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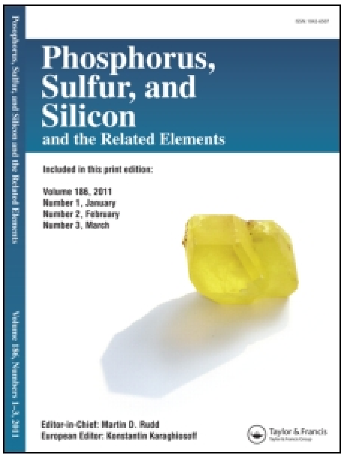

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Ali Souldozi[a]; Ali Ramazani[a]; Nader Noshiranzadeh[a]
[a] Chemistry Department, Zanzen University, Zanjan, Iran

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Dipotassium Hydrogen Phosphate Powder Catalyzed Stereoselective *O*-Vinylation of 1-(2-Hydroxy-1-naphthyl)-1-ethanone

Ali Souldozi
Ali Ramazani
Nader Noshiranzadeh
Chemistry Department, Zanzen University, Zanjan, Iran

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

Keywords 1-(2-Hydroxy-1-naphtyl)-1-ethanone; acetylenic esters; dipotassium hydrogen phosphate; triphenylphosphine; vinyltriphenylphosphonium salt

INTRODUCTION

The β-addition of nucleophiles to the vinyl 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] Silica gel as an additive promotes Wittig reactions of phosphorus ylides with aldehydes, including sterically hindered aldehydes to increase the rate and yields of alkenes.[4,5] In the past, we have established a convenient, one-pot method for preparing stabilized phosphorus ylides utilizing in situ generation of the phosphonium salts.[1,3] In this article, we report on the catalytic role of dipotassium hydrogen phosphate powder in the conversion of dialkyl 2-(1-acetyl-2-naphthyl)-3-[1,1,

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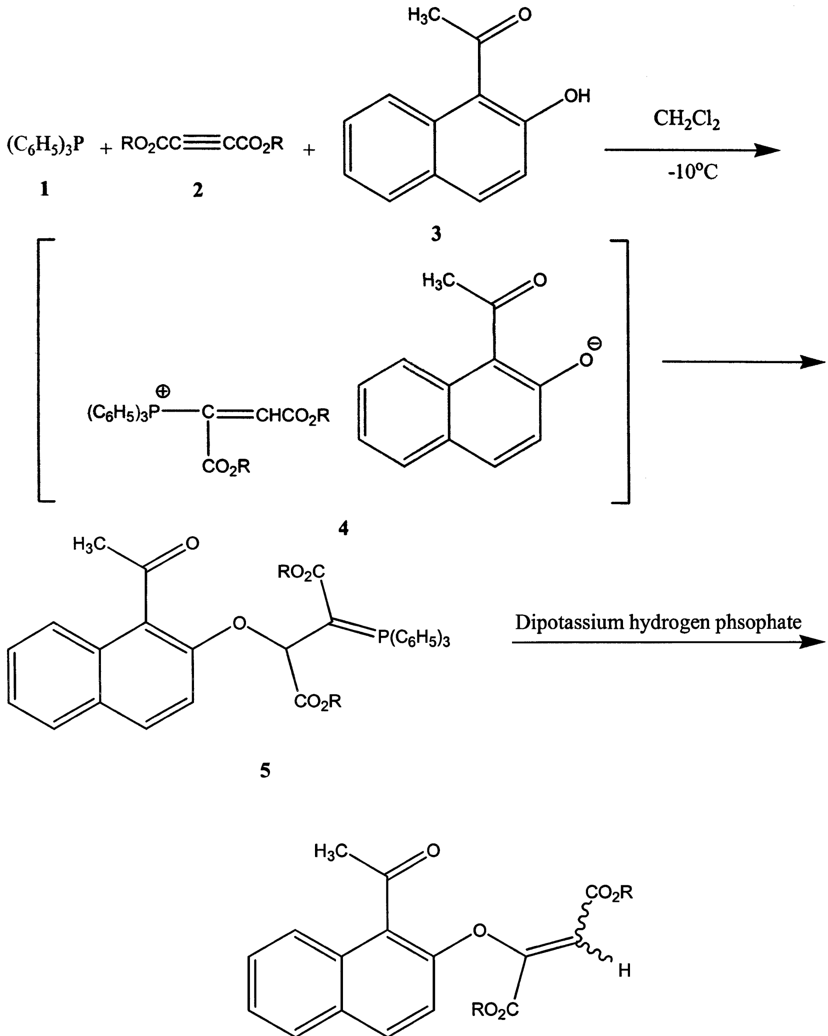
Address correspondence to Ali Ramazani, Zanjan University, Department of Chemistry, PO Box 45195-313, Zanjan, Iran. E-mail: aliramazani@gmail.com

1-triphenyl-λ^5-phosphanylidene)succinates (**5**) to dialkyl (*E*,*Z*)-2-(1-acetyl-2-naphthyl)-2-butenedioates (**6**) in solvent-free conditions under microwave irradiation and thermal conditions in fairly high yields (Scheme 1).



R	Me	R	Et
6a	*Z*	**6c**	*Z*
6b	*E*	**6d**	*E*

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

Dipotassium hydrogen phosphate powder was found to catalyze the conversion of the stabilized phosphorus ylides (**5**) to dialkyl (*E*,*Z*)-2-(1-acetyl-2-naphthyl)-2-butenedioates (**6**) under thermal and microwave conditions in a solventless system. TLC indicated that the reaction was completed in solid phase (dipotassium hydrogen phosphate) under microwave irradiation at microwave power 0.4 in 3 min and under thermal conditions at 100°C in 1 h. 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.

In summary, we have found that dipotassium hydrogen phosphate powder is able to catalyze the conversion of the stabilized phosphorus ylides **5** to to dialkyl (*E*,*Z*)-2-(1-acetyl-2-naphthyl)- 2-butenedioate (**6**) under thermal and microwave conditions in a solventless system (Scheme 1).

EXPERIMENTAL

Commerical oven butane M245 was used for microwave irradiation. IR spectra were recorded on Shimadzu IR-460 spectrometer. ^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–d

To a magnetically stirred solution of triphenylphosphine **1** (0.524 g, 2 mmol) and 1-(2-hydroxy-1-naphtyl)-1-ethanone **3** (0.372 g, 2 mmol) in CH_2Cl_2 (8 mL) dropwise a mixture of **2** (2 mmol) in CH_2Cl_2 (6 ml) was added at −10°C over 15 min. The mixture was allowed to warm to r.t. Dipotassium hydrogen phosphate powder (2 g) was added, and the solvent was evaporated. Dry dipotassium hydrogen phosphate and the residue were heated for 1 h 100°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 using ethyl acetate-light petroleum ether (2:10) as an eluent. The solvent was removed under reduced pressure, and products were obtained as colorless viscous oil (**6a–d**). The characterization data of compounds (**6a–d**) follow.

Dimethyl (Z)-2-(1-Acetyl-2-naphthyl)-2-butenedioate (6a)

Colorless viscous oil; Yield: 17.7%. IR (neat) (ν_{max}, cm^{-1}): 3054.72, 2985.29, 1720.21, 1643.07, and 1265.08. ^1H NMR ($CDCl_3$) δ_H: 2.67 (3H, s, $COCH_3$); 3.66 and 3.94 (6H, 2 s, 2 OCH_3); 6.71 (1H, s, vinylic); 6.98 (1H, d, $^3J_{HH} = 9.0$ Hz, arom); 7.25 (1H, d, $^3J_{HH} = 9.0$ Hz, arom); 7.53–7.58 (1H, m, arom); 7.80 (1H, d, $^3J_{HH} = 9.5$ Hz, arom); 7.85–7.89 (1H, m, arom) and 7.93 (1H, d, $^3J_{HH} = 9$ Hz, arom). ^{13}C NMR ($CDCl_3$) δ_C: 32.68 (CH_3 of $COCH_3$); 52.11 and 52.70 (2 OCH_3); 114.36 (=CH, vinylic); 124.30, 125.16, 128.18, 128.23, 129.97, and 131.48 (6CH, arom); 125.59, 130.44, 130.88, and 139.98 (4C arom); 150.69 (OC=, vinylic); 162.25 and 163.56 (2C=O, ester) and 203.78 (C=O, ketone).

Dimethyl (E)-2-(1-Acetyl-2-naphthyl)-2-butenedioate (6b)

Colorless viscous oil; Yield: 53.6%. IR (neat) (ν_{max}, cm^{-1}): 3054.72, 2985.29, 1720.21, 1643.07, and 1265.08. ^1H NMR ($CDCl_3$) δ_H: 2.67 (3H, s, $COCH_3$); 3.66 and 3.94 (6H, 2 s, 2 OCH_3); 5.24 (1H, s, vinylic); 6.98 (1H, d, $^3J_{HH} = 9.0$ Hz, arom); 7.25 (1H, d, $^3J_{HH} = 9.0$ Hz, arom); 7.53–7.58 (1H, m, arom); 7.80 (1H, d, $^3J_{HH} = 9.5$ Hz, arom); 7.85–7.89 (1H, m, arom) and 7.93 (1H, d, $^3J_{HH} = 9.0$ Hz, arom). ^{13}C NMR ($CDCl_3$) δ_C: 32.56 (CH_3 of $COCH_3$); 51.83 and 53.23 (2 OCH_3); 100.64 (=CH, vinylic); 119.29, 124.73, 126.63, 128.01, 128.40, and 130.14 (6CH, arom); 125.74, 130.28, 131.29, and 140.54 (4C arom); 148.76 (OC=, vinylic); 162.83 and 165.37 (2C=O, ester) and 202.16 (C=O, ketone).

Diethyl (Z)-2-(1-Acetyl-2-naphthyl)-2-butenedioate (6c)

Colorless viscous oil; Yield: 20.8%. IR (neat) (ν_{max}, cm^{-1}): 3054.72, 2985.29, 1712.49, 1635.53, and 1265.08. ^1H NMR ($CDCl_3$) δ_H:1.22 and 1.38 (6H, 2 t, $^3J_{HH} = 7.25$ Hz, 2CH_3 of 2Et); 2.69 (3H, s, $COCH_3$), 4.20 and 4.39 (4H, q, $^3J_{HH} = 7.25$ Hz, 2 OCH_2 of Et), 6.70 (1H, s, vinylic); 7.00 (1H, d, $^3J_{HH} = 9.0$ Hz, arom), 7.28 (1H, d, $^3J_{HH} = 9.0$ Hz, arom); 7.54–7.58 (1H, m, arom); 7.81 (1H, d, $^3J_{HH} = 9.5$ Hz, arom); 7.84–7.89 (1H, m, arom) and 7.94 (1H, d, $^3J_{HH} = 10.0$ Hz, arom). ^{13}C NMR ($CDCl_3$) δ_C: 13.89 and 13.97 (2CH_3 of Et); 32.71 (CH_3 of $COCH_3$); 61.15 and 62.53 (2OCH_3); 114.36 (=CH vinylic), 116.35, 124.32, 125.08, 128.20, 130.18, and 131.71 (6CH arom); 123.17, 130.11, 130.42, and 139.89 (4C arom);

150.66 (OC= vinylic); 161.75 and 163.26 (2C=O, ester); 203.46 (C=O, ketone).

Diethyl (E)-2-(1-Acetyl-2-naphthyl)-2-butenedioate (6d)

Colorless viscous oil; Yield: 46.39%. IR (neat) (ν_{max}, cm^{-1}): 3054.72, 2985.29, 1712.49, 1643.07, and 1265.08. ^{1}H NMR (CDCl$_3$) δ_H: 1.219 and 1.378 (6H, 2t, $^3J_{HH}$ = 7.3 Hz, 2CH$_3$ of 2Et); 2.69 (3H, s, COCH$_3$); 4.20 and 4.39 (4H, q, $^3J_{HH}$ = 7.3 Hz, 2 OCH$_2$ of 2 Et); 5.23 (1H, s, vinylic); 7.00 (1H, d, $^3J_{HH}$ = 9.0 Hz, arom); 7.28 (1H, d, $^3J_{HH}$ = 9.0 Hz, arom); 7.54–7.58 (1H, m, arom); 7.81 (1H, d, $^3J_{HH}$ = 9.5 Hz, arom); 7.84–7.89 (1H, m, arom) and 7.94 (1H, d, $^3J_{HH}$ = 10.0 Hz, arom). ^{13}C NMR (CDCl$_3$) δ_C: 13.84 and 14.02 (2CH$_3$ of 2 Et); 32.56 (CH$_3$ of COCH$_3$); 60.80 and 62.56 (2OCH$_3$); 100.94 (=CH vinylic), 119.41, 124.75, 126.55, 128.15, 128.37, and 132.05 (6CH arom); 125.66, 127.97, 131.37, and 140.31 (4C arom); 148.76 (OC= vinylic) and 162.38 and 164.87 (2 C=O, ester); 202.15 (C=O, ketone).

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