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C-Phosphorylation of Formamidines

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C-Phosphorylation of Formamidines

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V. OSHOVSKY and ANDREW A. TOLMACHEFF

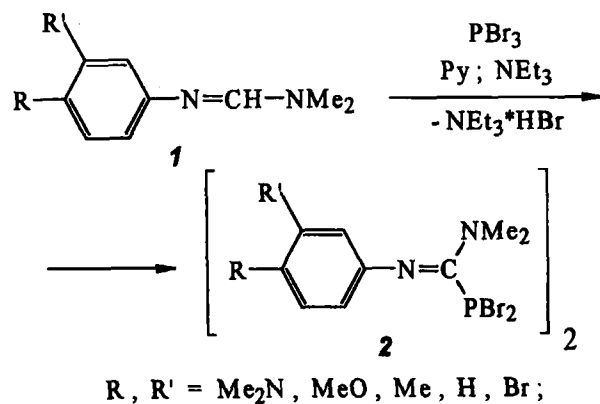
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C-Phosphorylation of formamidines by trivalent phosphorus halides was researched. Direction of the phosphorylation depends on nature of substituents at the amidine nitrogens. C-Phosphorylated products was shown to be of valuable possibilities to construct phosphorus-containing heterocycles.

Keywords: formamidines; C-phosphorylation; phosphorus-containing heterocycles

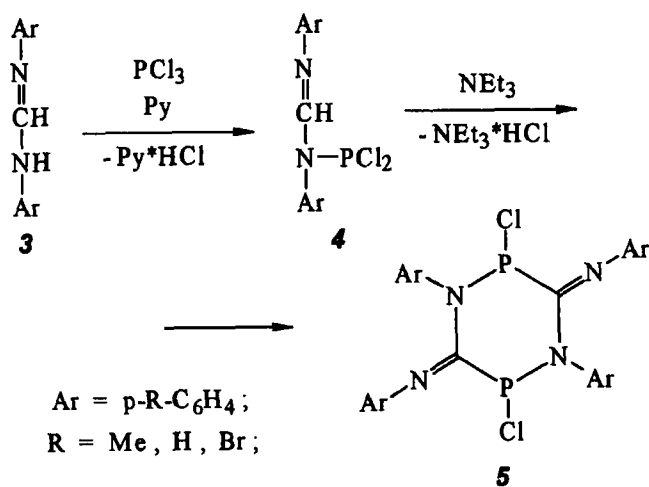
We have first realized C-phosphorylation of N,N,N'-trisubstituted formamidines and N,N'-disubstituted formamidines by trivalent phosphorus halides at the formamidine carbon atom. There is no information on similar reactions of formamidines with other electrophilic reagents in literature.

N¹,N¹-dimethyl-N²-arylformamidines **1** undergoes phosphorylation at the formamidine carbon atom to furnish dibromophosphine **2** (Scheme 1)^[1].



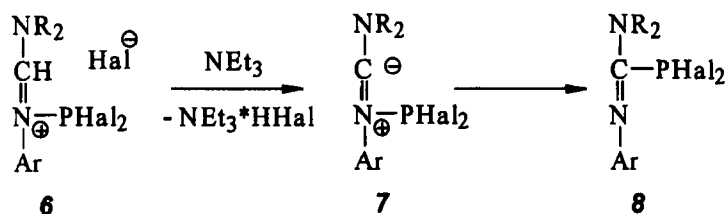
Scheme 1

In the case of N,N' -diarylformamidines **3** C-phosphorylation at the formamidine carbon atom is preceded by the classical formation of N-phosphorylated amidine **4**, what leads to 1,4,2,5 – diazadiphosphorinanes **5** (Scheme 2).



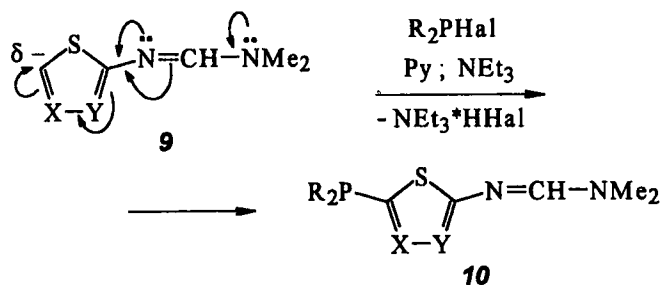
Scheme 2

Formation of the C—P bond is supposed to occur according to “ylide mechanism”, which consists in preliminary attack at the imine nitrogen atom, what considerably increases formamidine CH-acidity. It allows the formation of betaine **7** from **6** under action of comparatively weak base (triethylamine). The final dihalidophosphine **8** is formed by 1,2-N,C-phosphorotropic migration (Scheme 3).



Scheme 3

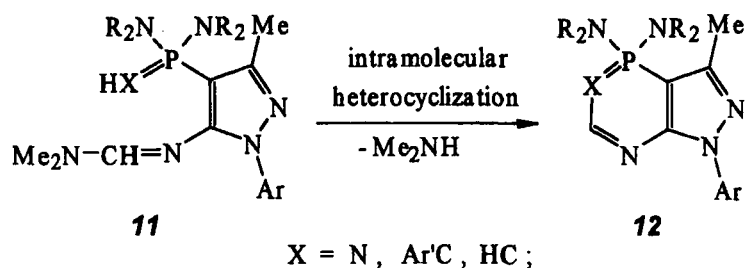
In the case of systems containing substituents with considerably alternated ordinary and double bonds **9**, amidine substituent acts as strong π -donor ($\sigma^\circ = -0.25$)^[2]. The phosphorylation of the systems **9** leads to introducing phosphorus substituent to heterocyclic moiety of the molecule with formation of amidinyldiarylposphines **10** (Scheme 4)^[3,4,5].



Scheme 4

In many of these cases the phosphorylation could be accomplished not only by $\text{P}(\text{Hal})_3$, but also by less reactive arylhalidophosphines and amidochlorophosphites (Scheme 4). Similar transformations have also been carried out with pyrazolyl- and 1,2,4-triazolylformamidines. Phosphorylation of N,N -dimethyl- N' -hetarylformamidines can also be used in syntheses of trihetarylphosphines.

Introduction of dihalidophosphino- moiety at the neighbour to the amidine position and its further transformation into reactive nucleophilic (ylide, phosphazohydride) function leads to compounds **11**, which undergo intramolecular transamination to furnish novel condensed heterocyclic systems **12** (Scheme 5)^[5].



Scheme 5

References

- [1] G.V. Oshovsky, A.M. Pinchuk, A.N. Chernega, I.I. Pervak, A.A. Tolmachev, *Mendelev. Commun.*, 1998, in print.
- [2] Eva D. Raczynska, M. Drapala, *J. Chem. Res. Synop.*, **2**, 54–55, 1993.
- [3] G.V. Oshovsky, A.A. Tolmachev, A.A. Yurchenko, A. S. Merkulov, A.M. Pinchuk, *Russ. Chem. Bull.*, **9**, 1998.
- [4] G.V. Oshovsky, F.F. Tolmachev, A.S. Merkulov, A.M. Pinchuk, *Khim. Geterotsikl. Soedin.*, **10**, 1422, 1997.
- [5] G.V. Oshovsky, A.M. Pinchuk, A.A. Tolmachev, in print.