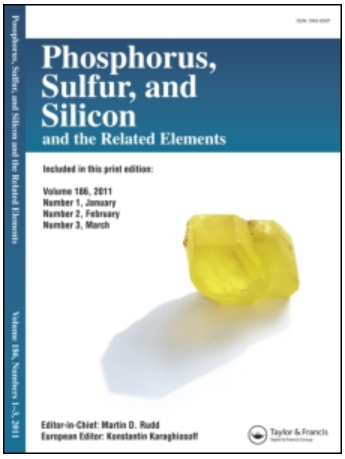

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Microwave-Induced Stereoselective Conversion of Stabilized Phosphorus Ylides to Electron Poor (*Z*)-*N*-Vinylimides in the Presence of Supported Catalysts on Silica Gel in Solvent-Free Conditions

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To cite this Article Kazemizadeh, Ali Reza , Ahmadi, Ebrahim , Marandi, Farzin and Ramazani, Ali(2007) 'Microwave-Induced Stereoselective Conversion of Stabilized Phosphorus Ylides to Electron Poor (*Z*)-*N*-Vinylimides in the Presence of Supported Catalysts on Silica Gel in Solvent-Free Conditions', Phosphorus, Sulfur, and Silicon and the Related Elements, 182: 12, 2855 — 2859
To link to this Article: DOI: 10.1080/10426500701521837
URL: http://dx.doi.org/10.1080/10426500701521837

Phosphorus, Sulfur, and Silicon, 182:2855–2859, 2007

ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426500701521837

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Supported catalyst on silica-gel were found to catalyze stereoselective conversion of dialkyl 2-(imido-N-yl)-3-triphenylphosphoranylidene)butanedioates to electron-poor (Z)-N-vinylimides in solvent-free conditions under microwave irradiation in 2 to 3 minutes in high conversions. The reaction is completely stereoselective.

Keywords Microwave irradiation; phosphorus ylide; supported catalysts; solvent-free conditions; (*Z*)-*N*-vinylimide

INTRODUCTION

Organophosphorus compounds have been extensively employed in organic synthesis[1–16] as useful reagents, as well as ligands in a number of transition metal catalysts.[17] β-Additions of nucleophiles to the vinyl group of vinylic phosphonium salts leading to the formation of new alkylidenephosphoranes has attracted much attention as a very convenient and synthetically useful method in organic synthesis.[18–30]

Received April 2, 2007; Accepted May 24, 2007.
The Zanjan University supported this work.
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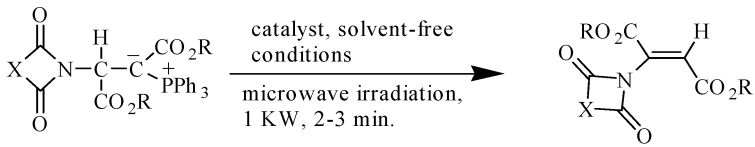
Phosphorus ylides are important reagents in synthetic organic chemistry, especially in the synthesis of naturally occurring products, compounds with biological and pharmacological activity.[6] Phosphorus ylides are a class of special type of zwitterions, which bear strongly nucleophilic electron rich carbanions. The electron distribution around the P^+–C^- bond and its consequent chemical implications had been probed and assessed through theoretical, spectroscopic and crystallographic investigations.[30] Proton affinity of these ylides can be used as a molecular guide to assess their utility as synthetic reagents and their function as ligands in coordination and organometallic chemistry.[17,30] The nucleophilicity at the ylidic carbon is a factor of essential mechanistic importance in the use of these ylides as Wittig reagents.

Some of the compounds containing *N*-vinyl group are monomers that free-radically polymerizes to produce water-soluble polymers with potentially useful properties. The monomers are probably the most practical precursors for preparation of poly(vinylamine). Poly(vinylformamide) is likely the best route to the generation of polyvinyl amine as useful and less toxic alternative to polyacrylamide and other cationic water-soluble polymers. poly(vinylformamide) is easily hydrolyzed under basic or acidic conditions to form poly(vinylamine).[31] Based on this subject, it seems that the prepared *N*-vinyl imides in this article may be used as interesting precursors for the synthesis of poly(glutamic acid) and polyimides by polymer chemists.

Waste prevention and environmental protection are major requirements in an overcrowded world of increasing demands. Synthetic chemistry continues to develop various techniques for obtaining better products with less environmental impact. One of the more promising approaches is solvent-free organic synthesis.[32] In this regard, solvent-free catalytic organic reaction has received tremendous attention in recent times.[33] In the past, we have established a convenient, one-pot method for preparing stabilized phosphorus ylides utilizing in situ generation of the phosphonium salts.[18–28] In this article, we report on the catalytic role of supported salts on silica gel in the stereoselective conversion of dialkyl 2-(imido-*N*-yl)-3-(triphenylphosphoranylidene)butanedioates (**1**)[28] to electron-poor (*Z*)-*N*-vinylimides (**2**)[27] in solvent-free conditions[34] under microwave irradiation in 2–3 minutes in high conversions (Scheme 1).

RESULTS AND DISCUSSION

The salts NaH_2PO_4, Na_2HPO_4, KH_2PO_4, K_2HPO_4, and $MnSO_4$—supported on silica-gel—were found to catalyze stereoselective conversion of dialkyl 2-(imido-*N*-yl)-3-triphenylphosphoranylidene)



1a-d **2a-d**

2	**a**	**b**	**c**	**d**
R	Me	Et	Me	Et
X	$(CH_2)_2$	$(CH_2)_2$	o-C_6H_4	o-C_6H_4

SCHEME 1

butanedioates (**1a–d**) to electron-poor (*Z*)-*N*-vinylimides (**2a–d**) in solvent-free conditions under microwave irradiation in 2–3 minutes at microwave power 1 KW in high conversions (Scheme 1). TLC indicated that the reactions were completed in the presence of these supported catalysts after 3 min for dialkyl 2-(2,5-dioxo-pyrrolidin-1-yl)-3-(triphenyl-λ^5-phosphoranylidene)-succinates (**1a–b**) and 2 minutes for dialkyl 2-(1,3-dioxo-1,3-dihydro-isoindol-2-yl)-3-(triphenyl-λ^5-phosphoranylidene)-succinates (**1c–d**). The reaction proceeds smoothly and cleanly under solvent-free conditions, and no side reactions were observed. In the absence of these supported catalysts, this reaction did not afford the corresponding compounds (**2a–d**), even at reflux temperature (toluene as solvent) after 24 h. We have also used NaH_2PO_4, Na_2HPO_4, KH_2PO_4, K_2HPO_4, and $MnSO_4$ supported on γ-Al_2O_3, and pure γ-Al_2O_3 (salt-free γ-Al_2O_3) in this reaction under microwave (1 KW, 6 min) conditions, but in all cases, the reactions did not occur. The mechanism of the conversion of **1a–d** to **2a–d** in the presence of the supported catalysts in solvent-free conditions has not been established experimentally. However, it seems that in this reaction, supported salts act as a general acid-base catalyst.[34] The structures of **2a–d** were deduced from their ^{1}H NMR, and ^{13}C NMR spectra. The reaction is completely stereoselective. The full characterization data of the compounds (**2a–d**) are given in our previous report.[27]

CONCLUSIONS

In summary, we have found that salts NaH_2PO_4, Na_2HPO_4, KH_2PO_4, K_2HPO_4, and $MnSO_4$—supported on silica gel—are able to catalyze stereoselective conversion of ylides **1a–d** to compounds **2a–d** in solvent-free conditions under microwave irradiation. The reaction is completely stereoselective. We believe the reported method offers a mild, simple,

and efficient route for the preparation of substituted electron-poor *N*-vinyl imides **2a-d**. Its ease of work up, high conversions, and short reaction times make it a useful addition to modern synthetic methodologies. 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 and ^{13}C NMR spectra were measured with a BRUKER DRX-500 AVANCE spectrometer at 500 and 125 MHz, respectively.

General Procedure for the Preparation of Supported Catalysts

A mixture of 0.54 mmol salt, 2.5 g silica-gel or γ-Al_2O_3,and 25 ml of distilled methanol was stirred at room temperature for 24 h. The mixture was filtered with sintered glass and then washed with 5 $\times$ 2.5 ml methanol. Then the catalyst was air dried and placed in an oven at 120°C for 2 h.

General Procedure for the Preparation of Compounds 2a–d

The powdered mixture of supported catalyst (2 g) and ylide **1** (1 mmol) were irradiated in the microwave oven at microwave power 1 KW(100%) for 2–3 min and then placed over a column of silica gel (10 g). The column chromatography was washed using ethyl acetate-light petroleum ether (1:9) as eluent. The solvent was removed under reduced pressure and products (**2a–d**) were obtained. The characterization data of the compounds (**2a–d**) are given in our previous report.[27]

REFERENCES

[1] O. I. Kolodiazhnyi, *Russ. Chem. Rev*., **66,** 225 (1997).
[2] K. M. Pietrusiewiz and M. Zablocka, *Chem. Rev*., **94,** 1375 (1994).
[3] J. I. G. Cadogan, *Organophosphorus Reagents in Organic Synthesis,* J. I. G. Cadogon, Ed. (Academic Press, New York, 1979).
[4] B. E. Maryanoff and A. B. Reitz, *Chem. Rev*., **89,** 863 (1989).
[5] R. A. Cherkasov and M. A. Pudovik, *Russ. Chem. Rev*., **63,** 1019 (1994).
[6] O. I. Kolodiazhnyi, *Phosphorus ylides, Chemistry and Application in Organic Synthesis* (Wiley-VCH, New York, 1999).
[7] H. J. Bestmann, *Angew. Chem*., **89,** 361 (1977).
[8] A. W. Johnson, *Ylide Chemistry* (Academic Press, London, 1966).

[9] G. Keglevich, H. Forintos, T. Körtvélyesi, and L. Tke, *J. Chem. Soc., Perkin Trans.*, **1,** 26 (2002).
[10] G. Keglevich, T. Körtvélyesi, H. Forintos, Á. Gy. Vaskó, V. Izvekov, and L. Tke, *Tetrahedron*, **58,** 372 (2002).
[11] G. Keglevich, T. Körtvélyesi, H. Forintos, and S. Lovas, *J. Chem. Soc. Perkin Trans.*, **2,** 1645 (2002).
[12] G. Keglevich, H. Forintos, A. Ujvári, T. Imre, K. Ludányi, Z. Nagy, and L. Tke, *J. Chem. Res.*, 432 (2004).
[13] G. Keglevich, T. Körtvélyesi, A. Ujvári, and E. Dudás, *J. Organomet. Chem.,* **690**,2497 (2005).
[14] G. Keglevich, E. Dudás, M. Sipos, D. Lengyel, and K. Ludányi, *Synthesis,* 1365 (2006).
[15] G. Keglevich, H. Forintos, and T. Körtvélyesi, *Current Org. Chem.*, **8,** 1245 (2004).
[16] V. Nair, C. Rajesh, A. U. Vinod, S. Bindu, A. R. Sreekanth, J. S. Mathess, and L. Balagopal, *Acc. Chem. Res*., **36,** 899 (2003).
[17] W. C. Kaska, Coord. Chem. Rev. **48,** 1 (1983).
[18] A. Ramazani, A. Abbasi Motejadded, and E. Ahmadi, *Phosphorus, Sulfur, and Silicon,* **181,** 233 (2006) and references cited therein.
[19] I. Yavari and A. Ramazani, *Synth. Commun.*, **27,** 1449 (1997).
[20] A. Ramazani and A. Bodaghi, *Tetrahedron Lett.*, **41,** 567 (2000).
[21] I. Yavari, A. Ramazani, and A. Yahya-Zadeh, *Synth. Commun.*, **26,** 4495 (1996).
[22] I. Yavari and A. Ramazani, *Phosphorus, Sulphur, and Silicon*, **130,** 73 (1997).
[23] A. Ramazani, A. Momeni-Movahhed, and F. Gouranlou, *Phosphorus, Sulphur, and Silicon,* **177,** 903 (2002).
[24] A. Ramazani, B. Mohammadi, and N. Noshiranzadeh, *Phosphorus, Sulphur, and Silicon,* **178,** 545 (2003).
[25] A. Ramazani, B. Mohammadi, and N. Noshiranzadeh, *Phosphorus, Sulphur, and Silicon,* **178,** 767 (2003).
[26] A. Ramazani, N. Noshiranzadeh, and B. Mohammadi, *Phosphorus, Sulphur, and Silicon,* **178,** 761 (2003).
[27] A. Ramazani, N. Noshiranzadeh, and B. Mohammadi, *Phosphorus, Sulphur, and Silicon,* **178,** 539 (2003).
[28] A. Ramazani and H. Ahani, *Phosphorus, Sulphur, and Silicon,* **170,** 181 (2001).
[29] K. Becker, *Tetrahedron*, **36**, 1717 (1980).
[30] D. E. C. Cobridge, *Phosphorus: An Outline of Chemistry, Biochemistry and Uses* (Elsevier, Amsterdam, 1995), 5th ed.
[31] E. J. Beckman, T. M. Chapman, C. G. Favero, C. C. Capelli, and H. E. Swift, *United States Patent*, 6965052, (2005).
[32] N. Deka, A.-M. Mariotte, and A. Boumendjel, *Green Chemistry*, **3,** 263 (2001).
[33] M. Kidwai, R. Venkataramanan, and B. Dave, *Green Chemistry*, **3,** 278 (2001).
[34] K. Tanaka and F. Toda, *Chem. Rev.*, **100,** 1025 (2000).