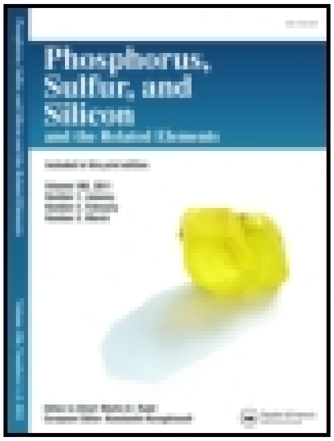
This article was downloaded by: [Nova Southeastern University]
On: 27 December 2014, At: 07:40
Publisher: Taylor & Francis
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



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

Synthesis of Four- and Five-Membered Heterocycles Derived from an Iminophosphorane

Naokazu Kano [a], Jia-Hua Xing [a], Azusa Kikuchi [a], Seiji Kawa [a] & Takayuki Kawashima [a]
[a] Department of Chemistry, Graduate School of Science, The University of Tokyo, Tokyo, Japan

Published online: 27 Oct 2010.

To cite this article: Naokazu Kano , Jia-Hua Xing , Azusa Kikuchi , Seiji Kawa & Takayuki Kawashima (2002) Synthesis of Four- and Five-Membered Heterocycles Derived from an Iminophosphorane, Phosphorus, Sulfur, and Silicon and the Related Elements, 177:6-7, 1685-1687, DOI: 10.1080/10426500212297

To link to this article: http://dx.doi.org/10.1080/10426500212297

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

Phosphorus, Sulfur and Silicon, 2002, Vol. 177:1685–1687

1042-6507/02 $12.00 + .00
DOI: 10.1080/10426500290092875

SYNTHESIS OF FOUR- AND FIVE-MEMBERED HETEROCYCLES DERIVED FROM AN IMINOPHOSPHORANE

Naokazu Kano, Jia-Hua Xing, Azusa Kikuchi, Seiji Kawa, and Takayuki Kawashima
Department of Chemistry, Graduate School of Science, The University of Tokyo, Tokyo, Japan

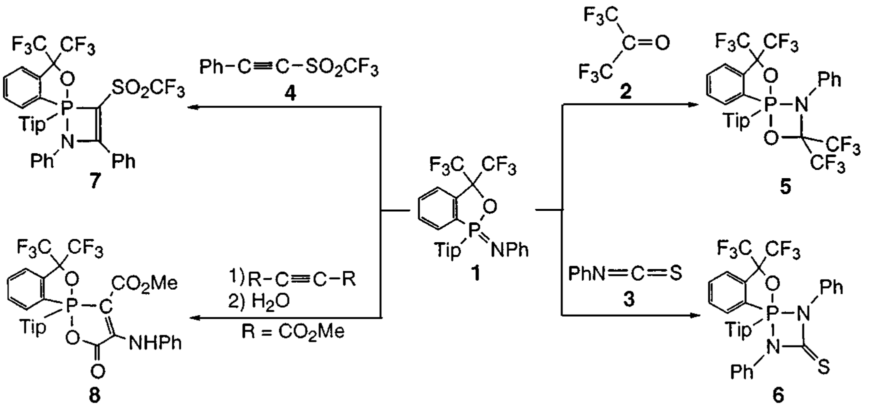
(Received August 3, 2001; accepted December 25, 2001)

*Reactions of an iminophosphorane bearing the Martin ligand with a ketone, an isothiocyanate, and an alkyne gave the corresponding cycloadducts, 1,3,2λ^5-oxazaphosphetidine, 1,3,2λ^5-diazaphosphetidine-4-thione, and 1,2λ^5-azaphosphetine, respectively, while that with dimethyl acetylenedicarboxylate (DMAD) and successive hydrolysis afforded the 1,2λ^5-oxaphosphole-(2*H*)-one. Thermal reactions of the cycloadducts were also studied.*

Keywords: Cycloaddition; heterocycles; iminophosphorane; phosphorane; thermolysis; x-ray analysis

There has been much interest in the chemistry of four-membered heterocycles containing both a pentacoordinate phosphorus atom and other heteroatom(s) in view of their unique structures and reactivities.[1] In the course of our study on such heteracyclobutanes, we have achieved the syntheses of 1,2λ^5-oxaphosphetanes[2] and 1,2λ^5-azaphosphetidines,[3] that is, the intermediates of Wittig reactions, by taking advantage of the Martin ligand. On the other hand, an iminophosphorane, which is a nitrogen analog of the phosphorus ylide, is expected to construct a variety of four-membered ring compounds by the cycloaddition with multiple bond compounds. We report here the syntheses and thermolyses of novel heterocycles bearing a pentacoordinate phosphorus atom derived from an iminophosphorane bearing the Martin ligand and a 2,4,6-triisopropylphenyl (denoted as Tip hereafter) group.

Address correspondence to Takayuki Kawashima, Department of Chemistry, Graduate School of Science, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-0033, Japan. E-mail: takayuki@chem.s.u-tokyo.ac.jp

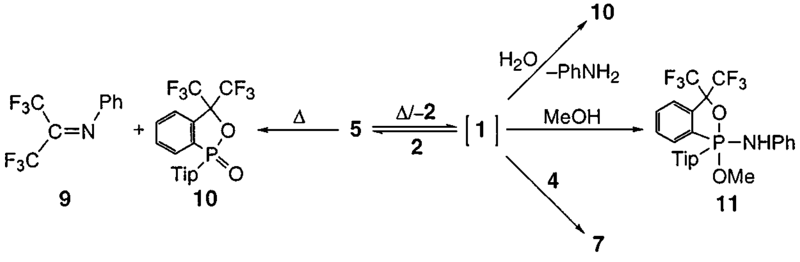


SCHEME 1

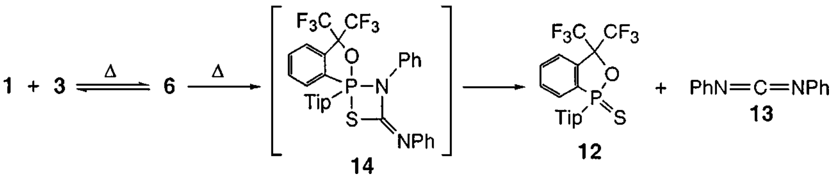
RESULTS AND DISCUSSION

Reactions of iminophosphorane **1** with hexafluoroacetone **2**, phenyl isothiocyanate **3**, and phenylethynyl trifluoromethyl sulfone **4** gave the corresponding cycloadducts, $1,3,2\lambda^5$-oxazaphosphetidine **5**,[4] $1,3,2\lambda^5$-diazaphosphetidine-4-thione **6**, and $1,2\lambda^5$-azaphosphetine **7**, respectively. Interestingly, successive treatment of **1** with dimethyl acetylenedicarboxylate (DMAD) and water afforded not the corresponding 1,2-azaphosphetine, but the $1,2\lambda^5$-oxaphosphol-5(2*H*)-one **8**[5] (Scheme 1). The structures of these products were established by x-ray crystallographic analyses. It is worth mentioning that the oxygen analog of 1,2-azaphosphetine, 1,2-oxaphosphete, is only an intermediate in the reactions of phosphine oxides and DMAD.[6]

The thermolysis of the four-membered ring compound **5** revealed the formation of the Wittig-type products, the corresponding imine **9** and cyclic phosphinate **10**. The existence of the equilibrium with the starting materials on the thermal conditions was found by the thermolyses



SCHEME 2



SCHEME 3

of **5** in the presence of water, methanol, and **4**, which gave **10**, methoxyphosphorane **11**, and **7**, respectively (Scheme 2).

The thermolysis of 1,3,2λ^5-diazaphosphetidine-4-thione **6**, afforded not only the starting materials, **1** and **3**, but also cyclic thiophosphinate **12** and diphenylcarbodiimide **13**. The formation of **12** and **13** strongly suggests the generation of the corresponding 1,3,2λ^5-thiazaphosphetidine **14** as an intermediate (Scheme 3).

1,2λ^5-Azaphosphetine **7** is thermally quite stable, in contrast to **5** and **6**. It did not decompose even upon heating at 180°C. It is inactive toward the Wittig reactions with benzaldehyde and phenyl isocyanate.

In summary, we have revealed that 1,3,2λ^5-oxazaphosphetidine **5** and 1,3,2λ^5-diazaphosphetidine-4-thione **6**, which were obtained from an iminophosphorane **1**, have two reactivities including the regeneration of **1**. Meanwhile, 1,2λ^5-azaphosphetine **7** is quite thermally stable.

REFERENCES

[1] (a) T. Kawashima and R. Okazaki, *Synlett*, 600 (1996). (b) T. Kawashima and R. Okazaki, In *Advances in Strained and Interesting Organic Molecules*, ed. B. Halton (JAI Press, Inc., Stamford, CT, 1999), Vol. 7, pp. 1–41, and references cited therein.

[2] (a) T. Kawashima, K. Kato, and R. Okazaki, *J. Am. Chem. Soc.*, **114,** 4008 (1992). (b) T. Kawashima, K. Kato, and R. Okazaki, *Angew. Chem., Int. Ed. Engl.*, **32,** 869 (1993).

[3] T. Kawashima, T. Soda, and R. Okazaki, *Angew. Chem., Int. Ed. Engl.*, **35,** 1096 (1996).

[4] N. Kano, X. J. Hua, S. Kawa, and T. Kawashima, *Tetrahedron Lett.*, **41,** 5237 (2000).

[5] N. Kano, J.-H. Xing, A. Kikuchi, and T. Kawashima, *Heteroatom Chem.*, **12,** 282 (2001).

[6] (a) G. Keglevich, H. Forintos, A. Szöllõsy, and L. Tõke, *Chem. Commun.*, 1423 (1999). (b) G. Keglevich, H. Forintos, A. Szöllõsy, and L. Tõke, *Tetrahedron*, **56,** 4823 (2000). (c) G. Keglevich, A. G. Vaskó, A. Dobó, K. Ludányi, and L. Tõke, *J. Chem. Soc., Perkin Trans.*, **1,** 1062 (2001). (d) G. Keglevich, H. Forintos, H. Szelke, T. Körtvelyesi, L. Kollár, and L. Tõke, *Phosphorus, Sulfur, Silicon Relat. Elem.*, in press.