

DIALKYL *N*-ALKOXY-*N*-(*N*'-ARYL(ALKYL)CARBAMOYL)PHOSPHORAMIDATES AND DIALKYL *N*-ALKOXY-*N*-(4-TOLUENESULFONUL)PHOSPORAMIDATES. SYNTHESIS AND STRUCTURE

Shtamburg V.G.¹, Klots E.A.,¹ Kravchenko S.V.,² Anishchenko A.A.³, Shishkina S.V.⁴, Mazepa A.V.⁵

¹Ukrainian State University of Science and Technologies

²Dnipro State Agrarian and Economic University sytailor@ukr.net

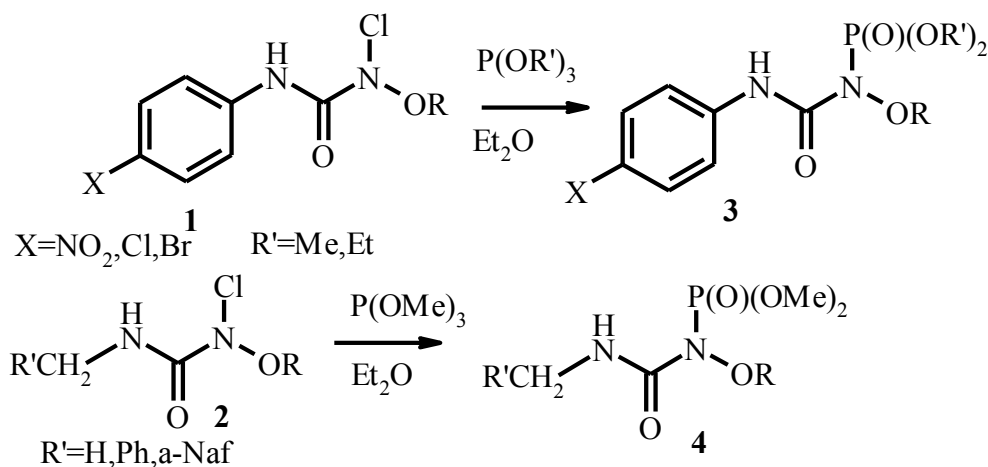
³O.Gonchar Dnipro National University

⁴Institute of Organic Chemistry of NAS of Ukraine

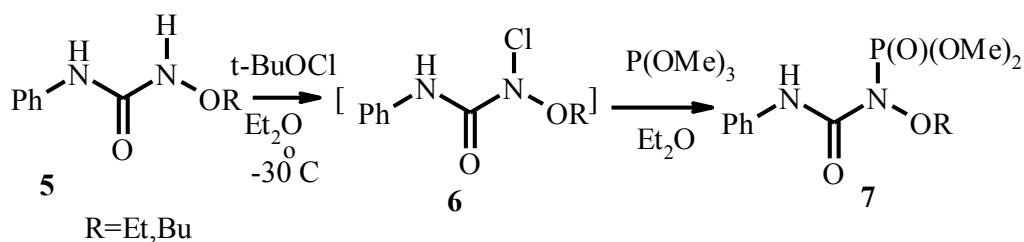
⁵A.V. Bogatsky Physico-Chemical Institute of NAS of Ukraine

Phosphoramidates and their derivatives are widely used in medicine, medicinal chemistry and agriculture. Molecules, containing P–N bond, are found in a large array biologically active natural products. While the synthetic routs to phosphoramidates are not limited now, the creating of new route to obtain could be useful. Urea and sulfonylamides are widely used in medicinal chemistry and drug design too. Thus, the creation of new synthetic route of compounds, which would simultaneously posses structural features of both phosphoramidates and ureas, or phosphoramidates and sulfonylamides it seems relevant.

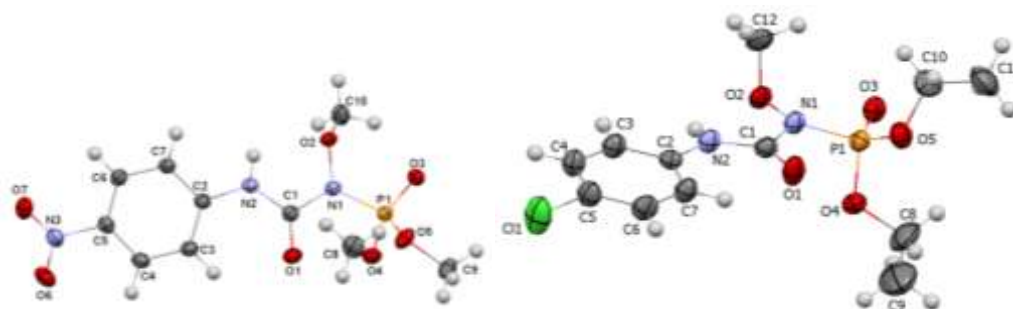
We have found that *N*-alkoxy-*N*-chloro-*N*'-arylureas **1** and *N*-alkoxy-*N*-chloro-*N*'-alkylureas **2** react with trialkyl phosphites in ether at room temperature with forming dialkyl *N*-alkoxy-*N*-(*N*'-arylcarbamoyl)phosphoramidates **3** and dialkyl *N*-alkoxy-*N*-(*N*'-alkylcarbamoyl)phosphoramidates **4**, respectively.



N-Alkoxy-*N*-chloro-*N*'-phenylureas cannot exist at room temperature. It was reported that *N*-methoxy-*N*-chloro-*N*'-phenylurea isomerizes into *N*-methoxy-*N*'-(4-chlorophenyl)urea at room temperature [1]. But we have obtained *N*-alkoxy-*N*-chloro-*N*'-phenylureas **6** by *t*-BuOCl chlorination of the *N*-alkoxy-*N*'-phenylureas at $-30^\circ C$ in ether. The subsequent treatment of *N*-alkoxy-*N*-chloro-*N*'-phenylureas **6** with trimethyl phosphite in these conditions yielded dimethyl *N*-alkoxy-*N*-(*N*'-phenylcarbamoyl)phosphoramidates **7** by one-pot synthesis.

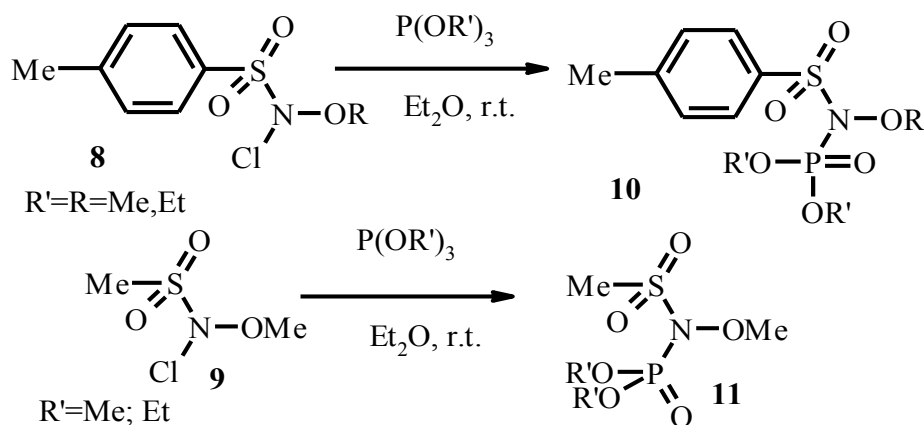


The structure of dialkyl *N*-alkoxy-*N*-(*N'*-arylcarbamoyl)phosphoramidates **3**, and dimethyl *N*-alkoxy-*N*-(*N'*-alkylcarbamoyl)phosphoramidates **4** has been proved by the ^1H , ^{13}C , ^{31}P NMR spectra and mass spectra. Also, the structure of some compound **3** has been confirmed by the single crystal X-ray diffraction (XRD) study.

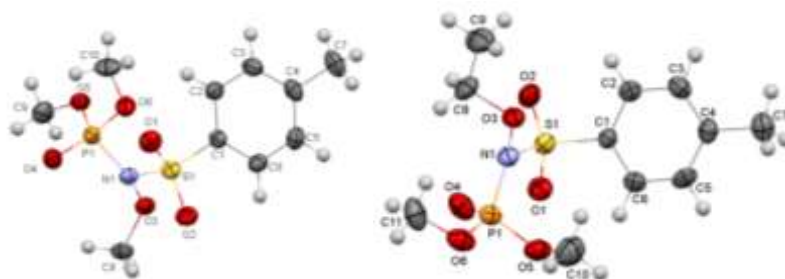


Molecular structure of dimethyl *N*-methoxy-*N*-(*N'*-4-nitrophenylcarbamoyl)phosphoramidate and diethyl *N*-methoxy-*N*-(*N'*-4-chlorophenylcarbamoyl)phosphoramidate

The interaction of *N*-alkoxy-*N*-(chloro)-*R*-sulfonylamides **8,9** with trialkyl phosphites selectively yields dialkyl *N*-alkoxy-*N*-4-toluenesulfonylphosphoramidates and dialkyl *N*-methoxy-*N*-methanesulfonylphosphoramidates **10,11** respectively.



The structure of dialkyl *N*-alkoxy-*N*-*R*-sulfonylphosphoramidates **10,11** has been proved by the ^1H , ^{13}C , ^{31}P NMR spectra and mass spectra. Also, the structure of some compound **10** has been confirmed by the single crystal X-ray diffraction (XRD) study.



Molecular structure of dimethyl *N*-methoxy-*N*-4-toluenesulfonylphosphoramidate and dimethyl *N*-ethoxy-*N*-4-toluenesulfonylphosphoramidate

1. Perronnet J., Demoute J.P. Approach to the 1-methoxy-2-benzimidazolinones. – Gazzet. Chim. Ital. – 1982. – 112. – P. 507–511.