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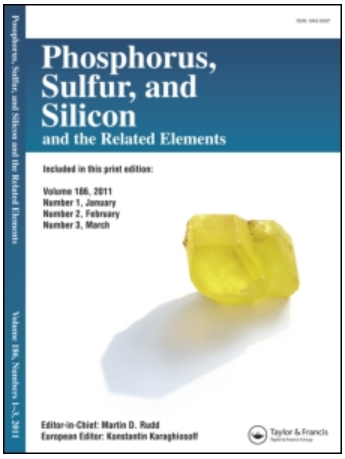

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
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Dipotassium Hydrogen Phosphate Powder Catalyzed Conversion of Dialkyl 2-(2,5-Dihydroxyphenyl)-3-(1,1,1-triphenyl-λ^5-phosphanylidene)succinates to Alkyl 6-Hydroxy-2-oxo-2*H*-chromen-4-carboxylates

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To cite this Article Souldozi, Ali , Ramazani, Ali and Noshiranzadeh, Nader(2006) 'Dipotassium Hydrogen Phosphate Powder Catalyzed Conversion of Dialkyl 2-(2,5-Dihydroxyphenyl)-3-(1,1,1-triphenyl-λ^5-phosphanylidene)succinates to Alkyl 6-Hydroxy-2-oxo-2*H*-chromen-4-carboxylates', Phosphorus, Sulfur, and Silicon and the Related Elements, 181: 3, 587 — 589
To link to this Article: DOI: 10.1080/10426500500269570
URL: http://dx.doi.org/10.1080/10426500500269570

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Phosphorus, Sulfur, and Silicon, 181:587–589, 2006
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ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426500500269570

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Protonation of the highly reactive 1:1 intermediates, produced in the reaction between triphenylphosphine and dialkyl acetylenedicarboxylates, by hydroquinone leads to vinyltriphenylphosphonium salts, which undergo an electrophilic substitution reaction with a conjugate base to produce corresponding stabilized phosphorus ylides. Dipotassium hydrogen phosphate powder was found to catalyze conversion of the stabilized phosphorus ylides to alkyl 6-hydroxy-2-oxo-2H-chromene-4-carboxylates under thermal or microwave irradiation in solvent-free conditions.

Keywords Dipotassium hydrogen phosphate; hydroquinone; acetylenic ester; triphenylphosphine; vinyltriphenylphosphonium salt

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INTRODUCTION

Coumarins are very well-known natural products and many such compounds exhibit high levels of biological activity.[1] They are used as anticoagulants and additives in food and cosmetics, and in the preparation of insecticides, optical brighteners, and dispered fluorescent and laser dyes.[2] Silica gel as an addative promotes the Wittig reactions of phosphorus ylides with aldehydes, including sterically hindered aldehydes to increase the rate and yields of alkenes.[3,4] In the past we have established a convenient, one-pot method for preparing stabilized phosphorus ylides utilizing in situ generation of phosphonium salt.[5–10] In this article, we report on the catalytic action of dipotassium hydrogen

Received May 10, 2005; accepted May 10, 2005.
This work was supported by Zanjan University.
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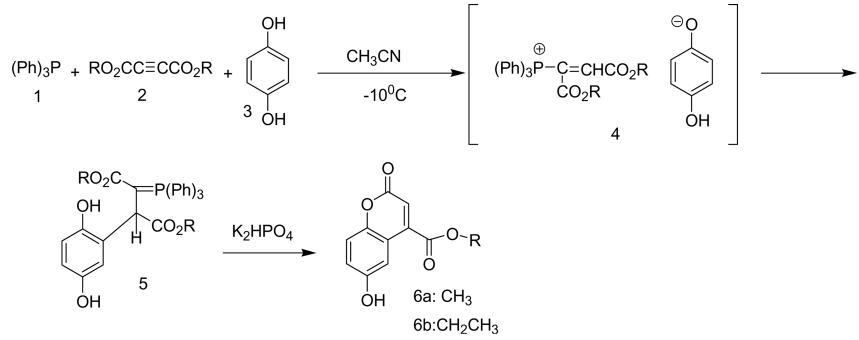
phosphate powder in the conversion of dialkyl 2-(2,5-dihydroxyphenyl)-3-(1,1,1-triphenyl-λ^5-phosphanylidene)succinates to alikyl 6-hydroxy-2-oxo-2*H*-chromene-4-carboxylates in solvent-free conditions under microwave irradiation and thermal conditions in fairly high yields (Scheme 1).



SCHEME 1

RESULTS AND DISCUSSION

The ylide **5** may result from an 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 carbanion **4** (Scheme 1). TLC indicated the formation of ylides **5** in CH_3CN.

Dipotassium hydrogen phosphate powder was found to catalyze the conversion of the stabilized phosphorus ylides **5** to alkyl 6-hydroxy-2-oxo-2*H*-chromene-4-carboxylates **6** under thermal or microwave irradiation in solvent-free conditions. TLC indicated that the reaction was completed in the solid phase (dipotassium hydrogen phosphate powder) under microwave irradiation at a microwave power of 0.5 after 3 min and in thermal conditions of 90°C after 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. The structures were deduced from their melting points IR and ^1H and ^{13}C NMR spectra. All of these data are the same as previously reported data for compound **6**.[11] Conversion of ylides **5** to coumarins **6** was reported in previously refluxing toluene.[11] In the refluxing toluene, the reaction time is fairly long (several hours).[11] In summary, we have found that dipotassium hydrogen phosphate powder is able to catalyze the conversion of the

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stabilized phosphorus ylides **5** to coumarins **6** under thermal and microwave conditions in a solventless 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. ^{1}H 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 hydroquinone **3** (0.22 g, 2 mmol) in CH_3CN (15 mL) a mixture of **2** (2 mmol) in CH_3CN (6 mL) at –10°C over 15 min was added dropwise. 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 at 90°C (or irradiated at microwave power 0.5 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 (1:2) as an eluent. The solvent was removed under reduced pressure and the products were obtained as pale yellow crystals (**6a:** m.p. 203.7–204.2°C, Yield, 64.45%; **6b:** m.p. 197.3–197.7°C, Yield, 59.79%.). The characterization data of the compounds (**6a–b**) are the as same as previously reported data for compounds **6**.[11]

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REFERENCES

[1] I. Jabin, N. D. Heindel, R. D. Rapp, and J. D. Laskin, *J. Heterocyclic Chem.*, **37,** 31 (2000).
[2] M. K. Potadar, S. S. Mohile, and M. M. Salunkhe, *Tetraheadron Lett.,* **42,** 9285 (2001).
[3] V. J. Patil and U. Maveres, *Tetraheadron Lett.,* **37,** 1281 (1996).
[4] C. Xu, G. Chen, C. Fu, and X. Huang, *Synth. Commun.*, **25,** 2229 (1995).
[5] A. Ramazani and A. Bodaghi, *Tetraheadron Lett.*, **41,** 567 (2000).
[6] I. Yavari and A. Ramazani, *Synth. Commun.*, **27,** 1385 (1997).
[7] I. Yavari, A. Ramazani, and A. Yahya-zadeh, *Synth. Commun.*, **26,** 4495 (1996).
[8] I. Yavari and A. Ramazani, *Phosphorus, Sulphur and Silicon*, **130,** 73 (1997).
[9] A. Ramazani, N. Shajari, and F. Gouranlou, *Phosphorus, Sulphur, and Silicon,* **174,** 223 (2001).
[10] A. Ramazani, A. Momeni-Movahhed, and F. Gouranlou, *Phosphorus, Sulphur, and Silicon*, **177,** 903 (2002).
[11] I. Yavari, M. Adib, and L. Hojabri, *Tetraheadron*, **57,** 7537 (2001).