

Synthesis, structure and properties of *N*-alkoxy-*N*-(1-pyridinium)urea salts, *N*-alkoxy-*N*-acyloxyureas and *N,N*-dialkoxyureas†

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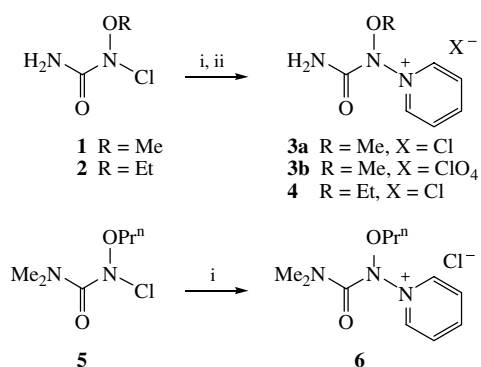
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N-Alkoxy-*N*-(1-pyridinium)urea salts **3**, **4** have been prepared, the conversions of *N*-acetoxy-*N*-methoxyurea **7** into *N,N*-dimethoxyurea **8** and of *N*-*n*-propyloxy-*N*-(1-pyridinium)-*N,N'*-dimethylurea chloride **6** into *N,N*-dimethoxy-*N,N'*-dimethylurea **11** were carried out. A high pyramidalicity of the amide nitrogen in O–N–X groups [X = N⁺C₅H₅, OMe, OC(O)C₆H₄Cl-*p*] has been revealed by XRD studies of ureas **3b**, **8** and *N*-*p*-chlorobenzoyloxy-*N*-*n*-butyloxyurea **9**.

The pyramidalicity of amide nitrogen was found earlier in acyclic anomeric amides² such as *N,N*-dialkoxy-*N,N'*-dimethylureas by the DNMR method³ and XRD studies in *N*-acyloxy-*N*-alkoxybenzamides,⁴ *N,N'*-diacyl-*N,N'*-dialkoxyhydrazines,⁵ *N*-acyloxy-*N*-alkoxyureas,^{6(a)} *N*-acyloxy-*N*-alkoxycarbamates^{6(a)} and *N*-chloro-*N*-alkoxyureas.¹ However, *N*-alkoxy-*N*-(1-pyridinium)urea salts have never been regarded as a kind of anomeric amides and the pyramidalicity parameters of unsubstituted *N,N*-dialkoxyureas were unknown.

We have synthesised salts **3**, **4**[‡] and **6** by nucleophilic substitution at nitrogen in *N*-chloro-*N*-alkoxyureas **1**, **2**, **5**^{1,7} and performed an XRD study of **3b** (Figure 1, Tables 1, 2).



Scheme 1 Reagents and conditions: i, Py, Et₂O, room temperature; ii, AgClO₄, MeCN.

In order to investigate the structure of the simplest *N,N*-dialkoxyurea by methanolysis of *N*-acetoxy-*N*-methoxyurea **7**, crystalline *N,N*-dimethoxyurea **8**¹ was obtained (Scheme 2) and studied by XRD analysis (Figure 2, Tables 1, 2).

Chlorides **3a**, **4** are stable at room temperature for 12 h and decompose at long-duration storage at –5 °C (10 weeks). Chloride **6** can be stored without decomposition at –5 °C for

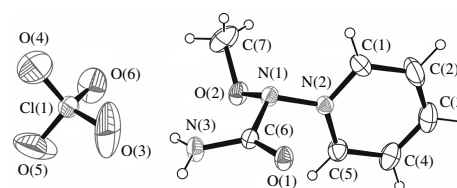
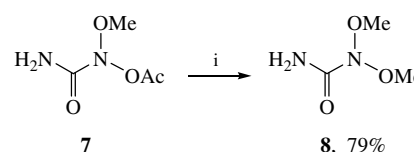


Figure 1 Molecular structure of **3b**. Selected bond lengths (Å) and bond angles (°): N(1)–C(6) 1.4515(19), N(3)–C(6) 1.3234(18), O(1)–C(6) 1.2218(17), N(1)–N(2) 1.4254(18), O(2)–N(1) 1.3999(17), O(2)–C(7) 1.442(3), N(2)–C(1) 1.341(2), N(2)–C(5) 1.341(2); O(2)–N(1)–N(2) 109.03(12), O(2)–N(1)–C(6) 113.03(12), N(2)–N(1)–C(6) 111.72(11), N(1)–O(2)–C(7) 108.94(18), C(5)–N(2)–N(1) 120.44(13), C(5)–N(2)–C(1) 123.61(16), C(1)–N(2)–N(1) 115.95(15).

more than one year, but it is very hygroscopic. Chloride **3a** was converted into more stable perchlorate **3b**. This allowed us to perform an XRD study⁸ at room temperature without any decomposition of the crystal. The results revealed that amide nitrogen in the O–N–N⁺ system has a pyramidal configuration (Figure 1, Tables 1, 2). The nitrogen pyramidalicity parameters as the sum of bond angles centered at this atom ($\Sigma\beta$) and the deviation of N(1) from the plane of three atoms it is bonded with (h_N) are given in Table 1. In *N*-alkoxy-*N*-(1-pyridinium)-urea salt **3b**, the N pyramidalicity degree is less as it was found for *N*-alkoxy-*N*-(1-pyridinium)-*N*-*tert*-alkylamine salts,⁸ but it is closer to N pyramidalicity in *N*-acetoxy-*N*-ethoxyurea^{6(a)} and methyl *N*-4-chlorobenzoyloxy-*N*-methoxycarbamate.^{6(a)} The decreasing nitrogen pyramidalicity degree in salt **3b** against the *N*-alkoxy-*N*-(1-pyridinium)-*N*-*tert*-alkylamine salt⁸ can be explained by stabilization of the planar configuration of amide



Scheme 2 Reagents and conditions: i, MeOH, room temperature.

† Asymmetric Nitrogen, Part 100. Geminal Systems, Part 57. Previous communication, see ref. 1.