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

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New accessible methods of synthesizing λ^5 -phosphines and 1,2- λ^5 -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.

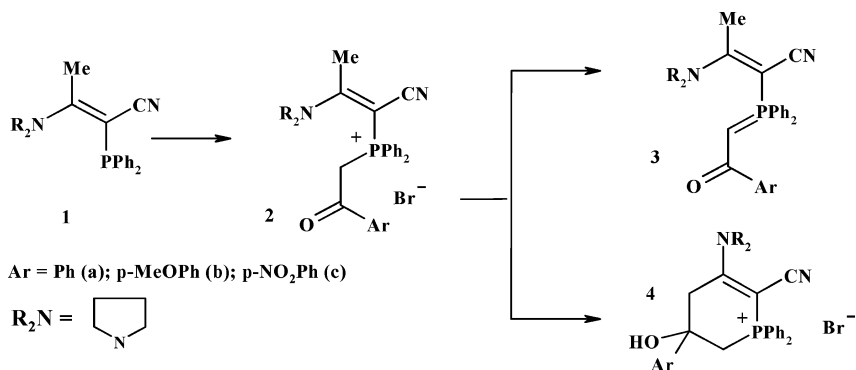
Keywords Phosphorylation; electrocyclization; λ^5 -phosphinines; 1,2- λ^5 -azaphosphinines

INTRODUCTION

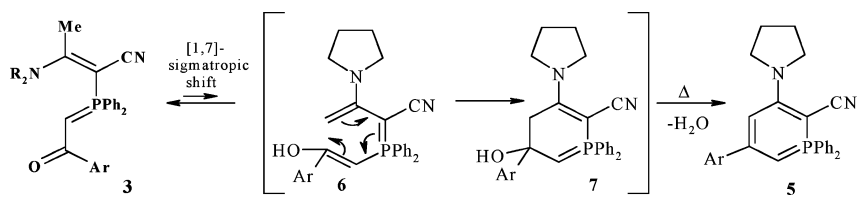
Development of a convenient synthetic procedure for phosphine **1** allowed us to prepare it in gram scale batches. Phosphine **1** and other trivalent phosphorus derivatives bearing the enamine residue were readily alkylated with a set of alkyl bromides affording phosphonium salts. In the reaction with 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).

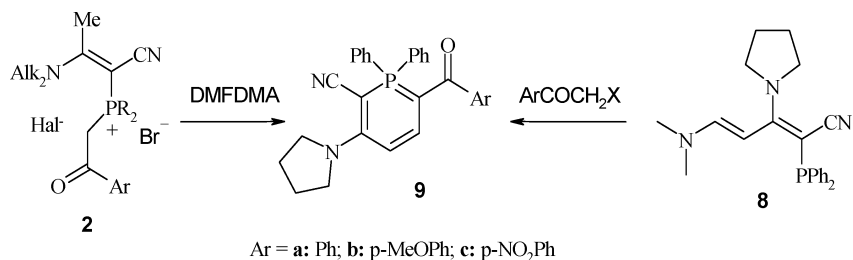
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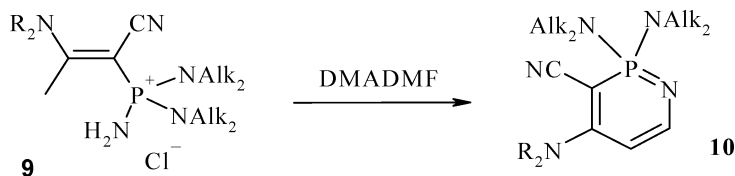
SCHEME 1



SCHEME 2



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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- [1] A. N. Kostyuk, Y. V. Svyaschenko, and D. M. Volochnyuk, *Tetrahedron*, **61**, 9263 (2005).
- [2] Y. V. Svyaschenko, A. N. Kostyuk, B. B. Barnych, and D. M. Volochnyuk, *Tetrahedron*, **63**, 5656 (2007).