This article was downloaded by: [Michigan State University] On: 18 January 2015, At: 01:33 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 and Thermolysis of Pentacoordinate 1,2-Azaphosphetidines

Takayuki Kawashima , Tomokazu Soda , Katsuhiro Kato & Renji Okazaki

<sup>a</sup> Department of Chemistry, Graduate School of Science , The University of Tokyo , 7-3-1 Hongo Bunkyo-ku, Tokyo 113, Japan

<sup>b</sup> Department of Chemistry, Graduate School of Science, The University of Tokyo, 7-3-1 Hongo Bunkyo-ku, Tokyo 113, Japan

<sup>c</sup> Department of Chemistry, Graduate School of Science , The University of Tokyo , 7-3-1 Hongo Bunkyo-ku, Tokyo 113, Japan

<sup>d</sup> Department of Chemistry, Graduate School of Science , The University of Tokyo , 7-3-1 Hongo Bunkyo-ku, Tokyo 113, Japan

Published online: 06 Aug 2008.

To cite this article: Takayuki Kawashima , Tomokazu Soda , Katsuhiro Kato & Renji Okazaki (1996) Synthesis and Thermolysis of Pentacoordinate 1,2-Azaphosphetidines, Phosphorus, Sulfur, and Silicon and the Related Elements, 109:1-4, 489-492, DOI: 10.1080/10426509608545197

To link to this article: <u>http://dx.doi.org/10.1080/10426509608545197</u>

### 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, sublicensing, systematic supply, or distribution in any form to anyone is expressly forbidden. Terms & Conditions of access and use can be found at <u>http://</u> www.tandfonline.com/page/terms-and-conditions

#### SYNTHESIS AND THERMOLYSIS OF PENTACOORDINATE **1,2-AZAPHOSPHETIDINES**

#### TAKAYUKI KAWASHIMA, TOMOKAZU SODA, KATSUHIRO KATO, AND **RENJI OKAZAKI**

Department of Chemistry, Graduate School of Science, The University of Tokyo 7-3-1 Hongo, Bunkyo-ku, Tokyo 113, Japan

Abstract Pentacoordinate 1,2-azaphosphetidines bearing the Martin ligand were synthesized by the intramolecular dehydration of the corresponding  $\beta$ -amino phosphine oxides with Mitsunobu reagent (Ph<sub>3</sub>P-EtO<sub>2</sub>CN=NCO<sub>2</sub>Et). The X-ray crystallographic analysis of 1,2,4,4,-tetraphenyl derivative shows that it has a distorted trigonal bipyramidal structure with oxygen and nitrogen atoms at apical positions. Their thermolyses gave the corresponding olefins along with a cyclic iminophosphorane, which was readily hydrolyzed to give the cyclic phosphinate and aniline.

#### INTRODUCTION

In the course of our study on oxetanes bearing a highly coordinate main group element at the neighboring position we achieved the syntheses and isolation of intermediates of pentacoordinate 1,2-oxaphosphetanes 1a,b,<sup>1</sup>, 1,2-oxasiletanides  $2,^2$  1,2-oxagermetanides  $3^{3}$  and 1,2-oxastannetanides  $4^{4}$  i.e., intermediates of the Wittig, Peterson, germanium-Peterson, and tin-Peterson reactions, respectively. Bestmann and Seng reported phosphorus ylides undergo the Wittig-type reaction with alkylideneamines instead of carbonyl compounds to give the corresponding olefins,<sup>5</sup> but there has been reported no evidence for the intermediates. We now report synthesis and thermolysis of pentacoordinate 1,2-azaphosphetidines which is formally derived from a phosphorus ylide and alkylideneamine.



#### **RESULTS AND DISCUSSION**

Sequential treatment of methylphenylphosphine oxide (5) having the Martin ligand<sup>6</sup> with 2.3 equiv of *n*-BuLi, with 2.4 equiv of benzylideneaniline (6) or diphenylmethyleneaniline (7) in THF at 0 °C, and then with aqueous NH<sub>4</sub>Cl gave a diastereomeric mixture of  $\beta$ -amino phosphine oxides 8a,b (52%) and 9 (44%) respectively. Intramolecular dehydration of 8a,b and 9 with Mitsunobu reagent<sup>7</sup> provided target molecules 10a,b and 11, respectively. Their <sup>1</sup>H, <sup>19</sup>F, and <sup>31</sup>P NMR spectral data are partially summarized in Table 1, indicating that 10a,b and 11 have a trigonal bipyramidal structure with nitrogen and oxygen atoms at apical positions. Compounds 10a,b were very moisture-sensitive and readily hydrolyzed to the starting 8a,b, but 11 could be isolated as colorless crystals (73%) by reprecipitation from CH<sub>2</sub>Cl<sub>2</sub> by the addition of ethanol, indicating that 4,4-diphenyl groups can protect sterically and efficiently the lone pair of the nitrogen atom.



The X-ray crystallographic analysis of 11 indicates that it has a distorted trigonal bipyramidal structure with nitrogen and oxygen atoms at apical positions, very similar to those of pentacoordinate 1,2-oxaphosphetanes 1a,b, 1,2-oxasiletanides 2, and 1,2-oxagermetanides 3 (Figure 1). The apical bond P-N (1.789(5) Å) is close to that (1.782(3) Å) of spiro-1,3,2-diazaphosphetidine 12,<sup>8</sup> but the P-O (1.796(5) Å) bond is

slightly longer than those of 1a, b.<sup>1</sup> The bond angle between two apical bonds deviates by 13.1(3)° from 180°. The phosphorus atom is placed in the equatorial plane and the torsion angle P-C-C-N is -0.1°, indicating that the four membered ring is almost planar. Interestingly, the nitrogen is trigonal and the plane of the benzene ring on the nitrogen is placed in the same plane of the four membered ring.

Table 1. 7	The <sup>1</sup> H,	<sup>19</sup> F and	<sup>31</sup> P NMR	Data of 10	a, b and 11.
------------	---------------------	---------------------	---------------------	------------	--------------

		δ( <sup>1</sup> H)	δ( <sup>19</sup> F)	δ( <sup>31</sup> P)		
Compounds	СН	IH'	CHN			
10a	3.49-3.55(m)	3.57-3.61(m)	4.57(m)	-73.5, -74.9 <sup>a)</sup>	-30.6	
10b	3.32(ddd) <sup>b)</sup>	4.10(ddd) <sup>c)</sup>	4.52(ddd) <sup>d)</sup>	-72.8, -75.2 <sup>a)</sup>	-30.2	
11	4.22(dd) <sup>e)</sup>	4.55(dd) <sup>f)</sup>	-	-73.6, -75.5 <sup>g)</sup>	-29.4	

a)  $A_3B_3$  like, not resolved. b)  ${}^2J(HP)= 21.1$  Hz,  ${}^2J=16.5$  Hz,  ${}^3J=5.0$  Hz. c)  ${}^2J(HP)= 19.6$  Hz,  ${}^2J=16.5$  Hz,  ${}^3J=8.7$  Hz. d)  ${}^3J(HP)= 12.2$  Hz,  ${}^3J=8.7$  Hz,  ${}^3J=5.0$  Hz. e)  ${}^2J(HP)= 19.6$  Hz,  ${}^2J=17.0$  Hz. f)  ${}^2J(HP)= 21.6$  Hz,  ${}^2J=17.0$  Hz. g) q,  ${}^4J(FF)=9.9$  Hz.



Figure 1. ORTEP drawing of 11.

Thermolysis of **10a,b** at 180 °C in a toluene- $d_8$  solution in the presence of Ph<sub>3</sub>P=O and EtO<sub>2</sub>CNHNHCO<sub>2</sub>Et as products gave a trace of styrene. When **11** ( $\delta$ (<sup>31</sup>P) -29.9) was dissolved in toluene- $d_8$ , another signal appeared at  $\delta$ (<sup>31</sup>P) -50.9, probably due to pseudorotamer **13** with the nitrogen being equatorial.<sup>9</sup> Heating of the solution at 200 °C for 5 d in a sealed tube gave quantitatively 1,1-diphenylethylene and the corresponding iminophosphorane **14**, which was hydrolyzed to the corresponding cyclic phosphinate **15** along with aniline.



#### REFERENCES

- a) T. Kawashima, K. Kato, and R. Okazaki, J. Am. Chem. Soc., <u>114</u>, 4008 (1992);
  b) T. Kawashima, K. Kato, and R. Okazaki, <u>Angew Chem., Int. Ed. Engl.</u>, <u>32</u>, 869 (1993);
- 2. T. Kawashima, N. Iwama, and R. Okazaki, J. Am. Chem. Soc., 114, 7598 (1992).
- 3. T. Kawashima, Y. Nishiwaki, and R. Okazaki, J. Organomet. Chem., in press.
- 4. T. Kawashima, N. Iwama, and R. Okazaki, J. Am. Chem. Soc., <u>115</u>, 2507 (1993).
- 5. H. J. Bestmann and F. Seng, Angew. Chem., 75, 475 (1965).
- The Martin ligand was introduced by using the dithio derivative of hexafluorocumyl alcohol: E. F. Perozzi, R. S. Michalak, G. D. Finguly, W. H. Stevenson, III, D. B. Dess, M. R. Ross, and J. C. Martin, J. Org. Chem., <u>46</u>, 1049 (1981).
- 7. For a review, see: O. Mitsunobu, Synthesis, 1981, 1.,
- H. W. Roesky, K. Ambrosius, M. Banek, and W. S. Sheldrick, <u>Chem. Ber.</u>, <u>113</u>, 1847 (1980).
- 9. NOE observed between the *ortho*-proton of the Martin ligand and one of 3-methylene protons indicates that two protons are close to each other, which is possible only in the case of the methylene-apical pseudorotamer.