

This article was downloaded by:

On: 27 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



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>

Dipotassium Hydrogen Phosphate Powder Catalyzed Synthesis of Alkyl 2-(2-Alkoxy-2-oxoethyl)dinaphtho[2,1-*d*:1,2-*f*][1,3]-dioxepin-2-Carboxylates from Stabilized Phosphorus Ylides in Solvent-Free Conditions

Ali Ramazani^a; Issa Amini^{bc}; Abdolhossain Massoudi^c

^a Chemistry Department, Zanzan University, Zanzan, Iran ^b Chemistry Department, Peyam Noor University of Abhar, Abhar, Iran ^c Chemistry Department, Peyam Noor University of Mashhad, Mashhad, Iran

To cite this Article Ramazani, Ali , Amini, Issa and Massoudi, Abdolhossain(2006) 'Dipotassium Hydrogen Phosphate Powder Catalyzed Synthesis of Alkyl 2-(2-Alkoxy-2-oxoethyl)dinaphtho[2,1-*d*:1,2-*f*][1,3]-dioxepin-2-Carboxylates from Stabilized Phosphorus Ylides in Solvent-Free Conditions', *Phosphorus, Sulfur, and Silicon and the Related Elements*, 181: 10, 2373 – 2376

To link to this Article: DOI: 10.1080/10426500600642783

URL: <http://dx.doi.org/10.1080/10426500600642783>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Dipotassium Hydrogen Phosphate Powder Catalyzed Synthesis of Alkyl 2-(2-Alkoxy-2-oxoethyl)dinaphtho[2,1-d:1,2-f][1,3]-dioxepin-2-Carboxylates from Stabilized Phosphorus Ylides in Solvent-Free Conditions

Ali Ramazani

Chemistry Department, Zanjan University, Zanjan, Iran

Issa Amini

Chemistry Department, Peyam Noor University of Abhar, Abhar, Iran;
and Chemistry Department, Peyam Noor University of Mashhad,
Mashhad, Iran

Abdolhossain Massoudi

Chemistry Department, Peyam Noor University of Mashhad,
Mashhad, Iran

The protonation of the highly reactive 1:1 intermediates, produced in the reaction of triphenylphosphine and dialkyl acetylenedicarboxylates, by 1,1-binaphthyl-2,2'-diol leads to vinyltriphenylphosphonium salts, which undergo a Michael addition reaction to produce the corresponding stabilized phosphonium ylides. Dipotassium hydrogen phosphate powder was found to catalyze the conversion of the stabilized phosphonium ylides to alkyl 2-(2-alkoxy-2-oxoethyl)dinaphtho[2,1-d:1,2-f][1,3]-dioxepin-2-carboxylates under solvent-free conditions using microwave (0.6 KW, 3 min) and thermal (100°C, 60 min) conditions.

Keywords 1,1-binaphthyl-2,2'-diol; dipotassium hydrogen phosphate; Michael addition; acetylenic esters; vinyltriphenylphosphonium salt; microwave irradiation

INTRODUCTION

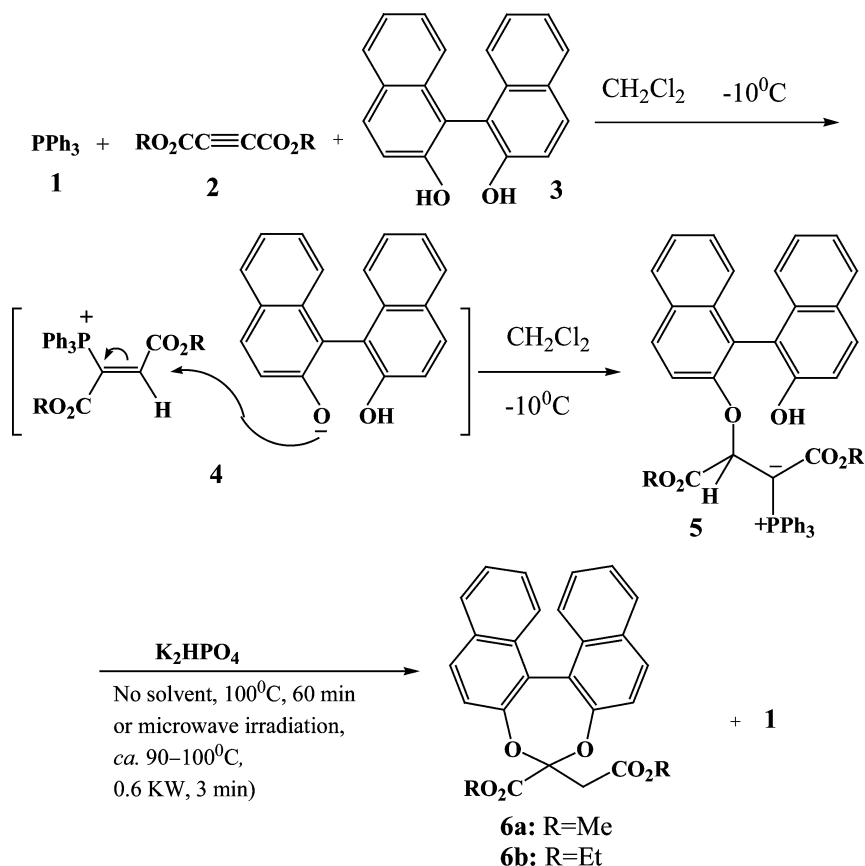
β -additions of nucleophiles to the vinyl group of vinylic phosphonium salts leading to the formation of new alkylidenephosphoranes have attracted much attention as a convenient and synthetically useful method

Received October 28, 2005; accepted February 7, 2006.

This work was supported by Zanjan University, Zanjan, Iran.

Address correspondence to Ali Ramazani, Zanjan University, Chemistry Department, P.O. Box 45195-313, Zanjan, Iran. E-mail: aliramazani@yahoo.com

in organic syntheses.^{1–3} 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.^{4,5} In the past we have established a convenient, one-pot method for the preparation of stabilized phosphonium 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 stabilized phosphonium ylides to alkyl 2-(2-alkoxy-2-oxoethyl)dinaphtho[2,1-*d*:1,2-*f*][1,3]-dioxepin-2-carboxylates under solvent-free conditions using microwave (0.6 KW, 3 min) and thermal (100°C, 60 min) conditions (Scheme 1).



SCHEME 1

RESULTS AND DISCUSSION

The ylides **5** may result from an initial addition of triphenylphosphine **1** on the acetylenic esters **2** and concomitant protonation of the 1:1 adducts by 1,1-binaphthyl-2,2'-diol **3**, followed by a Michael addition reaction of the vinyltriphenylphosphonium salts **4** so formed. TLC indicated the formation of the ylides **5**. Dipotassium hydrogen phosphate powder was found to catalyze the conversion of the stabilized phosphonium ylides **5** to alkyl 2-(2-alkoxy-2-oxoethyl)dinaphtho[2,1-d:1,2-f][1,3]-dioxepin-2-carboxylates **6** under solvent-free conditions using microwave (0.6 KW, 3 min) or thermal (100°C, 60 min) conditions (Scheme 1). We have also used SiO₂, KH₂PO₄, NaH₂PO₄, Na₂HPO₄, and (NH₄)H₂PO₄ in this reaction, but the yield of the product was low, and in some cases decomposition and several byproducts were observed. In the absence of the K₂HPO₄ powder, the powdered ylide **5** did not enter into a reaction under microwave irradiation at a power of 0.6 KW or under thermal (100°C, 60 min) conditions. Only decomposition of the starting materials was observed.

In summary, we have found that dipotassium hydrogen phosphate powder is able to catalyze the conversion of the ylides **5** to dioxepines **6** under solvent-free conditions⁶ (Scheme 1). Other aspects of this process are under investigation.

EXPERIMENTAL

Commercial oven butane M245 was used for microwave irradiation. ¹H and ¹³C NMR spectra were measured with a Bruker DRX-500 Avance spectrometer at 500 and 125 MHz, respectively. IR spectra were recorded on a Shimadzu IR-460 spectrometer.

The General Procedure for the Preparation of Ylides **5** and Compounds **6a,b**

To a magnetically stirred solution of triphenylphosphine **1** (1 mmol) and 1,1-binaphthyl-2,2'-diol **3** (1 mmol) in CH₂Cl₂ (4 mL), a mixture of **2** (1 mmol) in CH₂Cl₂ (3 mL) was added dropwise at -10°C over 15 min. The mixture was allowed to warm up to r.t. to afford intermediate **5**. Dipotassium hydrogen phosphate (1.5 g) was added, and the solvent was evaporated. The mixture was heated at 60°C for 100 min (yield for **6a** and **6b**, 37.1% and 32.4%, respectively) or irradiated in a microwave oven at a microwave power of 0.6 KW for 3 min (yield for **6a** and **6b**, 36.2% and 32.0%, respectively) and then placed over a column of silica gel powder (12 g). The column was washed with ethyl acetate-light

petroleum ether (1:10) as the eluent. The solvent was removed under reduced pressure, and the products were obtained as yellow crystals (**6a,b**) (Scheme 1). Characterization of the compounds (**6a,b**) is given below.

Methyl 2-(2-Methoxy-2-oxoethyl)dinaphtho[2,1-*d*:1,2-*f*][1,3]-dioxepin-2-carboxylate (**6a**)

Yellow crystals; m.p. = 185–186°C. ^1H NMR (CDCl_3) δ_{H} : 3.19 and 3.30 (2 H, AB-system, $^2J_{\text{HH}} = 15.5$ Hz, $\text{CH}_\text{A}\text{H}_\text{B}\text{CO}_2\text{Me}$), 3.79 and 3.84 (6 H, 2 s, 2 OCH_3), 7.1–8.0 (12 H, m, arom. H). ^{13}C NMR (CDCl_3) δ_{C} : 40.9 (CH_2 of $\text{CH}_2\text{CO}_2\text{Me}$); 52.2 and 53.0 (2 OCH_3); 111.5 ($(\text{O})_2\text{C}$); 121.8, 122.4, 125.3, 125.4, 126.0, 126.2, 127.0, 127.1, 128.28, 128.34, 129.9, and 130.0 (12 CH, arom.); 125.2, 125.9, 131.9, 131.97, 132.03, and 132.1 (6 C, arom.); 148.1 and 149.8 (2 OC, arom.); 167.0 and 168.3 (2 $\text{C}=\text{O}$ of esters). IR (KBr) (ν_{max} , cm^{-1}): 3062 and 2923 (C–H); 1713 ($\text{C}=\text{O}$, ester); 1619 ($\text{C}=\text{C}$, arom.).

Ethyl 2-(2-Ethoxy-2-oxoethyl)dinaphtho[2,1-*d*:1,2-*f*][1,3]-dioxepin-2-carboxylate (**6b**)

Yellow crystals; m.p. = 156–157°C. ^1H NMR (CDCl_3) δ_{H} : 1.31 and 1.33 (6 H, 2 t, $^3J_{\text{HH}} = 7.1$ Hz, 2 CH_3 of 2 Et); 3.17 and 3.28 (2 H, AB-system, $^2J_{\text{HH}} = 15.4$ Hz, $\text{CH}_\text{A}\text{H}_\text{B}\text{CO}_2\text{Et}$), 4.2–4.3 (2 H, m, OCH_2 of $(\text{O})_2\text{CCO}_2\text{Et}$); 4.31 (2 H, q, $^3J_{\text{HH}} = 7.1$ Hz, OCH_2 of $\text{CH}_\text{A}\text{H}_\text{B}\text{CO}_2\text{Et}$); 7.2–8.0 (12 H, m, arom. H). ^{13}C NMR (CDCl_3) δ_{C} : 14.07 and 14.09 (2 CH_3 of 2 Et); 41.2 (CH_2 of $\text{CH}_2\text{CO}_2\text{Et}$); 61.1 and 62.3 (2 OCH_2); 111.5 ($(\text{O})_2\text{C}$); 122.1, 122.6, 125.2, 125.4, 125.9, 126.1, 127.1, 127.2, 128.26, 128.33, 129.7, and 129.9 (12 CH, arom.); 125.2, 126.0, 131.89, 131.92, 132.0, and 132.1 (6 C, arom.); 148.3 and 149.9 (2 OC, arom.); 166.4 and 167.8 (2 $\text{C}=\text{O}$ of esters). IR (KBr) (ν_{max} , cm^{-1}): 3370, 2977, and 2939 (C–H); 1743 ($\text{C}=\text{O}$, ester); 1589 ($\text{C}=\text{C}$, arom.).

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*, Ed. J. I. G. Cadogan (Academic Press, New York, 1979).
- [3] A. Ramazani and A. Bodaghi, *Tetrahedron Lett.*, **41**, 567 (2000).
- [4] V. J. Patil and U. Mavers, *Tetrahedron Lett.*, **37**, 1281 (1996).
- [5] C. Xu, G. Chen, C. Fu, and X. Huang, *Synth. Commun.*, **25**, 2229 (1995).
- [6] K. Tanaka and F. Toda, *Chem. Rev.*, **100**, 1025 (2000).