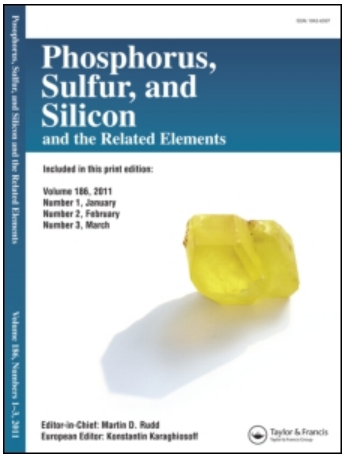


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Microwave Induced 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 the Presence of Silica Gel Powder in Solvent-Free Conditions

Ali Ramazani[a]; Ali Souldozi[a]
[a] Zanjan University, Zanjan, Iran

Online publication date: 27 October 2010

To cite this Article Ramazani, Ali and Souldozi, Ali(2003) 'Microwave Induced 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 the Presence of Silica Gel Powder in Solvent-Free Conditions', Phosphorus, Sulfur, and Silicon and the Related Elements, 178: 10, 2189 — 2192
To link to this Article: DOI: 10.1080/713744559
URL: http://dx.doi.org/10.1080/713744559

Phosphorus, Sulfur, and Silicon, 178:2189–2192, 2003

ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426500390228855

Taylor & Francis
Taylor & Francis Group

MICROWAVE INDUCED 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 THE PRESENCE OF SILICA GEL POWDER IN SOLVENT-FREE CONDITIONS

Ali Ramazani and Ali Souldozi
Zanjan University, Zanjan, Iran

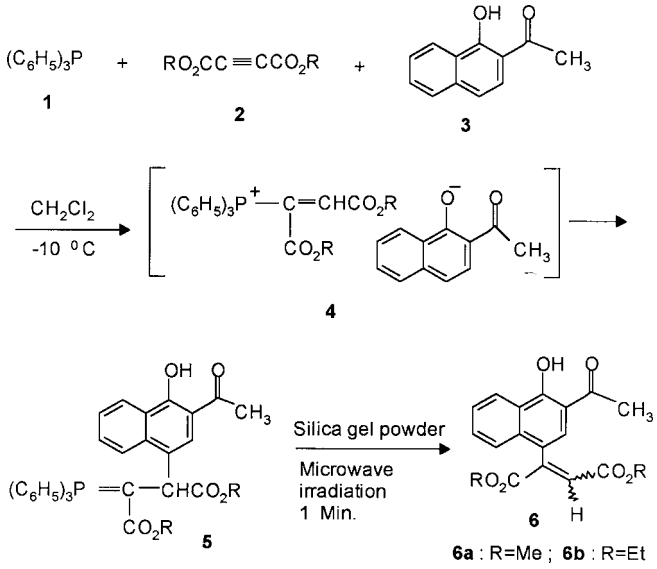
(Received April 29, 2003; accepted May 28, 2003)

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. Microwave 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 the presence of silica gel powder in solvent-free conditions.

Keywords: 1-Hydroxy-2-acetonaphthone; *C*-vinylation; microwave; silica gel; solvent-free conditions

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] In the absence of suitable catalysts, Wittig reactions of the stabilized phosphorus ylides are very slow.[2] 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 for 5–6 min. In the past we have established a convenient, one-pot method for preparing stabilized

This work was supported by the Zanjan University Research Council.
Address correspondence to Ali Ramazani, Chemistry Department, Zanjan University, P.O. Box 45195-313, Zanjan, Iran. E-mail: a-ramazani@mail.znu.ac.ir



SCHEME 1

phosphorus ylides utilizing in situ generation of the phosphonium salts.[3–7] Recently we have reported on the catalytic role of silica gel powder in the conversion of dialkyl 2-(3-acetyl-4-hydroxy-1-naphthyl)-3-(triphenylphosphoranylidene) butanedioates (**5**) to dialkyl 2-(3-acetyl-4-hydroxy-1-naphthyl)-2-butenedioates (**6**) in solvent-free conditions[8] at 90°C in fairly good yields[9] (Scheme 1). The use of microwave irradiation to bring about organic transformations has taken new dimensions in recent years.[10] In this article, we report on the catalytic role of microwave in conversion of dialkyl 2-(3-acetyl-4-hydroxy-1-napthyl)-3-(triphenylphosphoranylidene) butanedioates (**5**) to dialkyl 2-(3-acetyl-4-hydroxy-1-naphthyl)-2-butenedioates (**6**) in the presence of silica gel powder in solvent-free conditions (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. Microwave irradiation was found to catalyze conversion of ylides **5** to vinylated compounds (**6a–b**) in the presence of silica gel

powder in solvent-free conditions (Scheme 1). TLC indicated that the reactions were completed the in solid phase (silica gel powder) under microwave irradiation at microwave power 1 KW after 1 min. We also have used $NaHCO_3$, K_2CO_3, $MgSO_4$, $Mg(HSO_4)_2$, MgO, ZnO, $ZnSO_4$, Al_2O_3, $Al_2(SO_4)_3$, $KAl(SO_4)_2$ $NaHSO_4$, Na_2SO_4, $NaNO_2$, CuO, $CuNO_3$, $CuSO_4$, K_3PO_4, KH_2PO_4, K_2HPO_4, $FeSO_4$, $Mn(NO_3)_2$, $MnSO_4$, and MnO_2 powder instead of silica gel in this reaction, but no corresponding products **6** were observed and in all cases decomposition was observed. The structures **6a–b** were deduced from their melting points, IR and ^{1}H NMR spectra. All of these data are the same as our previously reported data for the compounds **6a–b**.[9]

In summary, we have found that microwave irradiation is able to catalyze conversion of ylides **5** to vinylated compounds **6** in the presence of silica gel powder in solvent-free conditions (Scheme 1). Other aspects of this process are under investigation.

EXPERIMENTAL

Commercial oven Butane M245 was used for microwave irradiation. Melting points were measured on an Electrothermal 9100 apparatus and are uncorrected. IR spectra were recorded on a Shimadzu IR-460 spectrometer. ^{1}H NMR spectra were measured with a BRUKER DRX-500 AVANCE spectrometer at 500 MHz.

*General procedure for the preparation of dialkyl 2-(3-acetyl-4-hydroxy-1-naphthyl)-2-butenedioates (**6a–b**):* 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 irradiated in the microwave oven at microwave power 1 KW (100%) for 1 min and then placed over a column of silica gel (5 g). The column was washed using ethyl acetate-hexane (1:3) as eluent. The solvent was removed under reduced pressure and the products were obtained as yellow solids (**6a–b**). The characterization data of the compounds (**6a–b**) are given in our previous report.[9]

REFERENCES

[1] V. J. Patil and U. Mavers, *Tetrahedron Lett.*, **37,** 1281 (1996).
[2] C. Xu, G. Chen, C. Fu, and X. Huang, *Synth. Commun.*, **25,** 2229 (1995).

[3] A. Ramazani and A. Bodaghi, *Tetrahedron Lett.*, **41,** 567 (2000).
[4] I. Yavari and A. Ramazani, *Synth. Commun.*, **27,** 1385 (1997).
[5] I. Yavari, A. Ramazani, and A. Yahya-Zadeh, *Synth. Commun.*, **26,** 4495 (1996).
[6] I. Yavari and A. Ramazani, *Phosphorus, Sulphur and Silicon*, **130,** 73 (1997).
[7] A. Ramazani, N. Shajari, and F. Gouranlou, *Phosphorus, Sulphur, and Silicon*, **174,** 223 (2001).
[8] K. Tanaka and F. Toda, *Chem. Rev.*, **100,** 1025 (2000).
[9] A. Ramazani, A. Momeni-Movahhed, and F. Gouranlou, *Phosphorus, Sulphur, and Silicon*, **177,** 903 (2002).
[10] S. Munavalli, D. K. Rohrbaugh, G. W. Wagner, F. R. Longo, and H. D. Durst, *Phosphorus, Sulphur, and Silicon*, **177,** 781 (2002).