

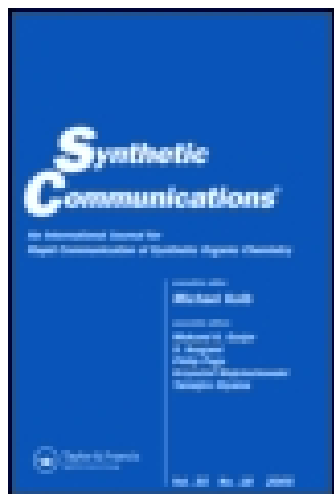
This article was downloaded by: [Stony Brook University]

On: 22 October 2014, At: 22:11

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:

<http://www.tandfonline.com/loi/lsyc20>

One-Pot Synthesis of 1-Alkynylphosphonates

Jun Mo Gil ^a, Jin Wuk Sung ^a, Chan Pil Park ^a & Dong Young Oh ^a

^a Department of Chemistry, Korea Advanced Institute of Science and Technology, 373-1, Kusung-Dong, Yusung-Gu, Taejon, 305-701, Korea
Published online: 22 Aug 2006.

To cite this article: Jun Mo Gil, Jin Wuk Sung, Chan Pil Park & Dong Young Oh (1997) One-Pot Synthesis of 1-Alkynylphosphonates, *Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry*, 27:18, 3171-3174, DOI: [10.1080/00397919708004175](https://doi.org/10.1080/00397919708004175)

To link to this article: <http://dx.doi.org/10.1080/00397919708004175>

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>

ONE-POT SYNTHESIS OF 1-ALKYNYLPHOSPHONATES

Jun Mo Gil, Jin Wuk Sung, Chan Pil Park and Dong Young Oh*

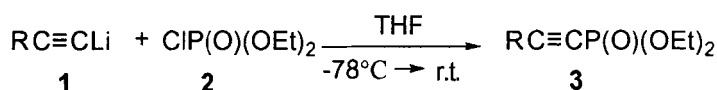
Department of Chemistry, Korea Advanced Institute of Science and Technology,
373-1, Kusung-Dong, Yüsung-Gu, Taejon, 305-701, Korea

Abstract: 1-Alkynylphosphonates **3** are prepared in a one-pot procedure from diethyl phosphorochloridates **2** and alkynyllithiums **1**, which are readily generated by the reaction of 1-alkynes with *n*-BuLi.

1-Alkynylphosphonates **3** have been used to synthesize a wide variety of unsaturated and saturated functional derivatives of organophosphorus compounds.¹ A literature survey on the preparation of 1-alkynylphosphonates **3** showed that some of the methods reported involve the preparation of explosive alkynyl bromides,² while other methods are either limited in scope or give low overall yields.³ Recently, we reported the preparation of 1-alkynylphosphonates by β -elimination of phosphates.⁴ The most widely used method of preparation involves the reaction of alkynylmagnesium bromides with dialkyl phosphorochloridates,^{5,6} but this method⁵ has some limitations. One of the limitations is the formation of side products, produced by attack of the alkynylmagnesium bromides on both the chloride and the alkoxide groups of dialkyl phosphorochloridates. Herein, we

*To whom correspondence should be addressed.

report an improved reaction which can overcome this limitation. 1-Alkynylphosphonates **3** are prepared in a one-pot procedure by reaction of diethyl phosphorochloridates **2** with alkynyllithiums **1**, which are readily generated by the reaction of 1-alkynes with *n*-BuLi (**Scheme**).



Scheme

Table. Preparation of 1-Alkynylphosphonates **3** (1~5)

entry	Product	yield, % ^a
1	$(\text{EtO})_2\text{P}(=\text{O})\text{C}\equiv\text{C}-n\text{-Bu}$	82 ^b
2	$(\text{EtO})_2\text{P}(=\text{O})\text{C}\equiv\text{C}-t\text{-Bu}$	92 ^c
3	$(\text{EtO})_2\text{P}(=\text{O})\text{C}\equiv\text{C}-n\text{-Hex}$	91 ^c
4	$(\text{EtO})_2\text{P}(=\text{O})\text{C}\equiv\text{C}-\text{Ph}$	86 ^c
5	$(\text{EtO})_2\text{P}(=\text{O})\text{C}\equiv\text{C}-\text{CH}_2\text{OBn}$	82 ^c

a isolated yields

b purification by distillation under reduced pressure

c purification by silica gel chromatography

The success of this method is explained by the reasonable assumption that the alkynyllithium is less nucleophilic than the alkynylmagnesium bromide and that the alkynyllithium can displace the chloride but not the alkoxide.

General Experimental Procedure

After stirring of a THF (30 ml) solution of distilled 1-alkyne **1** (10 mmol) with *n*-BuLi (10 mmol) for 1 h at -30 °C, distilled diethyl phosphorochloridate **2** (10 mmol) was added neat at -78 °C. The reaction mixture was stirred at -78 °C for 1 h and then at room temperature for 30 min. Saturated aqueous ammonium chloride solution (20 ml) was added and the aqueous layer was extracted with ethyl ether (50 ml x 3). The combined ether extracts were dried (MgSO₄) and evaporated, and 1-alkynylphosphonate **3** was obtained as the only isolable product. The resulting oils were purified by silica gel column chromatography or distillation under reduced pressure (**Table**).

Acknowledgement : We thank the Korea Science and Engineering Foundation for financial support.

REFERENCES

1. Miller, S. I.; Dickstein, J. I. *Acc.Chem. Res.* **1976**, *9*, 358. Saunders, B. C.; Simpson, P. J. *Chem. Soc.(C)* **1963**, 3351. Sauveur, F.; Collignon, N. *Phosphorus and Sulfur* **1983**, *14*, 34.
2. Ionin, B. I.; Petrov, A. A. *Zhur. Obshch. Khim.* **1962**, *32*, 2387.
3. Pudovik, A. N.; Aladzheva, I. M. *Zhur. Obshch. Khim.* **1963**, *33*, 707. Seyferth, D.; Paetsch, J. D. *J. Org. Chem.* **1969**, *34*, 1483. Hall, R. G.; Trippett, S. *Tetrahedron Lett.* **1982**, 23,2603.
4. Hong, J. E.; Lee, C-W.; Kwon, Y.; Oh, D. Y. *Synth. Commun.* **1996**, *26*, 1563.

5. Chatta, M. S.; Aguiar, A. M. *J. Org. Chem.* **1971**, *36*, 2719.
6. Burt, P. W.; Simpson, P. J. *Chem. Soc.(C)* **1971**, 2872. Sturtz, G.; Charrier, C.; Normant, H. *Bull. Soc. Chim. Fr.* **1966**, 1707.

(Received in the UK 18 February 1997)