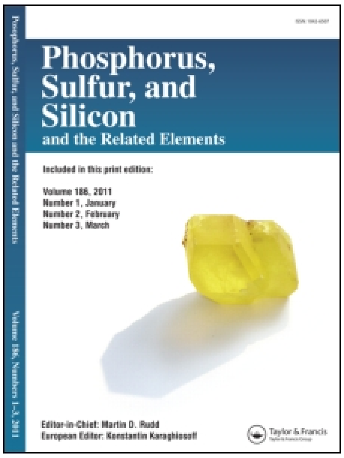

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

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To cite this Article Ramazani, Ali , Momeni-Movahhed, Abolfazl and Gouranlou, Farideh(2002) 'Silica Gel Catalyzed Stereoselective Conversion of Dialkyl 2-(3-acetyl-4-hydroxy-1-naphthyl)-3-(triphenylphosphoranylidene) butanedioates to Dialkyl 2-(3-acetyl-4-hydroxy-1-naphthyl)-2-butenedioates in Solvent-Free Conditions', Phosphorus, Sulfur, and Silicon and the Related Elements, 177: 4, 903 — 907

To link to this Article: DOI: 10.1080/10426500210658

URL: http://dx.doi.org/10.1080/10426500210658

Phosphorus, Sulfur and Silicon, 2002, Vol. 177:903–907
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1042-6507/02 $12.00 + .00

SILICA GEL CATALYZED STEREOSELECTIVE CONVERSION OF DIALKYL 2-(3-ACETYL-4-HYDROXY-1-NAPHTHYL)-3-(TRIPHENYLPHOSPHORANYLIDENE) BUTANEDIOATES TO DIALKYL 2-(3-ACETYL-4-HYDROXY-1-NAPHTHYL)-2-BUTENEDIOATES IN SOLVENT-FREE CONDITIONS

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(Received October 8, 2001)

Protonation of the highly reactive 1:1 intermediates, produced in the reaction between triphenylphosphine and dialkyl acetylenedicarboxylates, by 1-hydroxy-2-acetonaphthone leads to vinyltriphenylphosphonium salts, which undergo aromatic electrophilic substitution reaction with conjugate base to produce dialkyl 2-(3-acetyl-4-hydroxy-1-naphthyl)-3-(triphenylphosphoranylidene) butanedioates. Silica gel was found to catalyze conversion of dialkyl 2-(3-acetyl-4-hydroxy-1-naphthyl)-3-(triphenylphosphoranylidene) butanedioates to dialkyl 2-(3-acetyl-4-hydroxy-1-naphthyl)-2-butenedioates in solvent-free conditions at 90°C in fairly good yields.

Keywords: 1-hydroxy-2-acetonaphthone; acetylenic esters; silica gel; triphenylphosphine

INTRODUCTION

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.[1] Remarkable rate enhancements and dramatic reductions of reaction times in the Wittig reactions were observed[2] when a mixture of triphenylcarbethoxymethylene phosphorane, an aldehyde and silica gel was irradiated in a microwave oven

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This work was supported by the Zanjan University Research Council.

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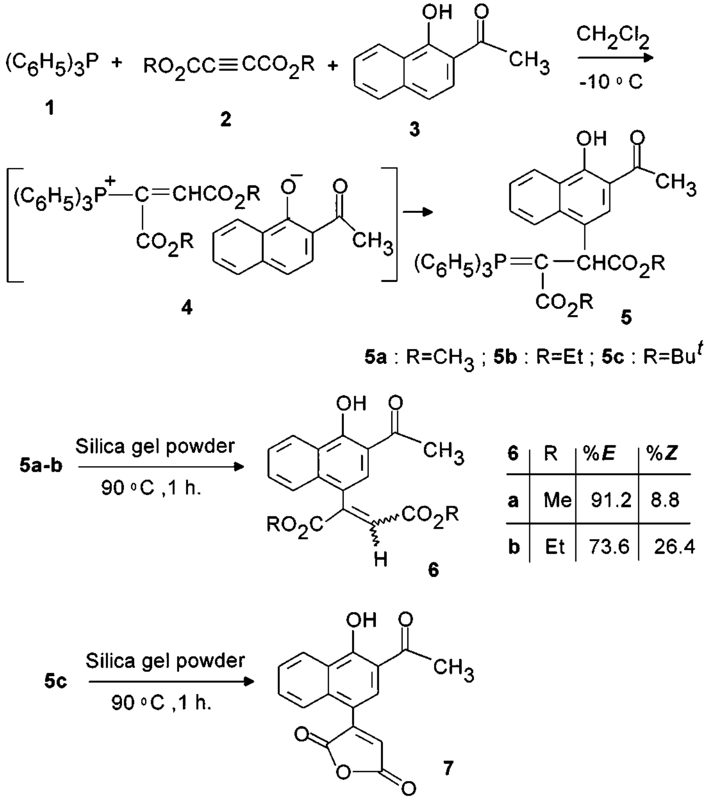
for 5–6 min. In the past we have established a convenient, one-pot method for preparing stabilized phosphorus ylides utilizing in situ generation of the phosphonium salts.[3–7] In this article, we report on catalytic rule of silica gel powder in the conversion of dialkyl 2-(3-acetyl-4-hydroxy-1-naphthyl)-3-(triphenylphosphoranylidene) butanedioates to dialkyl 2-(3-acetyl-4-hydroxy-1-naphthyl)-2-butenedioates in solvent-free conditions[8] at 90°C in fairly good yields (Scheme 1).



6	R	%*E*	%*Z*
a	Me	91.2	8.8
b	Et	73.6	26.4

SCHEME 1

RESULTS AND DISCUSSION

The ylide (**5**) may result from 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 to the aromatic ring at para position relative to the strong activating group (Scheme 1). TLC indicated formation of ylides **5** in CH_2Cl_2. Silica gel powder was found to catalyze conversion of ylides **5** to vinylated compounds (**6a–b** and **7**) in solvent-free conditions[8] at 90°C in fairly good yields (Scheme 1).

TLC indicated that the reaction was completed after 1 h. Under the same condition, ylide **5c** ($R{=}Bu^t$) was converted to anhydride **7** (Scheme 1). In the absence of silica gel powder, this reaction did not afford the corresponding compounds (**6a**) even at reflux temperature (toluene as solvent) after 24 h. TLC indicated that the solution contained unreacted ylide **5a**. The NMR spectra indicated that solution of compounds **6** ($CDCl_3$ as solvent) contained two geometrical isomers (***E*** and ***Z***) in unequal population. The relative percentages of geometrical isomers in $CDCl_3$ for each compound (**6**) (Scheme 1) were determined from their ^1H NMR spectra.[9] Spots of ***E*** and ***Z*** isomers (**6**) in TLC are very similar and have the same R_f. Therefore, we were not able to separate the ***E*** and ***Z*** isomers (**6**) from each other. The structures **6a–b** and **7** were deduced from their elemental analyses and their UV, IR, ^1H, and ^{13}C NMR spectra. The mass spectra of these compounds displayed molecular ion peaks at *m/z* of 328, 356, and 282 respectively.

In summary, we have found that silica gel powder is able to catalyze conversion of ylides **5** to compounds **6** and **7** in solvent-free conditions. Also a convenient, one-pot method for preparing stabilized ylides (**5a–c**) utilising in situ generation of the phosphonium salts is reported. Other aspects of this process are under investigation.

EXPERIMENTAL

Melting points were measured on an Electrothermal 9100 apparatus and are uncorrected. Elemental analyses were performed using a Heraeus CHN—O-Rapid analyzer. UV spectra were recorded on a Shimadzu UV-2100 spectrometer. IR spectra were recorded on a Shimadzu IR-460 spectrometer. ^1H and ^{13}C NMR spectra were measured with a BRUKER DRX-500 AVANCE spectrometer at 500 and 125 MHz respectively. Mass spectra were recorded on a Finnigan-Matt 8430 mass spectrometer operating at an ionization potential of 70 eV.

General Procedure for the Preparation of Ylides 5, Compounds 6a–b and Compound 7

To a magnetically stirred solution of triphenylphosphine **1** (0.262 g, 1 mmol) and 1-hydroxy-2-acetonaphthone **3** (0.186 g, 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 90°C and then placed over a column of silica gel (5 g). The column chromatography was washed using ethyl acetate-hexane (1:3) as eluent. The solvent was removed under reduced pressure and products were obtained as yellow solids (**6a–b** and **7**). The characterization data of the compounds (**6a–b** and **7**) are given below.

Dimethyl 2-(3-acetyl-4-hydroxy-1-naphtyl)-2-butendioate (6a, E/Z*)*

Yellow solid, m.p. 102.0–104.0°C; Yield: 71%. UV (EtOH 95%) ($\lambda_{max/nm}$, log ε): 216, 4.33; 236, 3.99; 258, 4.26. IR (KBr) (ν_{max}, Cm^{-1}) : 1722, 1634, 1218, 1130. ^1H NMR ($CDCl_3$) δ_H for *E*-isomer: 2.67 (3H, s, $COCH_3$), 3.53 and 3.76 (6H, 2s, 2 OCH_3), 7.31 (H, s, $=CHCO_2Me$), 7.50 (1H, S, H2, arom.), 7.51–7.6 (3H, m, H6–H8, arom.), 8.51 (1H, d, $^3J_{HH} = 7.7$ Hz, H5), 14.09 (1H, s, O—H···O=C). Observable δ_H for *Z*-isomer: 2.71 (3H, s, $COCH_3$), 3.71 and 3.85 (6H, 2s, 2 OCH_3), 6.21 (H, s, $=CHCO_2Me$), 14.01 (1H, s, O—H···O=C). ^{13}C NMR ($CDCl_3$) δ_C for *E*-isomer: 26.92 (CH_3); 51.98 and 53.12 (2 OCH_3); 124.59, 125.02, 125.24, 125.76, 126.07, and 130.55 (6 CH); 112.71, 122.28, 131.15, 135.49, and 143.13 (5C); 162.95 (C4); 165.12 and 166.94 (2C=O of ester), 204.21 (C=O, ketone). δ_C for the *Z*-isomer was not observed because its low population in the mixture. MS (m/z, %): 329 (M^++1, 5), 328 (M^+, 16); 268 (33); 229 (13); 195 (33); 139 (78); 115 (49); 89 (16); 59 (100). Found: C, 66.02; H, 5.05. $C_{18}H_{16}O_6$ requires C, 65.85; H, 4.88%.

Diethyl 2-(3-acetyl-4-hydroxy-1-naphtyl)-2-butendioate (6b, E/Z*)*

Yellow solid, m.p. 50.0–51.0°C; Yield: 67%. UV (EtOH 95%) ($\lambda_{max/nm}$, log ε): 214, 4.55; 236, 4.19; 258, 4.42. IR (KBr) (ν_{max}, Cm^{-1}): 1726, 1634, 1218, 1171. ^1H NMR ($CDCl_3$) δ_H for *E*-isomer: 0.90 (3H, t, $^3J_{HH} = 7.1$ Hz) and 1.24 (3H, t, $^3J_{HH} = 7.1$ Hz) (2CH_3 of 2Et), 2.68 (3H, s, $COCH_3$), 3.9–4.3 (4H, m, 2 OCH_2), 7.29 (1H, S, $=CHCO_2Et$), 7.50 (1H, s, H2), 7.51–7.73 (3H, m, H6–H8), 8.50 (1H, d, $^3J_{HH} = 8.3$ Hz, H5), 14.08 (1H, s, O—H···O=C). δ_H for *Z*-isomer: 1.31 (3H, t, $^3J_{HH} = 7.1$ Hz) and 1.36 (3H, t, $^3J_{HH} = 7.2$ Hz) (2CH_3 of 2Et), 2.75 (3H, S, $COCH_3$), 3.9–4.3 (4H, m, 2 OCH_2), 6.21 (1H, s, $=CHCO_2Et$), 7.74 (1H, s, H2), 7.51–7.73 (3H, m, H6–H8), 8.08 (1H, d, $^3J_{HH} = 8.4$ Hz, H5), 14.13 (1H, s, O—H···O=C). ^{13}C NMR ($CDCl_3$) δ_C for *E*-isomer: 13.75 and 14.10 (2CH_3 of 2 Et); 26.91 (CH_3 of COMe); 60.88 and 62.13 (2 OCH_2); 124.80, 124.90, 125.17, 125.72, 125.94, and 130.43 (6 CH); 112.64, 122.65, 131.48, 135.67, and

142.82 (5C); 162.87 (C4); 164.91 and 166.42 (2C=O of esters), 204.22 (C=O, ketone). δ_C for *Z*-isomer: 14.03 and 14.23 (2CH_3 of 2 Et); 26.94 (CH_3 of COMe); 60.89 and 62.15 (2 OCH_2); 125.25, 125.40, 125.58, 125.94, 126.49, and 130.45 (6 CH); 112.64, 124.98, 130.92, 134.44, and 146.64 (5C); 162.09 (C4); 163.33 and 164.83 (2C=O of esters), 204.25 (C=O, ketone). MS(m/z, %): 357 (M^++1, 10); 356 (M^+, 63); 311 (25); 282 (73); 237 (63); 195 (75), 139 (100); 115 (38); 69 (25). Found: C, 67.29; H, 5.67. $C_{20}H_{20}O_6$ requires C, 67.42; H, 5.62%.

3-(3-Acetyl-4-hydroxy-1-naphtyl)-2,5-furandione (7)

Yellow solid, m.p. 225.3–225.5°C; Yield: 51%. UV (EtOH 95%) ($\lambda_{max/nm}$, log ε): 299, 2.08; 309, 1.97; 371, 2.12. IR (KBr) (ν_{max}, Cm^{-1}): 1695, 1626, 1240. ^1H NMR ($CDCl_3$) δ_H:2.70 (3H, s, $COCH_3$), 6.05(1H, d, $^5J_{HH} = 1.5$ Hz, =CHCO—), 6.84 (1H, d, $^5J_{HH} = 1.5$ Hz, H2), 7.5–7.7 (3H, m, H6—H8), 8.51 (1H, d, $^3J_{HH} = 8.3$ Hz, H5), 14.06 (1H, s, O—H$\cdots$O=C). ^{13}C NMR ($CDCl_3$) δ_C: 26.91 (CH_3); 125.19, 125.26, 125.32, 126.08, 126.15 and 130.47 (6 CH); 112.64, 124.94, 132.57, 135.75, and 139.33 (5C); 162.90 (C4); 171.06 and 171.09 (2 C=O of anhydride), 204.19 (C=O of ketone). MS(m/z, %): 282 (M^+, 5); 279 (40); 256 (60); 241 (18); 211 (17); 169 (15); 167 (48); 149 (100); 138 (16); 57 (15); 43 (17). Found: C, 67.91; H, 3.41. $C_{16}H_{10}O_5$ requires C, 68.09; H, 3.55%.

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