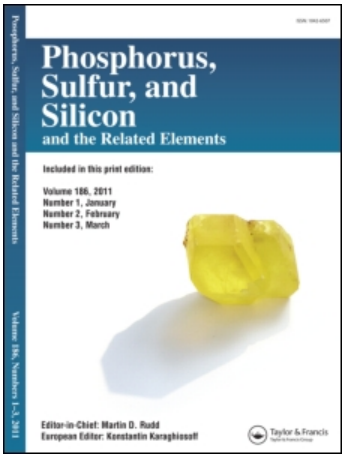

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C-Phosphorylation of Azoles in Synthesis of Novel Fused Phosphorus-Containing Heterocycles

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C-PHOSPHORYLATION OF AZOLES IN SYNTHESIS OF NOVEL FUSED PHOSPHORUS-CONTAINING HETEROCYCLES

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Keywords: Azole; fused phosphorus-containing heterocyclic systems; phosphorylation

Direct C-phosphorylation with phosphorus(III) halides in basic medium has proved to be an efficient and convenient method for the introduction of a variety of phosphorus functions in the electron-rich heteroaromatic[1] compounds. When applied to functionalized pyrroles,[2] this reaction has afforded a number of novel phosphorus-containing fused heterocycles. Herein, we report on our recent findings concerning the construction of phosphorus-containing fused heterocycles having azole nuclei.

Readily available derivatives of 5-amino-1-aryl-3-methylpyrazoles—amides, ureas, and azomethines[3]—have been subjected to the phosphorylation with P(III) halides in basic medium to produce bi- and even tricyclic (as in the last case) heterocyclic compounds having an endocyclic phosphorus atom (Figure 1).

We explored the same approach concerning 1,3-azoles, known to be phosphorylated via a different mechanism.[4] We have shown that the amide **5** (X = CH) reacts with phosphorus tribromide as well as with dibromophenylphosphine in basic medium to yield the 4,5-dihydrobenzo[*e*]imidazo[2,1-*c*][1,4,2]diazaphosphinine derivatives, which could be converted into P(V) derivatives **8** and **9**[5] (Figure 2).

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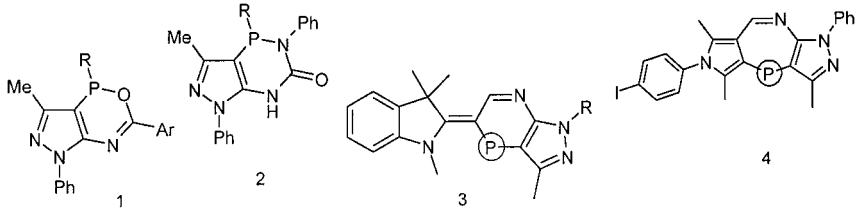

FIGURE 1

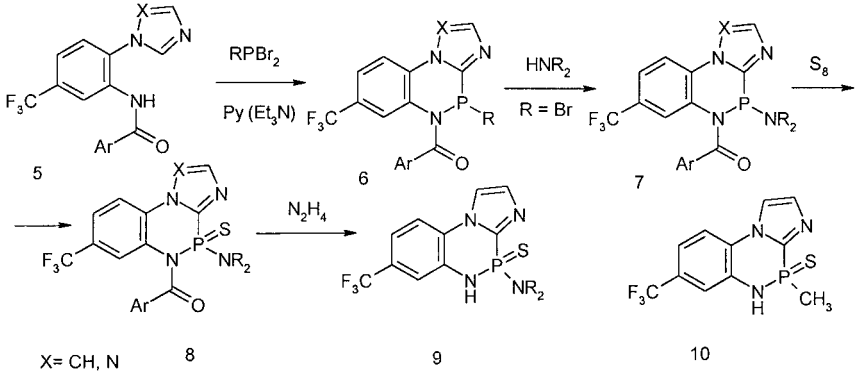

FIGURE 2

It has been found that the similar amide **5** (X = N) bearing the 1,2,4-triazole moiety could also be phosphorylated, although less activity of this compound is noted.

Moreover, phosphorus(V) acid chlorides, known as phosphorylating agents of less reactivity, were shown to react with the parent imidazolylaniline of **5** to furnish the 4,5-dihydrobenzo[*e*]imidazo[2,1-*c*][1,4,2]diazaphosphinine derivatives, such as **10**. The phosphorylation of the amide of 3,5-dimethoxybenzoic acid (**11**) with PBr_3 yielded the cyclic bromophosphonite **12**, which underwent intramolecular ring closure under heating to produce the pentacyclic compound **13** (Figure 3).

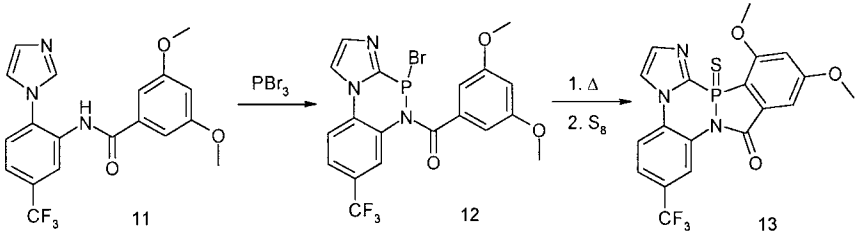

FIGURE 3

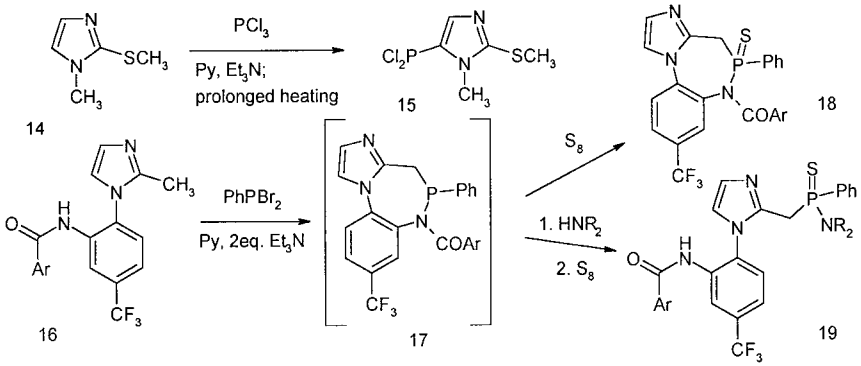

FIGURE 4

We have found very recently that imidazole can be phosphorylated not only at the *meso* position but also at position 5 when the preferred 2-position is blocked by an SCH_3 group, as in **14** (Figure 4). However, the reaction of the 2-methylimidazole derivative **16** with dibromophenylphosphine proceeded through the phosphorylation of the methyl group and resulted in the construction of a seven-membered heterocycle (**17**, **18**).

In conclusion, we have shown that in spite of the difference in the phosphorylation mechanisms, a number of functionalized derivatives of both pyrazoles and 1,3-azoles could be successfully employed in the design of phosphorus-containing fused heterocyclic systems via their reaction with phosphorus(III) halides.

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