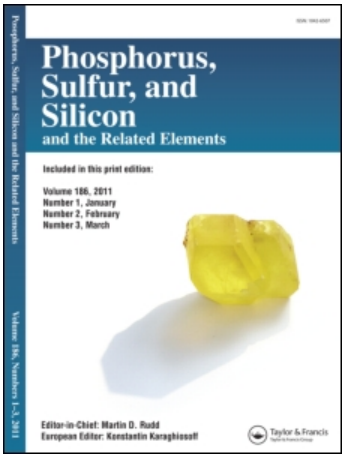

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The Theoretical and Experimental Investigation of the Halogencyclenes' Phosphorylation

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THE THEORETICAL AND EXPERIMENTAL INVESTIGATION OF THE HALOGENCYCLENES' PHOSPHORYLATION

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The phosphorylation reactions of the oxygen- and nitrogen-containing halocyclenes—3,4-dichloro-5-hydroxyfuranone, 3,4-dichloro-5-substituted pyrrolinon-2-ones and N-phenyl-4,5 dichloropyridazin-2-one by σ^3-phosphorus compounds—trialkylphoshphites, triphenylphosphine, and some P-functionalized derivatives of the trivalent phosphorus are studied. The reactions' mechanisms are discussed; the possible and preferable reactions' routes and the relative thermodynamic stabilities of the products and intermediates are estimated via the quantum-chemical methods.

Keywords: Arbusov reaction; halocyclenes; σ^3-phosphorus derivatives; phosphorylation; quantum-chemical calculations; reaction mechanism

The phosphorylation of halogencyclenes via the derivatives of trivalent phosphorus relates to a type of Arbuzov's reaction. In the first stage it usually occurs as nucleophilic vinil sustitution of halogen atom, linked with the heterocyclic carbon atom to give phosphonium or quasiphosphonium salts **2**. As we have shown earlier,[1] the further development of phosphorlation process occurs with the participation both of substituents at phosphorus atom and neighboring functional groups of heterocyclic fragment.

We have demonstrated[2] that methyl ester of mucochloric acid **1** (X=O, R=OMe) and 3,4,5-trichlorofuranon **1** (X=O, R=Cl) react with

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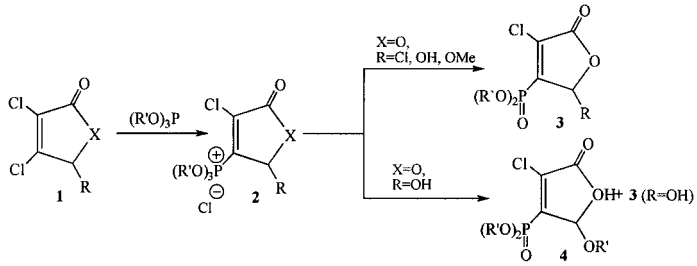
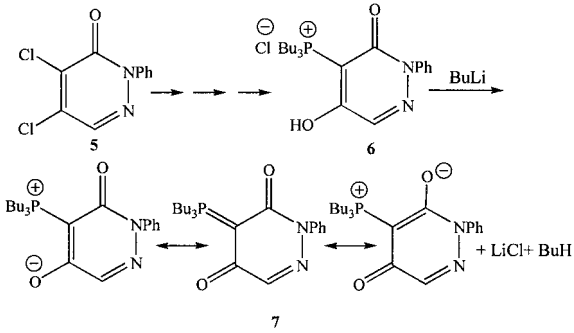
trialkylphosphites, substituting the chlorine atom at position 4 by dialkoxyphosphinoyl group and formation of 4-phosphorylated furanones **3** (X=O, R=OMe, Cl). Mucochloric acid **1** (X=O, R=OH) reacts with trialkylphospites another way: main reaction product is the mixture of β-phosphorylated mucochloric acid **3** (R=OH) and its alkyl ester **4**. They may be separated via column chromatography.



The nitrogen-containing analogue of mucoclhoric acid-3,4-dchloro-5-substituted pyrrolinones **1** (X=NH, R=OH, OMe, OBz) are unable to phosphorylate by treatment with trialkylphosphites and triphenylphosphine, even by heating till 150°C.

On the basis of the quantum-chemical calculations,[3] we have shown that the reasons for differences in the reactivity of both kind of heterocyclenes are connected with the difference of the LVMO energies. Pyrrolinones have a much higher located LVMO and are less sensitive to the nucleophilic attack than furanones

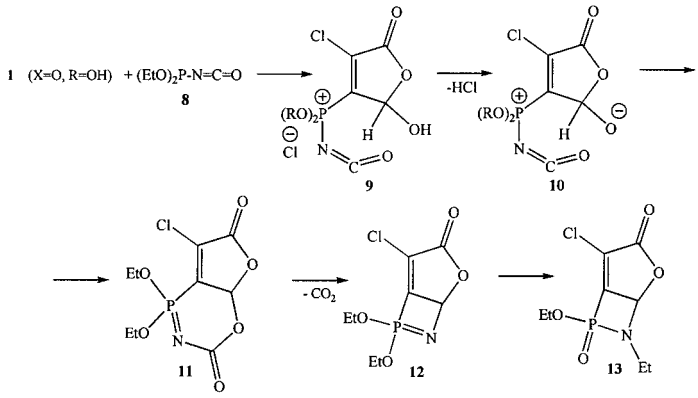
The attempts to phosphorylate the six-membered nitrogen-containing dihalocyclene-N-phenyl-dichloropyridazinone **5** were finished with no success. The reactions with trialkylphosphites and triphenylphosphine do not proceed at temperature range from 40 to 150°C. However, we have managed to obtain the phosphorylation product using lithium diphenylphosphide and tributylphosphine as the phosphorylating agents.



The quantum chemistry and X-Ray methods allow us to establish that the last reaction leads to the phosphonium salt **6**, which may be converted into betaine/ylide **7** by treatment with BuLi.[4]

We have shown that the synthetic potential of the phosphorylation reactions depends not only on the nature of the heterocyclic species but also from the functional groups linked with the σ^3-phosphorus atom. For instance, the phosphorisocyanatidites **8** were chosen as the phosphorylating agents. The synthetic versatility of these compounds is due, on the one hand, to the presence of nucleophilic σ^3-phosphorus atom, and the other hand to the tendency of isocyanato group to the nucleophilic addition and cycloaddition reactions.

It was detected[5] that hydroxyfuranone **1** already reacts with the isocyanate **8** at room temperature, forming the bicyclic phosphonamidate **13**. Reaction proceeds via the Arbuzov reaction route, intermediately forming the quaziphosphonium salt **9** and then—the betaine **10**, further cyclizing into the imine **11**. After decarboxylation of the last intermediate, the **12** rearrangement into the final product **13** takes place.



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