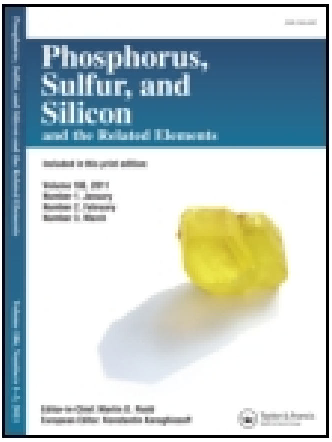
This article was downloaded by: [Florida Atlantic University]
On: 11 August 2015, At: 10:16
Publisher: Taylor & Francis
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: 5 Howick Place, London, SW1P 1WG



Click for updates

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gpss20

Convenient Synthesis of 1-(Trimethylsilyl)- and 1-(Trimethylstannyl)Vinylphosphonates and Their Synthetic Application

Yoshiharu Okada[a], Riho Urushihara[a] & Masato Nakamoto[a]
[a] Department of Biotechnology and Chemistry, Faculty of Engineering, Kinki University, TakayaHigashi-Hiroshima, Japan

Accepted author version posted online: 06 Dec 2014.

To cite this article: Yoshiharu Okada, Riho Urushihara & Masato Nakamoto (2015) Convenient Synthesis of 1-(Trimethylsilyl)- and 1-(Trimethylstannyl)Vinylphosphonates and Their Synthetic Application, Phosphorus, Sulfur, and Silicon and the Related Elements, 190:5-6, 922-924, DOI: 10.1080/10426507.2014.978327

To link to this article: http://dx.doi.org/10.1080/10426507.2014.978327

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.

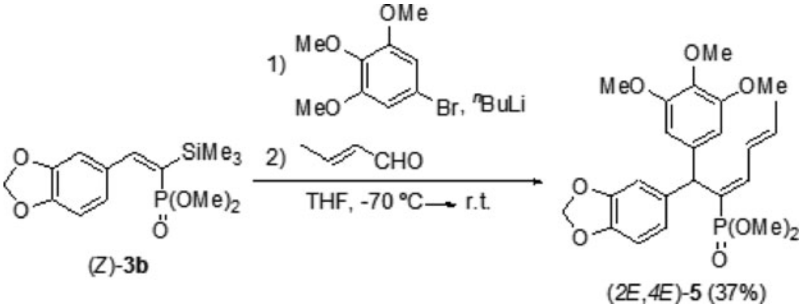
This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden. Terms &

Phosphorus, Sulfur, and Silicon, 190:922–924, 2015
Copyright © Taylor & Francis Group, LLC
ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426507.2014.978327

CONVENIENT SYNTHESIS OF 1-(TRIMETHYLSILYL)-AND 1-(TRIMETHYLSTANNYL)VINYLPHOSPHONATES AND THEIR SYNTHETIC APPLICATION

Yoshiharu Okada, Riho Urushihara, and Masato Nakamoto
Department of Biotechnology and Chemistry, Faculty of Engineering, Kinki University, Takaya, Higashi-Hiroshima, Japan

GRAPHICAL ABSTRACT



Abstract *Dimethyl 1,1-bis(trimethylsilyl)methylphosphonate was succeeded to react with aromatic aldehydes in the presence of methyl benzoate as additive to give the corresponding vinylphosphonates in moderate yields. Michael addition and subsequent Peterson olefination reaction of dimethyl (Z)-2-(3,4-methylenedioxyphenyl)-1-(trimethylsilyl)vinylphosphonate with 3,4,5-trimethoxyphenyllithium and crotonaldehyde afforded the corresponding (2E,4E)-1-(3,4,5-trimethoxyphenyl)-1-(3,4-methylenedioxyphenyl)-2-(dimethylphosphono)hexa-2,4-diene in 36% yield.*

Keywords Vinylphosphonates; vinylsilanes; vinylstannanes; Peterson reaction

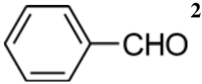
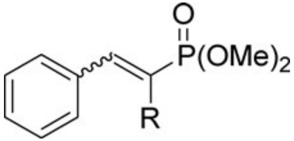
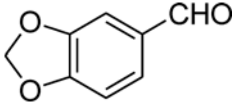
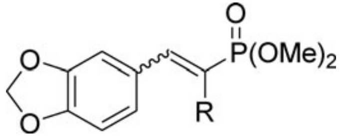
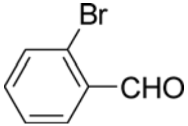
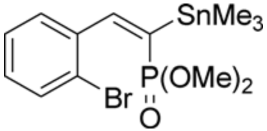
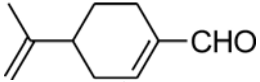
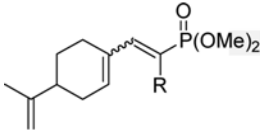
Organophosphorus, organosilicon, and organotin compounds are useful intermediates for organic synthesis. We became interested in the reactivity of multifunctionalized methylphosphonates with carbonyl compounds. We report here a convenient synthesis of vinylphosphonates with trimethylsilyl and trimethylstannyl groups in α-position from the multifunctionalized methylphosphonates with trimethylsilyl and trimethylstannyl groups **1a,b** (Figure 1).

Furthermore, the obtained vinylphosphonates were useful tandem reaction reagents, e.g., in Michael reaction—Horner–Wadsworth–Emmons reaction. The reactions of **1a,b**

Received 29 August 2014; accepted 15 October 2014.

Address correspondence to Yoshiharu Okada, Department of Biotechnology and Chemistry, Faculty of Engineering, Kinki University, Umenobe 1, Takaya, Higashi-Hiroshima 739-2116, Japan. E-mail: okadasan@hiro.kindai.ac.jp

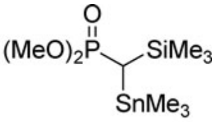
Table 1 Peterson Reaction of **1a,b** with carbonyl compounds **2a–d**.[1])

Entry	Phosphonate		Carbonyl Compound	Additive	Product (yield;%[2]), E/Z)
	1	R			
1	**1a**	$SiMe_3$	 **2a**	—	 **3a** (0)
2	**1a**	$SiMe_3$		Methyl benzoate	**3a** (79, 1/1.7)
3	**1a**	$SiMe_3$		NaF	**3a** (65, 1/1.2)
4	**1b**	$SnMe_3$		NaF	**4a** (42, 2.2/1)
5	**1a**	$SiMe_3$		Methyl benzoate	**3b** (64, 1/2)
6	**1b**	$SnMe_3$	 **2b**	Methyl benzoate	 **4b** (9, 1/1[3]))
7	**1b**	$SnMe_3$	 **2c**	NaF	 **4c** (52)
8	**1a**	$SiMe_3$	 **2d**	Methyl benzoate	 **3d** (53, 1/1.3)
9	**1b**	$SnMe_3$		NaF	**4d** (43, 1/1.3)

[1])All reaction was carried out under Ar atmosphere in THF at −70°C for 30 min, and then at room temperature for 12 h.

[2])Isolated yield. [3]) Determined by ^{1}H NMR.

1a



1b

Figure 1 Functionalized dimethyl methylphosphonates.

with carbonyl compounds **2a–d** in the presence of LDA in THF were carried out to give Peterson reaction products **3a–d** and **4a–d** [1]. The results are summarized in Table 1.

The reaction of **1a** with benzaldehyde **2a** did not give the desired product **3a**; only **1a** was recovered (entry 1). A similar reaction in the presence of methyl benzoate as an additive gave a mixture of (*E*)-**3a** and (*Z*)-**3a** in 28% and 51% yields, respectively (entry 2). Also, sodium fluoride as an additive was effective (entry 3). The structures of (*E*)-**3a–d**, (*Z*)-**3a–d**, (*E*)-**4a–d**, and (*Z*)-**4a–d** were assigned on the basis of their ^{1}H and ^{13}C NMR spectra. The ^{1}H NMR spectrum of (*E*)-**3b** shows a signal for olefinic proton at δ 8.22 (d, $J = 35.2$ Hz), while that of (*Z*)-**3b** shows the corresponding signal at δ 7.43 (d, $J = 60.8$ Hz).

Next, usage of a second functional group was investigated. Michael addition and subsequent Peterson reaction of (*Z*)-**3b** with 3,4,5-trimethoxyphenyllithium and crotonaldehyde afforded the desired (*2E,4E*)-**5** in 37% yield (Eq. (1)).

REFERENCES

1. Okada, Y.; Maruyama, T.; Tamura, S.; Kameoka, H.; Masuda, S.; Tokuda, Y.; Sakai, J.; Nomura, M. *Phosphorus, Sulfur, Silicon, Relat. Elem.* **2014,** 189, 778-790.