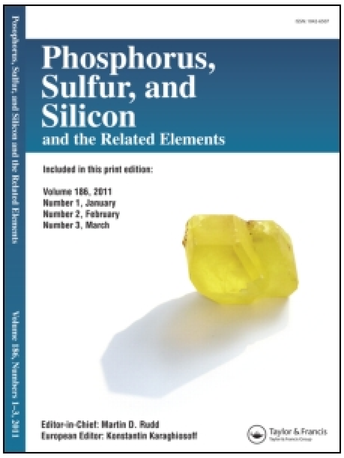

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Arbuzov Reaction in the Series of Halogenocyclenes: New Synthetical and Mechanistical Variants

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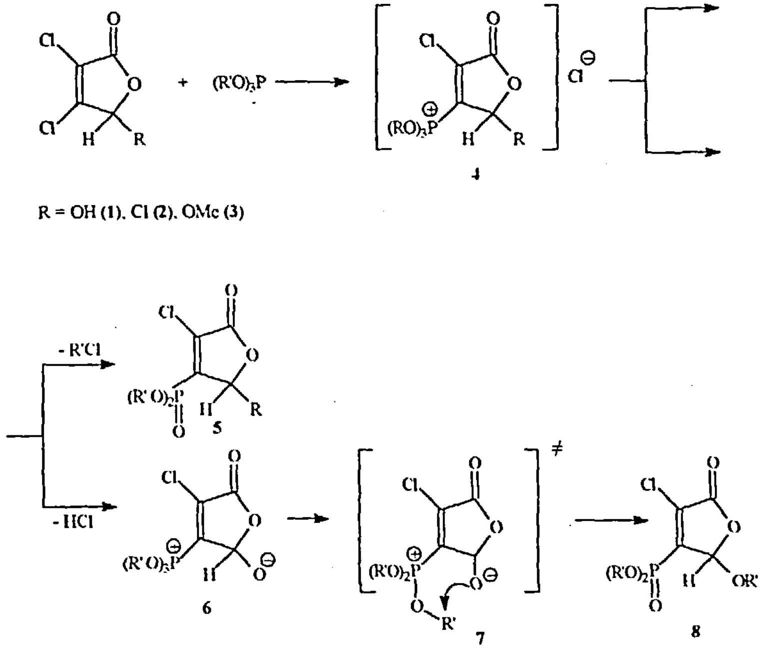
A new method of synthesis of phosphorylated furanones on the basis of tricoordinated phosphorus derivatives reaction with mucochloric acid and some of its derivatives is elaborated. The kinetic investigation of the reaction of phosphites (1, R = Me, Et, Pr, Bu, Ph) with mucochloric acid allowed to establish the reaction mechanism including competitive elimination of RCl or HCl from the obtaining intermediate. The ratio of these two possible reaction ways depends on the nature of substituents at phosphorus.

Keywords: phosphorylated furanones; Arbuzov reaction; kinetics investigation

The reaction of phosphites and other P(III)-derivatives with halogencyclenes is interesting and attractive method of synthesis of phosphorylated heterocycles. Interaction of P(III)-nucleophiles with mucocloric acid **1** and its derivatives **2** and **3** is the subject of the present work.

It was found [1,2] that furanones **2** and **3** react with trialkylphosphites, substituting the chlorine atom at C-4 position of furanones yielding phosphorylated furanone **5** (R = Cl, OMe).

Mucochloric acid **1** itself reacts with phosphites in another way, giving as main reaction product a mixture of β-phosphorylated 5-hydroxyfuranone (**5**, R = OH) and its 5-alkoxy derivative **8** (R' = Me, Et, Pr, Bu, Ph) [3].



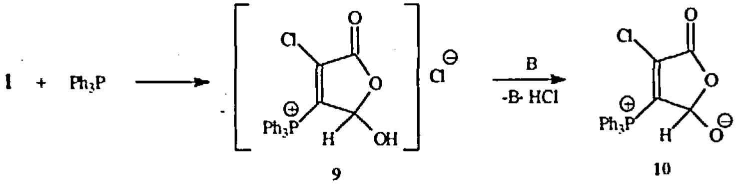
R = OH (1), Cl (2), OMe (3)

Kinetic and synthetical investigation of this reaction [3] allows to suggest the mechanism, involving on the first stage the nucleophilic substitution of chlorine atom by dialkoxyphosphinoyl group at C-4 with the formation of phosphonium intermediate 4. Its further stabilization carries out by two directions. First of them is the classical Arbuzov reaction and involves elimination of alkyl halide to form furanone 5.

Another direction consists in elimination of hydrogen chloride (non-classical Arbuzov reaction) to form betaine 6. Intramolecular dealkylation, involving transition state 7, leads to phosphonates 8.

Using ^{31}P NMR spectra we have established the ratio 5:8, which depends on the size of alkyl substituents R': Me 45:55; Et 63:37; Pr 69:31; Bu 84:16; Ph 100:0.

The intermediate formation of phosphonium salts of the type 4 was proved by isolation of stable phosphonium salt 9 in reaction of 1 with Ph_3P [4].

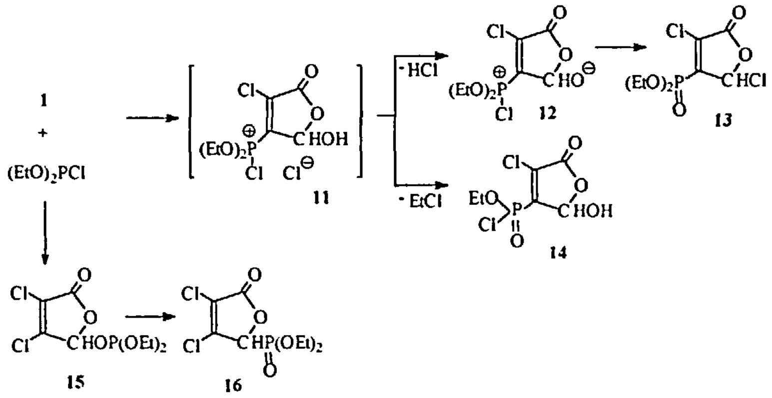


B = Et$_3$N. Ph$_3$P. Na$_2$CO$_3$

Salt **9** is capable to eliminate hydrogen chloride under the action of Et$_3$N, Na$_2$CO$_3$ and excess of Ph$_3$P. The structure of **9** was established by X-Ray analysis.

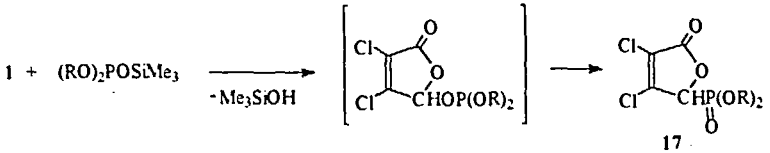
To include other reaction centers of **1** in the processes of phosphorylation we involved **1** into reaction with Ph$_2$PCl [4]. We expected that the reaction could occur either by a nucleophilic mechanism, like trialkylphosphites, or by esterification of Ph$_2$PCl by OH-group of **1**. We found that only the first path is realized.

When **1** and diethylclorophosphite reacted the multy-routs reaction took place [5].



Nucleophilic substitution of chlorine in β-position yields phosphonium salt **11**, which undergoes intramolecular rearrangement to 3,5-dichlorofuranone **13** via elimination of HCl and betaine **12** formation. At the same time the dealkylation of phosphonium center by the action of chloride-anion results furanone **14**.

Competitive reaction path involves substitution of of chlorine atom in chlorophosphite by hydroxy-group to yield furanonylphosphite **15** and then - 5-phosphinoylfuranone **16**. Reaction of **1** with phoshites, containing trimethylsilyl groups [6], occurs in a strictly chemoselective manner yielding 5-dialkoxyphosphinoyl-3,4-dichlorofuranone **17**.



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So, the presence of several active reaction centers in the molecule of **1** permits it to react with P(III)- derivatives by different pathways. It allowed us to propose new methods of synthesis of phosphorylated derivatives of **1** and other chlorofuranones.

Acknowledgments

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