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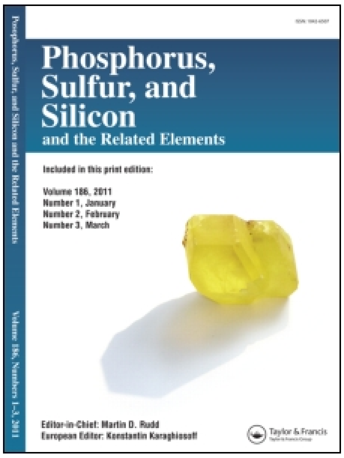

Phosphorus, Sulfur, and Silicon and the Related Elements

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C-Phosphorylation of Formamidines

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To cite this Article Pinchuk, Alexander M. , Merkulov, Anatoly S. , Oshovsky, Gennady V. and Tolmachev, Andrew A.(1999) 'C-Phosphorylation of Formamidines', Phosphorus, Sulfur, and Silicon and the Related Elements, 144: 1, 713 — 716

To link to this Article: DOI: 10.1080/10426509908546344

URL: http://dx.doi.org/10.1080/10426509908546344

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Phosphorus, Sulfur and Silicon, 1999, Vol. 144-146, pp. 713-716
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Printed in Malaysia

C-Phosphorylation of Formamidines

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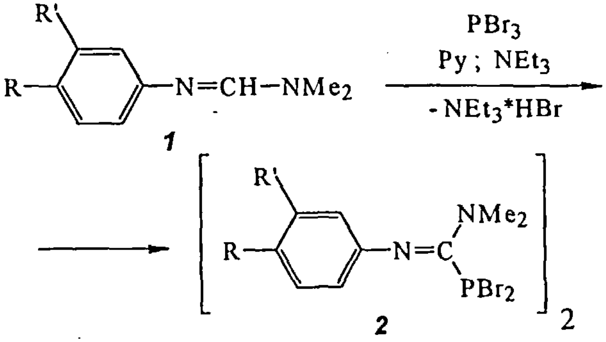
C-Phosphorylation of formamidines by trivalent phosphorus halides was researched. Direction of the phosphorylation depends on nature of substituents at the amidine nitrogens. C-Phosphorylated products was shown to be of valuable possibilities to construct phosphoruscontaining heterocycles

Keywords: formamidines; C-phosphorylation; phosphoruscontaining 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.

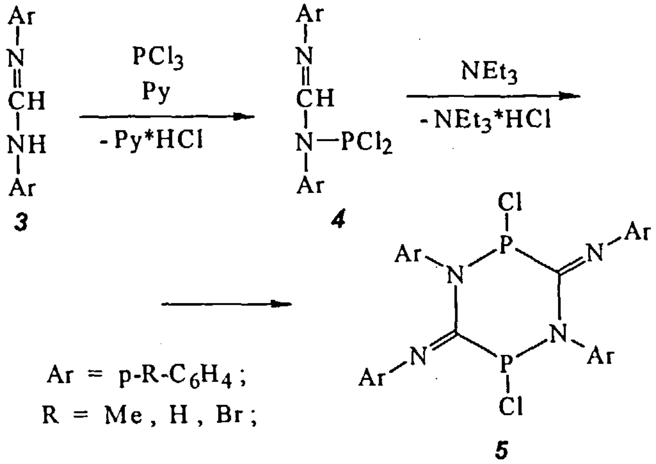
N^1,N^1-dimethyl-N^2-arylformamidines ***1*** undergoes phosphorylation at the formamidine carbon atom to furnish dibromophosphine ***2*** (Scheme 1)[1].



R , R' = Me_2N , MeO , Me , H , Br ;

Scheme 1

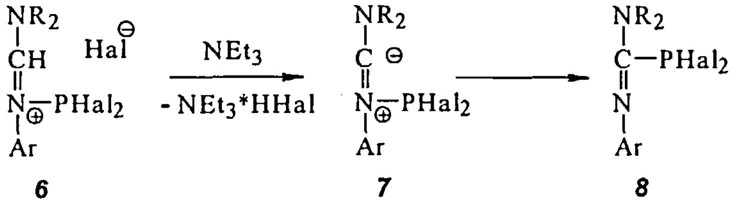
In the case of N,N'-diarylformamidines **3** C-phosphorylation at the formamidine carbon atom is preceded by the classical formation of N-phosphorylated amidine **4**, what leads to 1,4,2,5 – diazadiphosphorinanes **5** (Scheme 2).



Ar = p-R-C_6H_4 ;
R = Me , H , Br ;

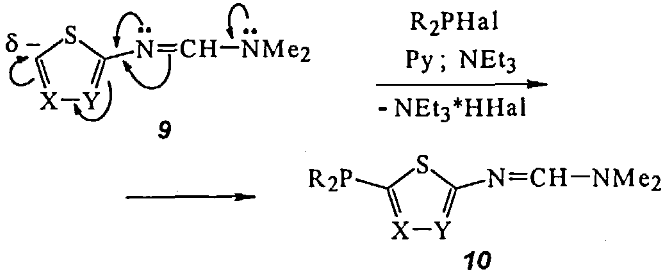
Scheme 2

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 (σ° = -0.25)[2]. The phosphorylation of the systems **9** leads to introducing phosphorus substituent to heterocyclic moiety of the molecule with formation of amidinylhetarylphosphines **10** (Scheme 4)[3,4,5].

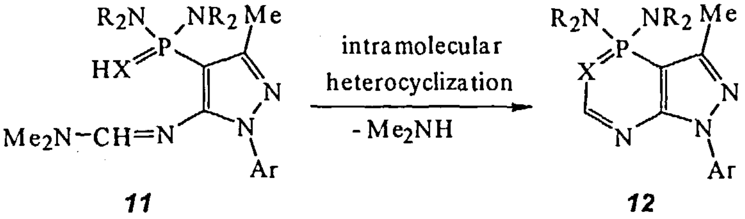


R = Hal, Et_2N, Ph ; X, Y = N, HC, R'C ;

Scheme 4

In many of these cases the phosphorylation could be accomplished not only by $PHal_3$, 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].



11 **12**

X = N, Ar'C, HC;

Scheme 5

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