This article was downloaded by: [Johann Christian Senckenberg] On: 05 September 2014, At: 04:03 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



# Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry

Publication details, including instructions for authors and subscription information: <u>http://www.tandfonline.com/loi/lsyc20</u>

# Microwave Heating in Synthesis: Preparation of Allyldiphenylphosphine Oxide

Raymond J. Giguere <sup>a</sup> & Brad Herberich <sup>a</sup> <sup>a</sup> Department of Chemistry and Physics , Skidmore

<sup>a</sup> Department of Chemistry and Physics, Skidmore College, Saratoga Springs, New York, 12866-1632 Published online: 18 Nov 2011.

To cite this article: Raymond J. Giguere & Brad Herberich (1991) Microwave Heating in Synthesis: Preparation of Allyldiphenylphosphine Oxide, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 21:21, 2197-2201, DOI: <u>10.1080/00397919108055453</u>

To link to this article: http://dx.doi.org/10.1080/00397919108055453

## PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the "Content") contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages,

and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden. Terms & Conditions of access and use can be found at http://www.tandfonline.com/page/terms-and-conditions

### MICROWAVE HEATING IN SYNTHESIS: PREPARATION OF ALLYLDIPHENYLPHOSPHINE OXIDE

Raymond J. Giguere\* and Brad Herberich1

Department of Chemistry and Physics, Skidmore College, Saratoga Springs, New York 12866-1632

Abstract: A new one-pot synthesis of allyldiphenylphosphine oxide has been developed using a tandem Sn2' / Michaelis-Arbuzov sequence. The application of microwave heating lowers the reaction time significantly.

Yamamoto's preparation of allyldiphenylphosphine oxide, a synthetic reagent that has been studied extensively in his group, is a two-step method beginning with allyl alcohol and chlorodiphenylphosphine.<sup>2a</sup> This method produces allyldiphenylphosphine oxide in a 65-73% yield. In repeating this work our research group has been frustrated by inconsistent results, therefore an alternative synthesis has been developed.<sup>2b-d</sup> The new one-step preparation is the reaction of commercially available ethyl diphenylphosphinite **1** and allyl bromide to afford product yields between 82-88%. The reaction is accomplished overnight under mild room

<sup>\*</sup> To whom correspondence should be addressed

Conditions	<b>Isolated Yield(%)</b> (250 mg scale)
Co RT, 24 h 130 °C, 1 h	onventional 82 85
Ν	licrowave
3 min	82
(205- 275 °C) 2 min	86
(177-205 °C) 1 min	83
(177-205 °C)	

<u>Table I</u>

temperature conditions<sup>3</sup> or can be accelerated by microwave heating (Table I) and thereby completed in one minute.



The proposed mechanism is a Sn2' reaction of ethyl diphenylphosphinite 1 and allyl bromide 2 followed by an intermolecular Michaelis-Arbuzov reaction of intermediate 3 and the bromide ion.

**Conclusion**: The new one-step preparation of allyldiphenylphosphine oxide is a facile and direct synthesis. Allyldiphenylphosphine oxide finds use as a Wittig reagent to prepare terminal 1,3-dienes from aldehydes.<sup>4</sup>

#### **Experimental:**

General. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Varian Gemini 200 spectrometer in solutions of deuterated chloroform with TMS as internal standard. UV-Vis spectra were recorded on a Hewlett Packard 8452A diode array spectrophotometer.

Conventional. Ethyl diphenylphosphinite (0.20 ml, 210.4 mg, 1.04 mmole) was added to allyl bromide (0.10 ml, 137.8 mg, 1.14 mmole) in a round bottomed flask. The flask was stoppered and allowed to stand overnight without stirring. The next day white crystals appeared. The ethyl bromide was removed by rotary evaporation and the crystals triturated with 5 ml of pentane, filtered, and dried under vacuum to give allyldiphenylphosphine oxide (197.5 mg, 0.816 mmole, 85% yield) as white plates. The product is pure as recovered but may be recrystallized from cyclohexane, if desired. Mp: 97-99 °C (lit.<sup>4</sup> 94-95 °C). TLC (silica gel; 1% MeOH/ EtOAc)  $R_f = 0.29$ . <sup>1</sup>H-NMR (200 MHz), 7.83-7.71 (m, 4H), 7.59-7.41 (m, 6H), 5.94-5.69 (m, 1H), 5.24-5.17 (m, 1H), 5.17-5.08 (m,1H), 3.23-3.09  $(qt, J= 7.4 Hz, J=1.2 Hz, 2H); {}^{13}C-NMR (200 MHz) 132.3, 132.2,$ 

131.8, 131.5, 131.3, 129.1, 128.8, 127.5, 127.3, 121.5, 121.3, 36.9, 35.5. (Additional <sup>13</sup>C peaks due to phosphorous-carbon coupling); UV (CH<sub>2</sub>Cl<sub>2</sub>,  $\lambda_{max}$ ): 248 nm.

A thick-walled ampule (10 ml capacity) is Microwave. charged with ethyldiphenylphosphinite (0.20 ml, 210.4 mg, 1.04 mmol) and allyl bromide (0.10 ml, 137.8 mg, 1.14 mmol) and sealed under vacuum. The tube is strapped with melting point capillaries each charged with compounds of known melting point (between 158-277 °C).6 The tube is then buried in a bed of vermiculite held in a Corian container<sup>7</sup> and placed in a commercial microwave oven (Sanyo EM-2500LA) contained in a fume hood. The sample is irradiated for the indicated time (Table I) with the hood sash completely down, allowed to cool briefly and carefully removed from the oven (Caution: Use a protective shield and thick insulative gloves). The tube is carefully removed from the Corian container, allowed to cool The contents are transferred to a round bottomed and opened. flask using dichloromethane as a solvent and the product isolated in the manner described above. Isolated yields are found in Table I.

Acknowledgement: Brad Herberich gratefully acknowledges support for this research by the Council on Undergraduate Research Academic-Industrial Undergraduate Research Partnership (AIURP) Fellowship sponsered by Pfizer Central Research (1990).

### References:

1. Academic-Industrial Undergraduate Research Partnership Fellowship recepient 1990. Presented by Brad Herberich at the Fifth National Conference on Undergraduate Research, California Institute of Technology, April 1991, Abstract No. CHM. II. 2D.

 (a) Ikeda, Y.; Ukai, J.; Ikeda, N.; Yamamoto, H. Tetrahedron Lett. 1987, 43, 723. and references therein. For other methods see: (b) Collins, D. J.; Mollard, S.-A.; Rose, N.; Swan, J. M. Aust. J. Chem. 1974, 27, 2365. (c) Grayson, J. I.; Warren S.; Zaslona, A. T. J. Chem. Soc. Perkin Trans. I 1987, 967. (d) Lu, X.; Zhu, J.; Huang, J.; Tao, X. J. Molecular Catalysis 1987, 41, 235.

3. We have scaled up the reaction to 10 g and received a 88% yield.

(Received in USA 17 June, 1991)