This article was downloaded by: [Gebze Yuksek Teknoloji Enstitïsu] On: 25 December 2014, At: 10:14 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.tandfonline.com/loi/gpss20

Synthetic Utilization of a-Phosphonovinyl Anions

Toru Minami , Ryoji Kouno , Tatsuo Okauchi , Mitsuharu Nakamura & Junji Ichikawa

^a Department of Applied Chemistry , Kyushu Institute of Technology , Sensuicho, Tobata, Kitakyushu 804-0015, Japan

^b Department of Applied Chemistry , Kyushu Institute of Technology , Sensuicho, Tobata, Kitakyushu 804-0015, Japan

^c Department of Applied Chemistry , Kyushu Institute of Technology , Sensuicho, Tobata, Kitakyushu 804-0015, Japan

^d Department of Applied Chemistry , Kyushu Institute of Technology , Sensuicho, Tobata, Kitakyushu 804-0015, Japan

^e Department of Applied Chemistry , Kyushu Institute of Technology , Sensuicho, Tobata, Kitakyushu 804-0015, Japan Published online: 17 Mar 2008. To cite this article: Toru Minami , Ryoji Kouno , Tatsuo Okauchi , Mitsuharu Nakamura & Junji Ichikawa (1999) Synthetic Utilization of α -Phosphonovinyl Anions, Phosphorus, Sulfur, and Silicon and the Related Elements, 144:1, 689-692, DOI: <u>10.1080/10426509908546338</u>

To link to this article: http://dx.doi.org/10.1080/10426509908546338

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

Synthetic Utilization of α-Phosphonovinyl Anions

TORU MINAMI, RYOJI KOUNO, TATSUO OKAUCHI MITSUHARU NAKAMURA and JUNJI ICHIKAWA

Department of Applied Chemistry, Kyushu Institute of Technology, Sensui-cho, Tobata, Kitakyushu 804–0015, Japan

The α -phosphonovinyl anions, generated in situ from treatment of β -hetero-substituted vinylphosphonates **1a-c** with LDA (or LTMP), were trapped with various electrophiles such as chlorotriorganosilanes, chlorotrimethylgermane, chlorotriorganotins, dimethyl disulfide, and halogen to afford the corresponding β -hetero-substituted α -functionalized vinylphosphonates **2–14** in good to excellent yields. The Friedel-Crafts reaction of α -(silyl) or α -(germyl)phosphonoketene dithioacetals **2**, **9** or **4** with acid chlorides gave α -acylated phosphonoketene dithioacetals **15–19** in 53–91 % yields. The palladium-catalyzed cross-coupling reaction of β -ethoxy- α -(tributylstannyl)vinylphosphonate **13** with a variety of organic halides (R = acyl, allyl, aryl etc.) provided β -ethoxy- α -substituted vinylphosphonates **20–25** in good to moderate yields. The palladium-mediated cross-coupling reaction of α -(ido)-vinylphosphonates **7**, **14** with terminal acetylenes afforded α -alkynylated vinylphosphonates **26– 29** in 69–83 % yields.

Keywords: α -phosphonovinyl anions; α -(triorganomatal)vinylphosphonates; α -(alky-nyl)vinylphosphonates; Pd-catalyzed cross-coupling; Friedel-Crafts reacton

INTRODUCTION

Vinylphosphonates containing various functional groups have been widely studied due to their synthetic and biological usefulness.^[11] We have recently reported the generation of α -carbanions of phosphonoketene dithioacetals and their synthetic application to dithioallenes.^[21] We report here a new convenient synthesis of various vinylphosphonates containing synthetically useful substituents such as organometallic groups and halogen on the α -carbon via α -phosphono-stabilized vinyl anions, and also the synthesis of a new class of vinylphosphonates via functional group transformation of the resulting α -functionalized vinylphosphonates.

Results and Discussion

The 2,2-(ethylenedithio)-1-phosphonovinyl anion, generated from phosphonoketene dithioacetal 1a and lithium 2,2,6,6-tetramethylpiperidide (LTMP) at -78 °C for 1h, was

treated with a wide variety of electrophiles to provide α -functionalized phosphonoketene dithioacatals 2-8 in good yields (eq 1).



In the case of acyclic dithioacetal 1b, a THF solution of LTMP was inversely added to the mixture of 1b and an electrophile (Me₃SiCl or Bu₃SnCl) at -78 °C to give the expected α -triorganometal-substituted phosphonoketene dithioacetal 9 or 10 in good yields (eq 2).

Treatment of 1c with LDA in THF at -78 °C followed by addition of an electrophile similarly led to α -substituted β -(ethoxy)vinylphosphonates 11-14 in high yields (eq 3).



We next tried to develop multipurpose vinylphosphonates via the above prepared α -functionalized vinylphosphonates. The Friedel-Crafts reaction of 2, 4 and 9 with acid chlorides (2 equiv) / AlCl₃ (2 equiv) led to α -acylated phosphonoketene dithioacetals 15-19 in 53-91 % yields (eq 4).



Since the synthesis of α -acylated β -(ethoxy)vinylphosphonates are not accessible by the Friedel-Crafts reaction of **11** with acid chlorides as above, the Stille crosscoupling reaction of **13** with benzoyl chloride in the presence of Pd(PPh₃)₄ (4 mol%) and CuCN (9 mol%) was carried out to give the desired α -benzoylated β -(ethoxy)vinylphosphonate **20** (eq 5). Similar treatment of **13** with various organic halides produced cross-coupling products **21-25** (eq 5).



We have also attempted to synthesize a new class of enyne compounds containing phosphorus and hetero functional group. The palladium-mediated cross-coupling reaction of 7 and 14 with terminal acetylenes in THF at room temperature afforded the desired enyne compounds 26-29 in good yields (eq 6). The above results have indicated that the palladium-mediated cross-coupling reaction of α -(iodo)vinylphosphonates with terminal acetylenes has no limitation in functionalities on the vinylphosphonates and the acetylenes.



Furthermore, oxdative homo-coupling of the terminal alkyne 30 derived from 27 produced the expected diene-diyne derivative 31 in excellent yield (93 %)(eq 7).



(ii) Cu(OAc)₂ (4.4 equiv), THF-pyridine-EtOH, 70 °C, 30 min, 93 %.

References

- [1] T. Minami and J. Motoyoshiya Synthesis 333 (1992).
- [2] T. Minami, T. Okauchi, H. Matsuki, M. Nakamura, J. Ichikawa, and M. Ishida J. Org. Chem. 61, 8132 (1996).