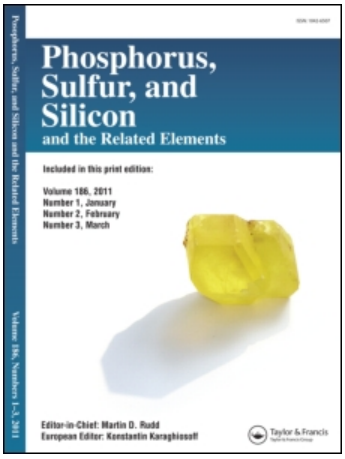

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

C-Phosphorylation of Azoles with Trivalent Phosphorus Halides

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To cite this Article Pinchuk, Alexander M. , Tolmachev, Andrew A. , Kostyuk, Alexander N. , Yurchenko, Alexander A. and Sviridon, Angelika I.(1996) 'C-Phosphorylation of Azoles with Trivalent Phosphorus Halides', Phosphorus, Sulfur, and Silicon and the Related Elements, 109: 1, 477 — 480
To link to this Article: DOI: 10.1080/10426509608545194
URL: http://dx.doi.org/10.1080/10426509608545194

Phosphorus, Sulfur, and Silicon, 1996, Vols. 109–110, pp. 477–480
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C-PHOSPHORYLATION OF AZOLES WITH TRIVALENT PHOSPHORUS HALIDES

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Abstract Simple method of C-phosphorylation of azoles by trivalent phosphorus halides in the pyridine solution have been developed. Hetaryldihalogen, dihetarylhalogen-, trihetarylphosphines, which were transformed into new types of P(III) and P(IV) derivatives, have been synthesized. Features of their reaction ability stipulated by the influence of hetaryl residues are found.

INTRODUCTION

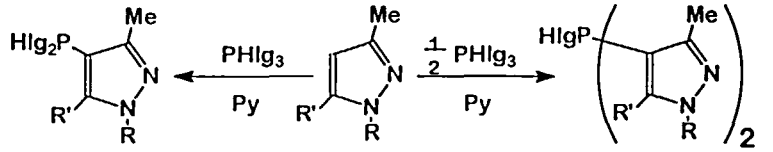
We have found C-phosphorylation's conditions of pyrrole, furan, thiphene derivatives [1] and related compounds. We have ascertained that the method of phosphorylation can be extended to phosphorylation of pyrazole and imidazole derivatives, their benzanalogs and more complicated heteroaromatic condensed systems, containing azole fragment.

RESULTS AND DISCUSSION

Pyrazoles **1** are easily phosphorylated by phosphorus (III) halides (Hlg = Cl, Br) in the pyridine solution at the fourth position. One or two pyrazole residue can be introduced at a single phosphorus atom.

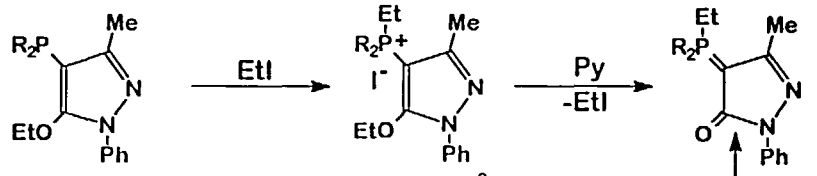
Proceeded from halogenphosphines **2** and **3** different derivatives were prepared. Among them, compounds **4** containing the alkoxy group at the fifth position

of the ring possess an especial reaction ability, namely, under heating or action of alkylhalides they are rearranged into ylids 5 [2].



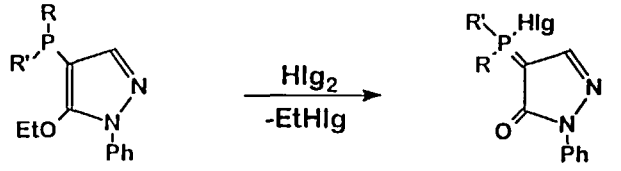
Hlg = Cl, Br ; R= Me, Ph ; R' = AlkO, Alk, Cl

3 1 2



4 5

The rearrangement discovered was used for synthesis of P-halides **6a,b** [3].

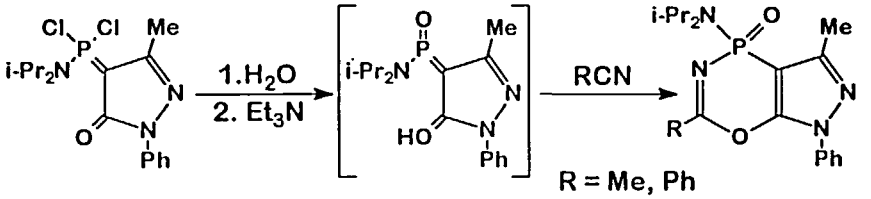


a: R = R' = Ph, R_2N ; Hlg = Cl, Br ;
b: R = i-Pr_2NH, R' = Cl ; Hlg = Cl ;

6 a,b

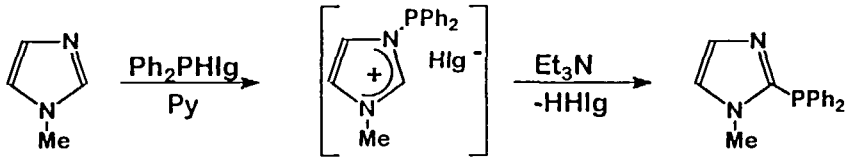
Chlorine atoms in the P-chlorides **6a,b** are sufficiently mobile and easily substituted under action of O,N,S-nucleophiles. In the case of dichloroylids, the derivatives containing double P=E bond (E = N, O, S) are formed. Reactions of dichloroylide **6b**, when P=E bond is formed under action of one mole of a nucleophile, present particular interest. For example, the reaction of **6b** with one mole of water directs to the formation of the derivative of a methylene(oxo)phosphorane (7), which have been transformed into novel types of phosphopruscontaining heterocycles

(8) under action of nitriles.



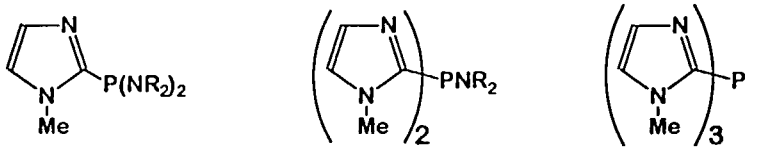
6b 7 8

Phosphorylation of N-substituted imidazoles by trivalent phosphorus halides proceeds into the stage of formation of N-phosphinoimidazolium salts **10**, which are transformed into resulted phosphines, such as, for example, **11**.



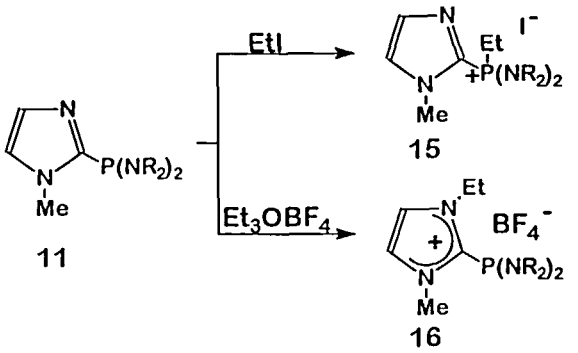
9 10 11

Phosphines **12-14** are formed depending from the ratio of N-methylimidazole and phosphorus (III) halides in the reaction [4].

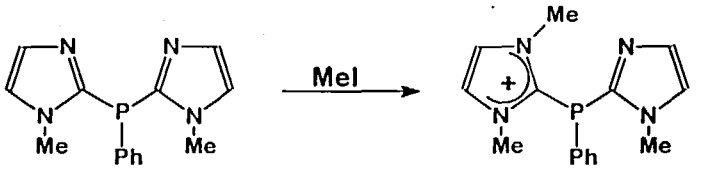


12 13 14

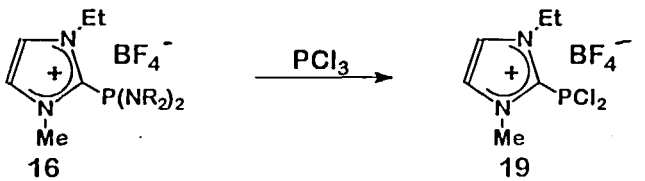
Phosphines **12-14** display unusual properties in the reactions of alkylation [5]. Either phosphonium salts (**15**) or imidazolium ones (**16**) are formed depending from hardness and softness of an alkylation reagent used.



Alkylation proceeds at the nitrogen atom even under action of methyliodide in the case of phosphine **17**.



Reaction of imidazolium salt **16** and phosphorus trichloride directs to the novel type of dichlorophosphines **19** which can be used for the synthesis of different derivatives.



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