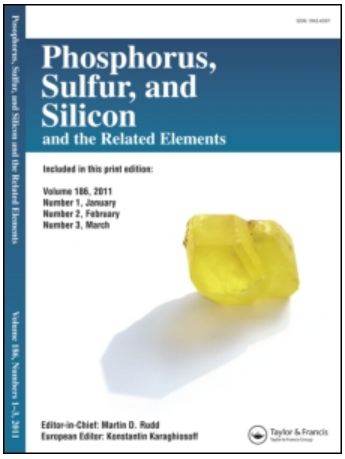

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Interaction of 2-Alkoxy-3-Alkyl-1,3,2-Oxazaphosphinanes with Alkyl Chloroformates

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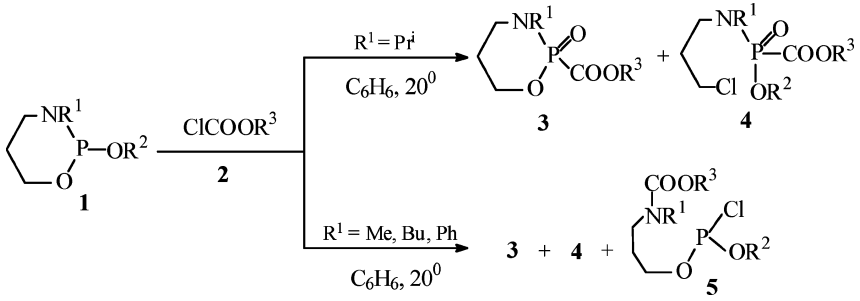
Depending on steric hindnanus at the nitrogen atom interaction of 2-alkoxy-3-alky(aryl)-1,3,2-oxazaphosphinanes with alkyl chloroformates proceeds according to the Arbuzov reaction or with the formation of acyclic chlorofosphites.

Keywords 1,3,2-oxazaphosphines; alkyl chlolformated; Arbuzov reaction; phosphoryl formic acid derivatives; chlorophosphites

1,3,2-Oxazaphosphinane analogues of phosphoryl formic acid derivatives could be of interest as biologically active compounds. In this connection the reaction of phosphinanes (**1**) with alkyl chloroformates (**2**) was investigated.



In contrast to the interaction of phosphinanes **1** with haloacetic acid derivatives,[1] the reaction of esters **1** with chloroformates (products and

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their yields ratio) drastically depends not only on the structure of the substituent R^2 in ester group but also on the structure of the substituent R^1 at the nitrogen atom. When $R^1 = i$-Pr the reaction proceeds only with the formation of two main products of the Arbuzov rearrangement – without (**3**) and with (**4**) opening of the cycle, and yields ratios depend noticeably on the structure of R^2 (according to NMR ^{31}P data **3** and **4** ratios are from 94:6 for R^2 = Me to 24.5:75.5 for $R^2 = i$-Pr). But when R^1 = Me, Bu or Ph along with the Arbuzov reaction products **3** and **4** the formation of chlorophosphite (**5**) takes place. When R^1 is Me or Ph chlorophosphite **5** becames the main product of the reaction (the ratio of **5** to **3**+**4** is 72:28) and for R^1 = Bu this ratio is 15:85. The ratio between **5** and **3**+**4** also depends on the polarity of the solvent and temperature. We suppose the main factor determining the reaction pathway and yields ratio of products is the steric hindrances at the nitrogen atom. The structure of chlorophosphites **5** was verified by the conversion into phosphorothioates or amidophosphorothioate. The structure of the latter was confirmed by X-ray data.

REFERENCE

[1] A. E. Shipov, G. K. Genkina, P. V. Petrovskii, and T. A. Mastryukova, *Russ. Chem. Bull. Int. Ed.,* **53,** 1996 (2004).