N-ALKOXY-*N*-(DIMETHOXYPHOSPHORYL)UREAS AND Z-*N*-ALKOXY-1-(DIMETHOXYPHOSPHORYLOXY)BENZIMIDATES

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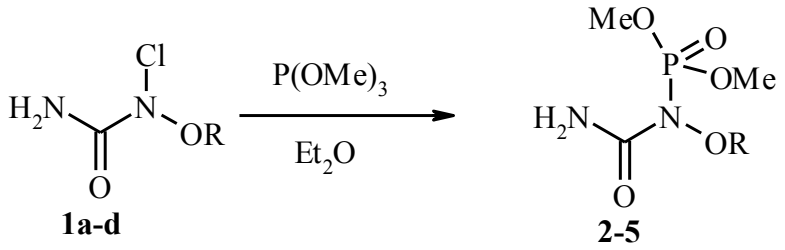
The possibility of the nucleophilic substitution of the chlorine atom in *N*-alkoxy-*N*-chloroureas and in *N*-alkoxy-*N*-chlorobenzamides allow to create the new reaction strategies that give access to such new biological relevant scaffolds

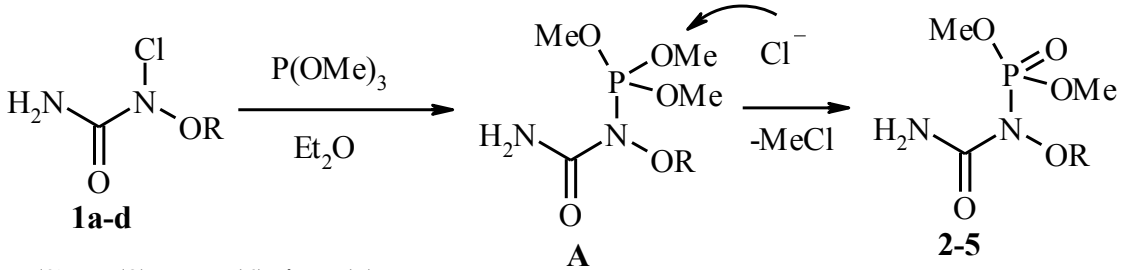
We have studied the interaction of trimethyl phosphite with *N*-alkoxy-*N*-chloroureas. The *N*-alkoxy-*N*-chloroureas **1a-d** react with trimethyl phosphite in ether selectively forming the *N*-alkoxy-*N*-(dimethoxyphosphoryl)ureas **2**–**5**.



1a-d **2-5**

R=Me(**1a**,**2)**, Et(**1b**,**3**), n-Bu(**1c**,**4**), i-Pr(**1d**,**5**)

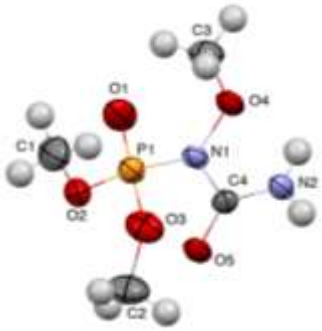
It may be proposed this is another possible mechanism of *N*-alkoxy-*N*-phosphorylureas **2**–**5** formation.



1a-d **A** **2-5**

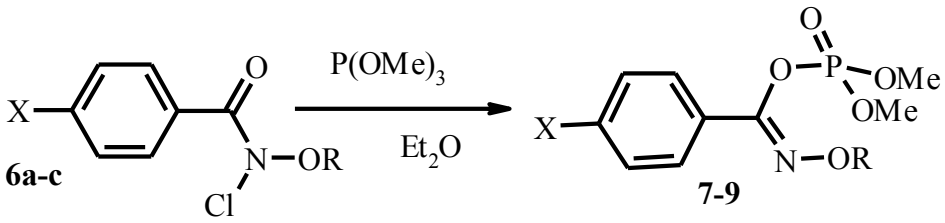
R=Me(**2)**, Et(**3**), n-Bu(**4**), i-Pr (**5**)

The structure of *N*-alkoxy-*N*-phosphorylureas **2**–**5** has been proved by the ^{1}H, ^{13}C, ^{13}P NMR spectra and mass spectra. Also, the structure of compounds **2,4** has been confirmed by the XRD study.



Molecular structure of *N*-methoxy-*N*-(dimethoxyphosphoryl)urea **2**.

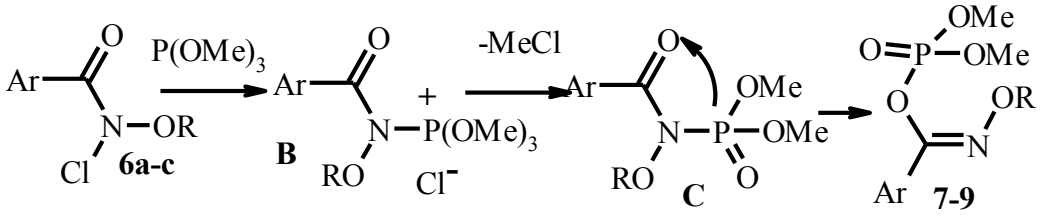
Also we have studied the interaction of trimethyl phosphite with *N*-alkoxy-*N*-chlorobenzamides. *N*-Alkoxy-*N*-chlorobenzamides **6a-c** selectively react with trimethyl phosphite in ether leading to the selective formation of Z-*N*-alkoxy-1-(dimethoxyphosphoryloxy)benzimidates **7–9**.



X=NO_2, R=Me **(6a,7)**

X=H, R=Me(**6b**,**8**),Et(**6c**,**9**)

This is supposed to be another possible mechanism of compounds **7**–**9** formation. At the first stage the labile intermediates **B** formed. At the second stage the *O*-demethylation of the intermediates **B** by the chloride anion takes place (this is the new kind of Arbuzov reaction). It yields the unstable intermediates **C**. Then the N–O-migration of dimethoxyphosphoryl group takes place yielding compounds **7**–**9**. The driving force behind this migration could be the creation of a robust P–O bond.



The structure of Z-*N*-alkoxy-1-(dimethoxyphosphoryloxy)benzimidates **7**–**9** has been proved by the ^{1}H, ^{13}C, ^{13}P NMR spectra and mass spectra. Also, the structure of compound **7** has been confirmed by XRD study.