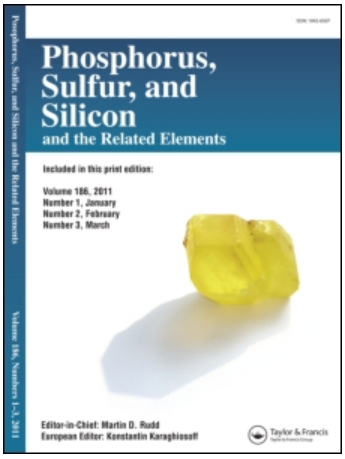

Phosphorus, Sulfur, and Silicon and the Related Elements

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Synthesis and Properties of λ^5-Phosphinines and λ^5-Azaphosphinines

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New accessible methods of synthesizing λ5-phosphines and 1,2-λ5-azaphosphinines by cyclocondensation of phosphorylated derivatives of linear enamines bearing at the α-position an electron-accepting substituent and a methyl group at the α-position was developed.

Keywords Phosphorylation; electrocyclization; λ5-phosphinines; 1,2-λ5-azaphosphinines

INTRODUCTION

Development of a convenient synthetic procedure for phosphine **1** allowed us to prepare it in gram scale batches. Phosphine **1** and other trivalent phosphorus derivatives bearing the enamine residue were readily alkylated with a set of alkyl bromides affording phosphonium salts. In the reaction with DMFDMA these salts were transformed into λ^5-phosphinines.[1] The phosphonium salts **2** were found to react differently with bases. While the salts **2** upon treatment with aqueous sodium hydroxide transformed into stable ylides **3**, heating the salts **2** with a catalytic amount of triethylamine lead to cyclic phosphonium salt **4**[2] (Scheme 1).

We have investigated various reaction conditions under which both the ylides **3** and the phosphonium salts **4** were converted into λ^5-phosphinines **5**. Thus, we have found that heating ylides **3** neat at 150°C in vacuo for **5** min resulted in the corresponding phosphinines 5 in moderate yields. Thus, one can conclude that ylide **3** undergoes thermal cyclization leading to cyclic ylide **7** followed by dehydration thus affording the final phosphinines **5** (Scheme 2).

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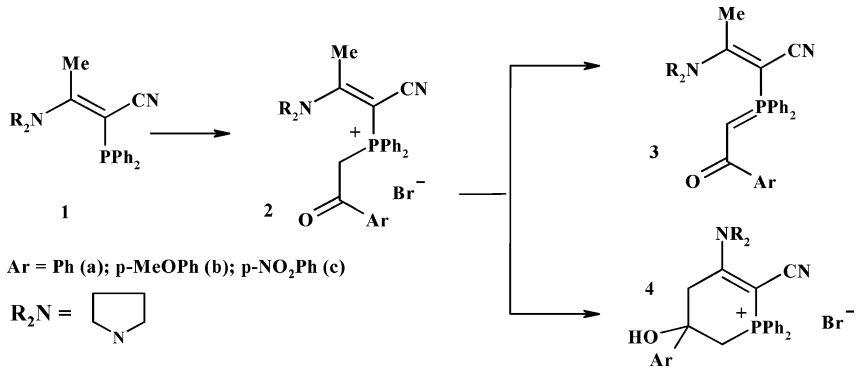
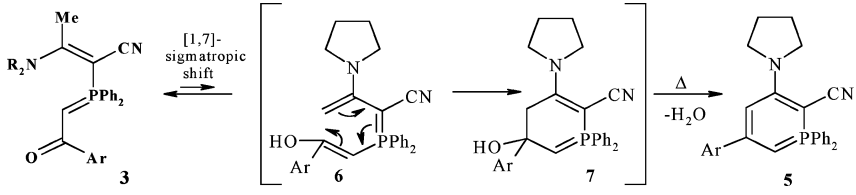


SCHEME 1



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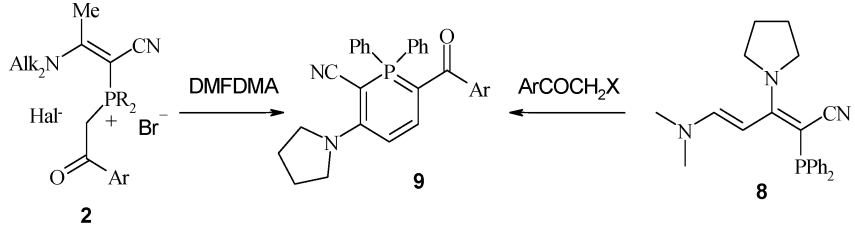

SCHEME 3

SCHEME 4

The treatment of phosphonium salt **2** with DMFDMA gave phosphinine 9. Also, these compounds could be prepared by an alternative method, namely by the reaction of dienamine **8** with bromoacetophenones at room temperature (Scheme 3).

This approach was successfully applied for the synthesis of λ^5-azaphosphinines **10** (Scheme 4).

Thus, a novel approach to λ^5-phosphinines and λ^5-azaphosphinines was proposed.

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