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# Phosphorus, Sulfur, and Silicon and the Related Elements

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Alexander M. Pinchuk; Andrew A. Tolmachev; Alexander N. Kostyuk; Alexander A. Yurchenko; Angelika I. Sviridon

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C-PHOSPHORYLATION OF AZOLES WITH TRIVALENT PHOSPHORUS HALIDES

ALEXANDER M. PINCHUK, ANDREW A. TOLMACHEV, ALEXANDER N. KOSTYUK, ALEXANDER A. YURCHENKO, ANGELIKA I SVIRIDON

Institute of Organic Chemistry of the Ukrainian National Academy of Sciences; Murmanskaya Str., 5, KIEV-94, 253660, UKRAINE.

Abstract Simple method of C-phosphorylation of azoles by trivalent phosphorus halides in the pyridine solution have been developed. 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].

HIg<sub>2</sub>P 
$$\stackrel{\text{Me}}{\underset{R}{\text{N}}}$$
  $\stackrel{\text{Hig}}{\underset{R}{\text{PH}}}$   $\stackrel{\text{Me}}{\underset{R}{\text{PH}}}$   $\stackrel{\text{Hig}}{\underset{R}{\text{PH}}}$   $\stackrel{\text{Me}}{\underset{R}{\text{PH}}}$   $\stackrel{\text{Hig}}{\underset{R}{\text{PH}}}$   $\stackrel{\text{Me}}{\underset{R}{\text{N}}}$   $\stackrel{\text{Hig}}{\underset{R}{\text{PH}}}$   $\stackrel{\text{Me}}{\underset{R}{\text{N}}}$   $\stackrel{\text{Hig}}{\underset{R}{\text{PH}}}$   $\stackrel{\text{Me}}{\underset{R}{\text{N}}}$   $\stackrel{\text{Hig}}{\underset{R}{\text{N}}}$   $\stackrel{\text{Me}}{\underset{R}{\text{N}}}$   $\stackrel{\text{Hig}}{\underset{R}{\text{N}}}$   $\stackrel{\text{Me}}{\underset{R}{\text{N}}}$   $\stackrel{\text{Hig}}{\underset{R}{\text{N}}}$   $\stackrel{\text{Me}}{\underset{R}{\text{N}}}$   $\stackrel{\text{Hig}}{\underset{R}{\text{N}}}$   $\stackrel{\text{Me}}{\underset{R}{\text{N}}}$   $\stackrel{\text{Hig}}{\underset{R}{\text{N}}}$   $\stackrel{\text{Hig}}{\underset{R}{\text{N}}}$   $\stackrel{\text{Ne}}{\underset{R}{\text{N}}}$   $\stackrel{\text{Hig}}{\underset{R}{\text{N}}}$   $\stackrel{\text{Ne}}{\underset{R}{\text{N}}}$   $\stackrel{\text{Hig}}{\underset{R}{\text{N}}}$   $\stackrel{\text{Ne}}{\underset{R}{\text{N}}}$   $\stackrel{\text{Hig}}{\underset{R}{\text{N}}}$   $\stackrel{\text{Ne}}{\underset{R}{\text{N}}}$   $\stackrel{\text{Hig}}{\underset{R}{\text{N}}}$   $\stackrel{\text{Ne}}{\underset{R}{\text{N}}}$   $\stackrel{\text{Ne}}{\underset{R}{\text{N}}}$   $\stackrel{\text{Ne}}{\underset{R}{\text{N}}}$   $\stackrel{\text{Hig}}{\underset{R}{\text{N}}}$   $\stackrel{\text{Ne}}{\underset{R}{\text{N}}}$   $\stackrel{\text{Ne}}{\underset{R}{\text{Ne}}}$   $\stackrel{\text{Ne}}{\underset{R}{\text{N}}}$   $\stackrel{\text{Hig}}{\underset{R}{\text{Ne}}}$   $\stackrel{\text{Ne}}{\underset{R}{\text{Ne}}}$   $\stackrel{\text{Ne}$ 

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

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.

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.

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

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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