

N-ALKOXY-N-(DIMETHOXYPHOSPHORYL)UREAS, SYNTHESIS AND STRUCTURE

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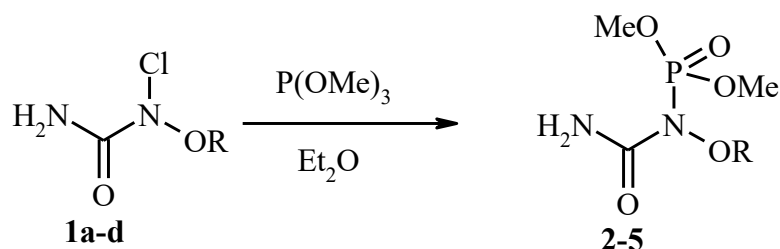
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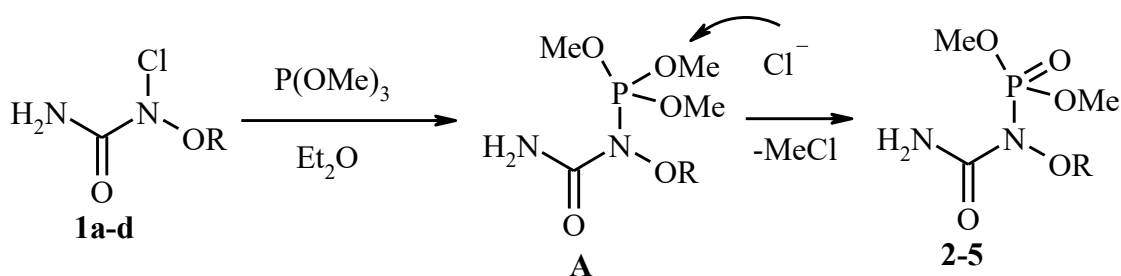
The *N*-alkoxy-*N*-chloroureas **1a-d** react with trimethyl phosphite selectively forming the *N*-alkoxy-*N*-phosphorylureas **2-5** [1]. The ureas **2-5** may be regarded as new biologically relevant scaffolds.



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

The obtained *N*-alkoxy-*N*-(dimethoxyphosphoryl)ureas **2-5** are the products of the nucleophilic substitution at nitrogen. This reaction is a new synthetic route to the *N*-phosphorylureas.

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

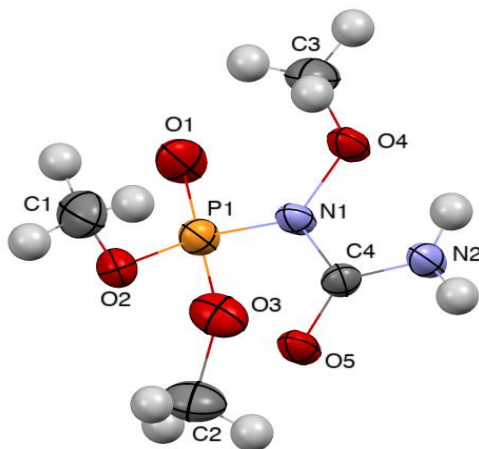


R=Me(**2**), Et(**3**), n-Bu(**4**), i-Pr (**5**)

At the first stage the labile *N*-alkoxy-*N*-(trimethoxyphosphonium)urea chlorides **A** are formed by the nucleophilic substitution at the nitrogen in the *N*-alkoxy-*N*-chloroureas **2a-c**. At the second stage the *O*-demethylation of the intermediate **A** by the chloride anion takes place (this is the kind of Arbuzov reaction). It yields *N*-alkoxy-*N*-(dimethoxyphosphoryl)ureas **2-5**.

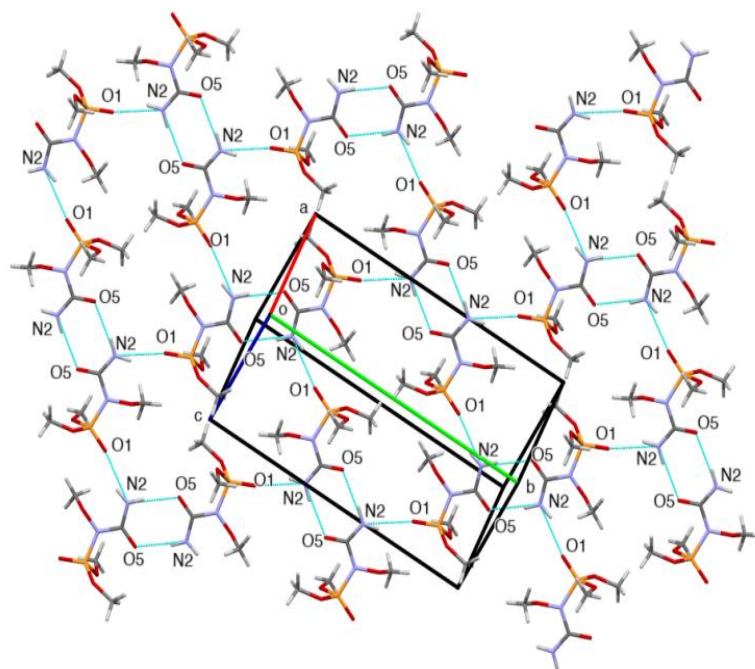
The structure of *N*-alkoxy-*N*-phosphorylureas **2-5** has been proved by the ¹H, ¹³C, ¹³P

NMR spectra and mass spectra. Also, its structure of compounds **2,4** has been confirmed by the XRD study [1].



Molecular structure of *N*-methoxy-*N*-(dimethoxyphosphoryl)urea **2** according to X-ray diffraction data. Thermal ellipsoids are shown with 50% probability.

In compounds **2, 4** both nitrogen atoms have planar configuration. The carbamoyl group and the N–O bond lie within the plane. Thus, it has been found that *N*-alkoxy-*N*-(dimethoxyphosphoryl)ureas have a number of structural features different from those of anomeric ureas [2-5].



The layer formed by hydrogen bonds (cyan dotted lines) between molecules *N*-methoxy-*N*-(dimethoxyphosphoryl)urea **2**.

Thus, the possibility of the N–P bond formation by *N*-alkoxy-*N*-chloroureas interaction with *P*-nucleophiles had become clear. This result has a significant value for the better understanding of the synthetic importance of *N*-alkoxy-*N*-chloroureas.

References:

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