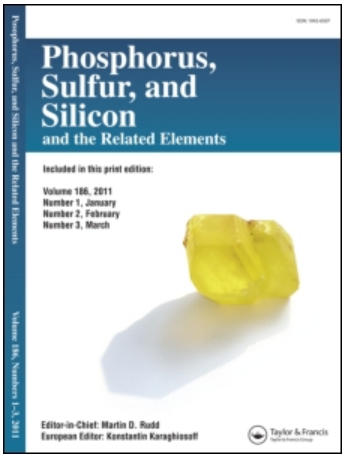

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Synthesis of Four- and Five-Membered Heterocycles Derived from an Iminophosphorane

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

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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

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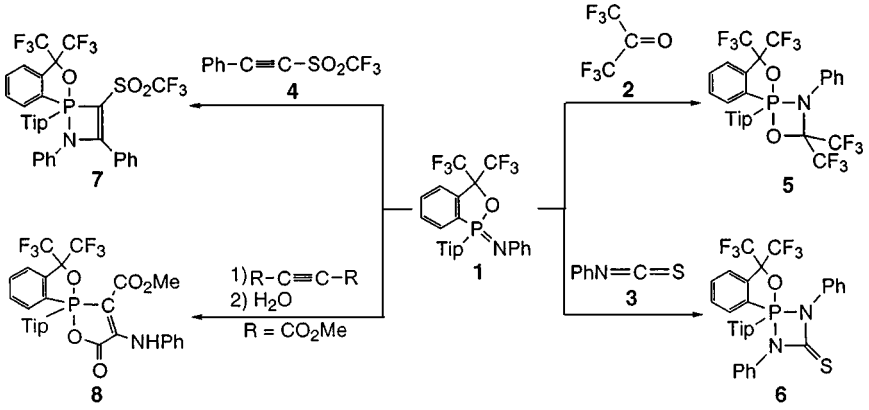
*Reactions of an iminophosphorane bearing the Martin ligand with a ketone, an isothiocyanate, and an alkyne gave the corresponding cycloadducts, 1,3,2λ^5-oxazaphosphetidine, 1,3,2λ^5-diazaphosphetidine-4-thione, and 1,2λ^5-azaphosphetine, respectively, while that with dimethyl acetylenedicarboxylate (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

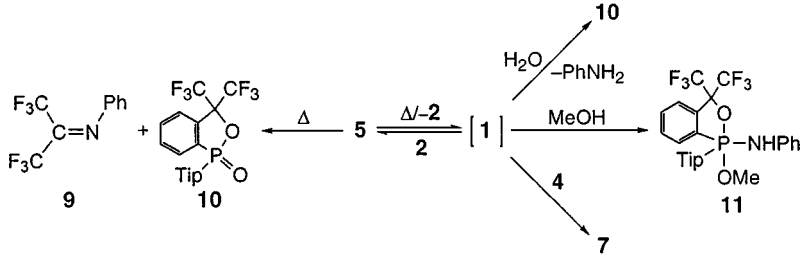


SCHEME 1

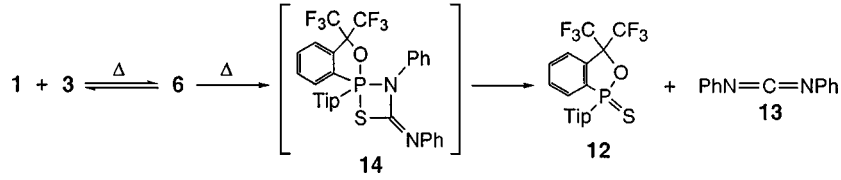
RESULTS AND DISCUSSION

Reactions of iminophosphorane **1** with hexafluoroacetone **2**, phenyl isothiocyanate **3**, and phenylethynyl trifluoromethyl sulfone **4** gave the corresponding cycloadducts, 1,3,2λ^5-oxazaphosphetidine **5**,[4] 1,3,2λ^5-diazaphosphetidine-4-thione **6**, and 1,2λ^5-azaphosphetine **7**, respectively. Interestingly, successive treatment of **1** with dimethyl acetylenedicarboxylate (DMAD) and water afforded not the corresponding 1,2-azaphosphetine, but the 1,2λ^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.

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