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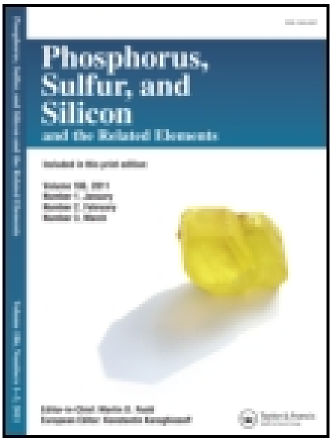

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Intramolecular Cyclization of a Phosphinoazide: Transformation of 1,2,3,4-Triazaphosphole into 1,2,4-Diazaphosphole

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INTRAMOLECULAR CYCLIZATION OF A PHOSPHINOAZIDE: TRANSFORMATION OF 1,2,3,4-TRIAZAPHOSPHOLE INTO 1,2,4-DIAZAPHOSPHOLE

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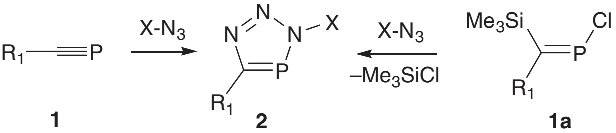
Abstract *Carbanion **4** generated from phosphane azide **3** undergoes intramolecular cyclization to give 1,2,3,4-triazaphosphole **5**, which rearranges into 1,2,4-diazaphosphole **8**.*

Keywords Azides; carbanions; 1,2,4-diazaphosholes; 1,2,3,4-triazaphospholes; ylides

INTRODUCTION

It is known that phosphaalkynes **1** and some phosphaalkenes **1a** are able to participate in [3+2] cycloaddition reactions with azides to give 1,2,3,4-triazaphospholes **2** (Scheme 1).[1,2] However, this reaction is restricted by the accessibility of phosphaalkynes and phospaalkenes, the stabilization of which requires sterically demanding substituents.



R_1=bulky substituens; X=H, CH_3, C_6H_5, CH_2CN, $SiMe_3$, CO_2Me

Scheme 1

RESULTS AND DISCUSSION

We have found that generation of a carbanionic center in the α-position to the phosphane azide moiety may lead to the intramolecular cyclization into 1,2,3,4-triazaphospholes. For example, the addition of DBU to phosphane azide **3** led to its intramolecular cyclization into triazaphosphole **5** in 85% yield (Scheme 2). It is possible that this is a particular

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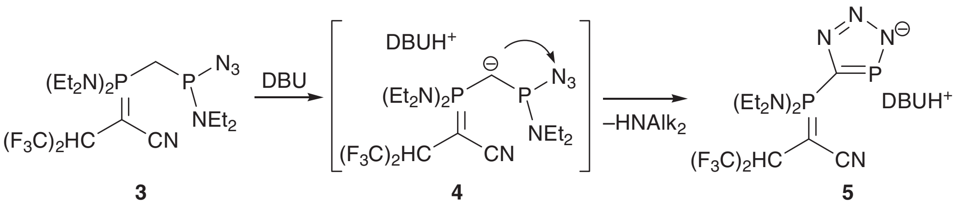
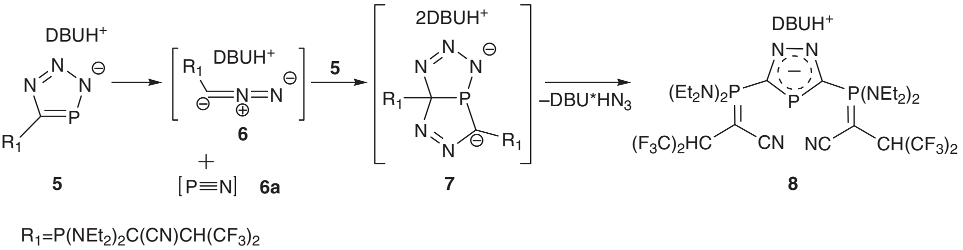


Scheme 2

example of a more general reaction that can be used for the synthesis of other 1,2,3,4-triazaphospholes. The presence of an activated methylene group in the α-position to the phosphane center is the necessary condition for the generation of carbanions.

Starting phosphane azides can be easily obtained from chlorophosphanes and trimethylsilyl azide. For example, phosphane azide **3** was quantitatively synthesized and without purification was used for the synthesis of **5**. The ^{31}P-NMR spectrum of the reaction mixture after addition of DBU displays two clear doublets of compound **5**. The chemical shift of 238 ppm is typical for the two-coordinate phosphorus atom in such compounds.[1–4] The intramolecular cyclization of intermediate carbanion **4,** which is accompanied by the elimination of diethylamine, is probably much more rapid in comparison with the rate of its formation. For this reason **4** cannot be registered by the ^{31}P-NMR spectroscopy.

Triazaphosphole **5** cannot be isolated from the reaction mixture because it rearranges spontaneously into 1,2,4-diazaphosphole **8**. This kind of transformation has not been experimentally observed earlier. There is one example known of the synthesis of 1,2,4-diazaphosphole by the reaction of triazaphospholes and diazo alkanes.[4] The decomposition of a 1,2,3,4-triazaphosphole with the formation of diazo alkane and polymeric product $(PN)_n$ has also been postulated in two works.[2,3] We suppose that the mechanism of the rearrangement of triazaphosphole **5** into 1,2,4-diazaphosphole **8** should be accounted for by the combination of these two previously described processes (Scheme 3). Triazaphosphole **5** decomposes first into diazo compound **6**, which then adds to the starting triazaphosphole with the formation of bicyclic intermediate **7**. Due to the presence of the cation $[DBU^*H]^+$, intermediate **7** undergoes an interesting elimination of DBU^*HN_3 yielding 1,2,4-diazaphosphole **8**. DBU^*HN_3 and diazaphosphole **8** can be separately isolated from the reaction mixture. The polymeric product $(PN)_n$ **6a** resulting from the decomposition of triazaphosphole **5** was identified in the reaction mixture as a broad signal in the ^{31}P-NMR spectrum at +55 ppm.



Scheme 3

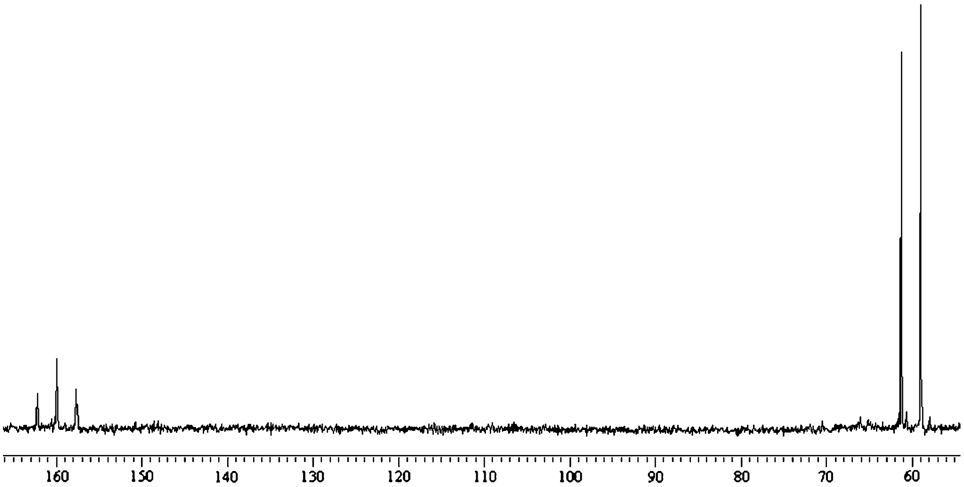


Figure 1 ^{31}P-NMR spectrum of diazaphosphole **8**.

Diazaphosphole **8** was isolated in 50% yield. This compound displays the characteristic ^{31}P-NMR spectrum (Figure 1), consisting of a doublet at 60 ppm and a triplet at 160 ppm with a ratio of 2:1. The low field value corresponds to the two-coordinate phosphorus atom and coincides with the literature data.[1a,2,3] The high-resolution mass spectrum of diazaphosphole **8** with electrospray ionization displayed intensive signals of the anionic and cationic parts of the molecule.

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