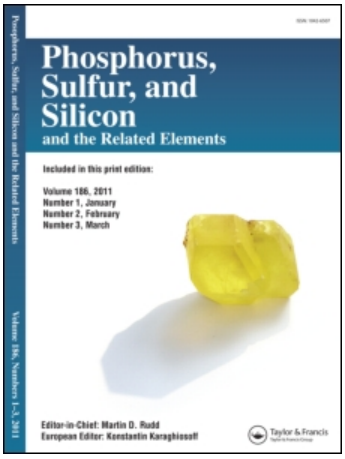
This article was downloaded by:
On: *28 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



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

Manganese Dioxide is an Efficient Catalyst for the Stereoselective Conversion of Dialkyl 2-(Imido-*N*-yl)-3-(triphenylphosphoranylidene)butanedioates to Electron-Poor (*Z*)-*N*-vinylimides in Solvent-Free Conditions

Ali Ramazani; Ebrahim Ahmadi

Online publication date: 18 June 2010

To cite this Article Ramazani, Ali and Ahmadi, Ebrahim(2003) 'Manganese Dioxide is an Efficient Catalyst for the Stereoselective Conversion of Dialkyl 2-(Imido-*N*-yl)-3-(triphenylphosphoranylidene)butanedioates to Electron-Poor (*Z*)-*N*-vinylimides in Solvent-Free Conditions', Phosphorus, Sulfur, and Silicon and the Related Elements, 178: 12, 2659 — 2661

To link to this Article: DOI: 10.1080/714040979

URL: http://dx.doi.org/10.1080/714040979

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.

Phosphorus, Sulfur, and Silicon, 178:2659–2661, 2003
Copyright © Taylor & Francis Inc.
ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426500390248385

Taylor & Francis
Taylor & Francis Group

MANGANESE DIOXIDE IS AN EFFICIENT CATALYST FOR THE STEREOSELECTIVE CONVERSION OF DIALKYL 2-(IMIDO-*N*-YL)-3-(TRIPHENYLPHOSPHORANYLIDENE)-BUTANEDIOATES TO ELECTRON-POOR (*Z*)-*N*-VINYLIMIDES IN SOLVENT-FREE CONDITIONS

Ali Ramazani and Ebrahim Ahmadi
Zanjan University, Zanjan, Iran

Downloaded At: 10:38 28 January 2011

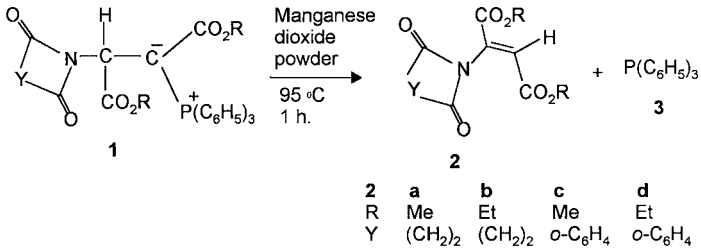
*Manganese dioxide was found to catalyze stereoselective conversion of dialkyl 2-(imido-*N*-yl)-3-(triphenylphosphoranylidene)butanedioates to electron-poor (Z)-N-vinylimides in solvent-free conditions at 95°C in high coversions.*

Keywords: Catalyst; manganese dioxide; phosphorus ylide; solvent-free conditions; (*Z*)-*N*-vinylimide

Organophosphorus compounds have been used extensively in organic synthesis as useful reagents as well as ligands of a number of transition metal catalysts.[1] 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.[1–11] In the past we have established a convenient, one-pot method for preparing stabilized phosphorus ylides utilizing in situ generation of the phosphonium salts.[1–11] In this article, we report on the catalytic rule of manganese dioxide powder in the stereoselective conversion of dialkyl 2-(imido-*N*-yl)-3-(triphenylphosphoranylidene)butanedioates (**1**)[11] to electron-poor (*Z*)-*N*-vinylimides (**2**)[10] in solvent-free conditions[13] at 95°C with high coversions (Scheme 1).

This work was supported by Zanjan University.

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

RESULTS AND DISCUSSION

Manganese dioxide powder was found to catalyze stereoselective conversion of ylides **1**[11] to electron-poor (*Z*)-*N*-vinylimides (**2**)[10] in solvent-free conditions[13] at 95°C with high coversions (Scheme 1).[10–11] TLC indicated that the reaction was completed after 1 h. The reaction proceeds smoothly and cleanly under solvent-free conditions[15] at 95°C (in all cases the reaction works efficiently with high coversions) and no side reactions were observed. In the absence of manganese dioxide powder, this reaction did not afford the corresponding compounds (**2a**) even at reflux temperature (toluene as solvent) after 24 h. TLC indicated that the solution contained unreacted ylide **1a**.[11]

We also have used Al_2O_3, $CuSO_4$, $ZnSO_4$, Na_2SO_4, $NaNO_3$, $Cu(NO_3)_2$, $Mn(NO_3)_2$, and K_2CO_3 powder instate of manganese dioxide in this reaction, but no corresponding product **2** was observed, and in all cases decomposition was observed. The structures of **2a–d** were deduced from their ^{1}H NMR and ^{13}C NMR spectra and via x-ray single crystal (for **2c**) structure determination.[12]

In summary, we have found that manganese dioxide powder is able to catalyze stereoselective conversion of ylides **1**[11] to compounds **2**[10] in solvent-free conditions. Other aspects of this process are under investigation.

EXPERIMENTAL

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 500 and 125 MHz respectively.

Downloaded At: 10:38 28 January 2011

General Procedure for the Preparation of Compounds 2a–d

The powdered mixture of dry manganese dioxide (2 g) and ylide **1**[11] (1 mmol) was heated for 1 h at 95°C and then placed over a column of silica gel (12 g). The column chromatography was washed using ethyl acetate-light petroleum ether (1:9) as eluent. The solvent was removed under reduced pressure and the products (**2a–d**) were obtained. The characterization data of the compounds (**2a–d**) are given in our previous report.[10]

REFERENCES

[1] I. Yavari and A. Ramazani, *Synth. Commun.*, **27,** 1449 (1997).
[2] A. Ramazani and A. Bodaghi, *Tetrahedron Lett.*, **41,** 567 (2000).
[3] I. Yavari, A. Ramazani, and A. Yahya-Zadeh, *Synth. Commun.*, **26,** 4495 (1996).
[4] I. Yavari and A. Ramazani, *Phosphorus, Sulphur, and Silicon*, **130,** 73 (1997).
[5] A. Ramazani, N. Shajari, and F. Gouranlou, *Phosphorus, Sulphur, and Silicon*, **174,** 223 (2001).
[6] A. Ramazani, A. Momeni-Movahhed, and F. Gouranlou, *Phosphorus, Sulphur, and Silicon*, **177,** 903 (2002).
[7] A. Ramazani, B. Mohammadi, and N. Noshiranzadeh, *Phosphorus, Sulphur, and Silicon*, **178,** 545 (2003).
[8] A. Ramazani, B. Mohammadi, and N. Noshiranzadeh, *Phosphorus, Sulphur, and Silicon*, **178,** 767 (2003).
[9] A. Ramazani, N. Noshiranzadeh, and B. Mohammadi, *Phosphorus, Sulphur, and Silicon*, **178,** 767 (2003).
[10] A. Ramazani, N. Noshiranzadeh, and B. Mohammadi, *Phosphorus, Sulphur, and Silicon*, **178,** 539 (2003).
[11] A. Ramazani and H. Ahani, *Phosphorus, Sulphur, and Silicon*, **170**, 181 (2001).
[12] A. Ramazani, A. Morsali, and N. Noshiranzadeh, *Z. Kristallogr. NCS*, **218**, 0000 (2003).
[13] K. Tanaka and F. Toda, *Chem. Rev.*, **100,** 1025 (2000).

Downloaded At: 10:38 28 January 2011