

[1] A. Ramazani, L. Yousefi, E. Ahmadi, and A. Souldozi, *Phosphorus, Sulfur, and Silicon,* **179,** 1459 (2004) and references cited therein.

[2] J. I. G. Cadogan, Organophosphorus Reagents in Organic Synthesis, J. I. G. Cadogon, ed. (Academic Press, New York, 1979).

[3] K. P. C. Vollhardt, *Synthesis*, 765 (1975) and references cited therein.

[4] A. Ramazani and M. Mohammadi-Vala, *Phosphorus, Sulphur, and Silicon*, **176,** 243 (2001).

[5] A. Ramazani, *Phosphorus, Sulphur, and Silicon*, **178,** 1839 (2003).