DECARBAMOYLATION OF *N*-ALKOXY-*N*-(4-DIMETHYLAMINOPYRIDIN-1-IUM-1-YL)UREA CHLORIDES IN DIMETHYLSULFOXIDE AS A ROUTE TO 1-ALKOXYAMINO-4-DIMETHYLAMINOPYRIDINIUM CHLORIDES

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Keywords: *N*-alkoxy-*N*-(pyridin-1-ium-1-yl)urea chlorides; decarbamoylation; 1-alkoxyamino-4-dimethylaminopyridinium chlorides; structure; O-N-N geminal systems; dimethylsulfoxide.

Decarbamoylation of *N*-alkoxy-*N*-(4-dimethylaminopyridin-1-ium-1-yl)urea chlorides in dimethylsulfoxide takes place with the formation of 1-alkoxyaminopyridinium chlorides. The nature of *N*-alkoxy substituents has a great influence on decarbamoylation efficiency. Decarbamoylation of *N*-*n*-butyloxy-*N*-(4-dimethylaminopyridin-1-ium-1-yl)urea chloride at 20 ºC occurs with the selective formation of 1-*n*-butyloxyamino-4-dimethylaminopyridinium chloride. *N*-Methoxy-*N*-(4-dimethylaminopyridin-1-ium-1-yl)urea chloride is stable in dimethylsulfoxide at 20 ºC, but it forms selectively 1-methoxyamino-4-dimethylaminopyridinium chloride at 82 ºC in 1 h. *N*-Ethoxy-*N*-(4-dimethylaminopyridin-1-ium-1-yl)urea chloride is also stable in dimethylsulfoxide at 20 ºC, but it converts into 1-ethoxyamino-4-dimethylaminopyridinium chloride at 100 ºC under heating for 3 h.

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INTRODUCTION

Five types of 1-alkoxyaminopyridinium salts are known: *N*-alkoxy-*N*-(pyridin-1-ium-1-yl)-*N*-*tert*-alkylamine salts (**1**),[1-3] *N*-alkoxy-*N*-(pyridin-1-ium-yl)urea salts (**2**),[3-6] *N*-alkoxy-*N*-(1-pyridinium)carbamate chlorides(**3**),[7] *N*-alkoxy-*N*-(pyridin-1-ium-1-yl)benzamide chlorides(**4**)[3] and unsubstituted 1-alkoxyamino-4-dimethylamino-pyridinium salts **5**[8,9] (Figure 1).

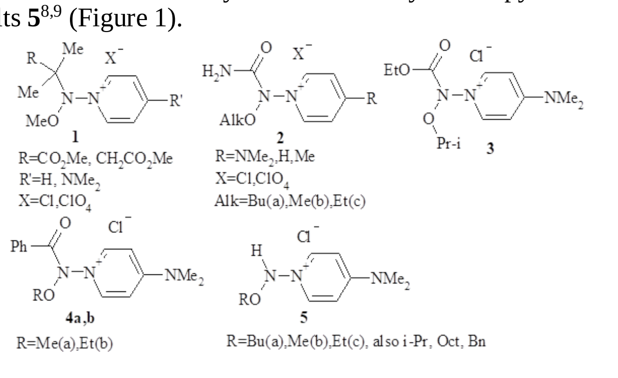

Figure 1. The known types of 1-alkoxyaminopyridinium salts **1-5**

Compounds **1–4** were synthesized by the interaction of appropriate *N*-alkoxy-*N*-chloroamines and *N*-alkoxy-*N*-chloroamides with pyridines[1-9] (Figure 2).

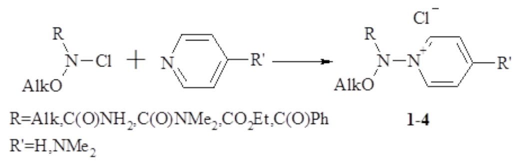

Figure 2. Synthesis of compounds **1 – 4**

1-Alkoxyamino-4-dimethylaminopyridinium salts **5** were synthesized by the reaction of methyl *N*-alkoxy-*N*-chlorocarbamates with 4-dimethylaminopyridine (DMAP).[8,9] Evidently, this reaction carries out via formation of unstable intermediates **3'** (Figure 3).[8]

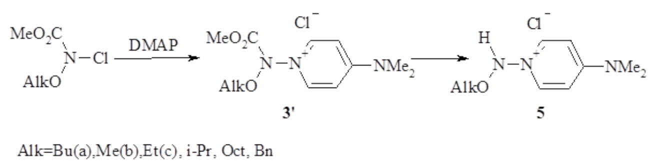

Figure 3. The most convenient synthesis of 1-alkoxyamino-4-dimethylaminopyridinium salts **5**.[8,9]

There are other synthesis methods for preparation of compounds **5,** for example, decarbamoylation of urea derivatives **2** with bases as sodium acetate and ammonia, or potassium fluoride [9]or the reaction of AcONa and benzamide **4a**[9] (Figure 4).

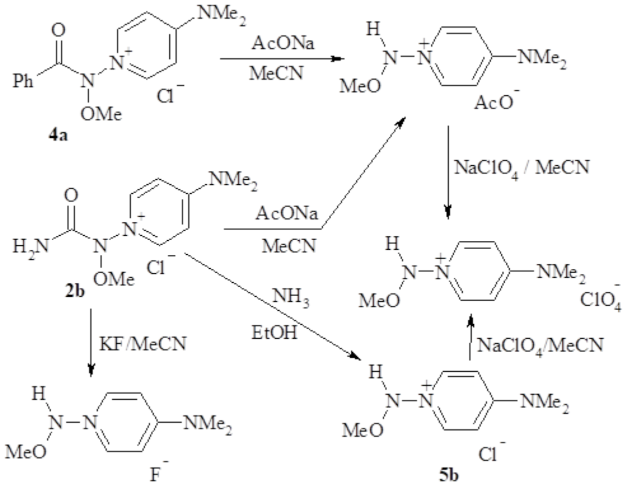

Figure 4. Other synthesis routes of 1-alkoxyaminopyridinium salts (**5**)

1-Alkoxyaminopyridinium salts **1**–**5** are relatively stable compounds contrary to *N*-alkoxy-*N*-aminoamides which are destabilized by $n_{N'} \rightarrow \sigma^*_{N-O(Alk)}$ orbital interaction ("anomeric effect").[10-13]

Our previous XRD studies confirmed that 4-dimethylamino substituted 1-alkoxyaminopyridinium salts (**1**–**3** and **5**) predominantly exist in their quinonoid form (**B**)[3,6-9] (Figure 5). In pyridinium moiety the N–C(2), the N–C(6), the C(3)–C(4) and the C(4)–C(5) bonds are elongated and the C(2)–C(3) and the C(5)–C(6) bonds are shortened comparably to the same bonds in pyridine and at 4-position unsubstituted 1-alkoxyaminopyridinium salts (**1**,**2**). In compounds **1**–**3** and **5** the C(4)–NMe$_2$ bond is strongly shortened and is near to the length of a C=N double bond.

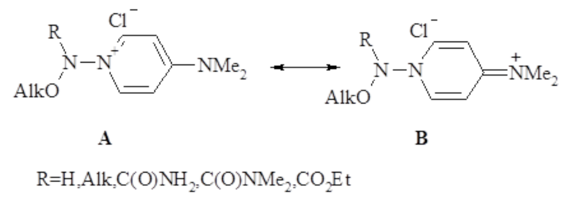

Figure 5. Quinonoid deformation of pyridine ring in 1-alkoxyamino-4-dimethylaminopyridinium salts

EXPERIMENTAL

300 MHz ^{1}H NMR spectra were recorded on a VARIAN VXR-300 spectrometer, 400 MHz ^{1}H NMR spectra were recorded on a VARIAN JEMINI 400 spectrometer with Me$_4$Si as an internal standard. Mass spectrum was recorded on VG 770-70EQ spectrometer in FAB regime. The solvents were purified and dried according to standard procedures. Dimethylsulfoxide (DMSO) was distilled *in vacuo* at 4 Torr. Benzene was dried by boiling and distillation over Na.

1-*n*-Butyloxyamino-4-dimethylaminopyridinium chloride (5a).

The solution of *N*-*n*-butyloxy-*N*-(4-dimethyl-aminopyridin-1-ium-1-yl)urea chloride[6] **2a** (0.238 mmol, 68.8 mg) in freshly distilled dimethylsulfoxide (1 mL) was kept at 16 °C during 150 h, then dry benzene (13 mL) was added. The benzene-phase was separated; the liquid residue was mixed with benzene (3 mL), then after 20 h the benzene-phase was separated. The obtained residue was dried *in vacuo* at 20 °C (2 Hgmm for 5 h), and then it was extracted by CH$_2$Cl$_2$ (8 mL). The CH$_2$Cl$_2$-extract was evaporated *in vacuo* giving 1-*n*-butyloxyamino-4-dimethylaminopyridinium chloride **5a** (50.6 mg, 80 %) as a white solid, which was identified by its ^{1}H NMR spectra and mass spectrum.[8]

^{1}H NMR (400 MHz, CDCl$_3$) δ = 0.901 (3H, t, ^3J= 7.4 Hz, NO(CH$_2$)$_3$Me), 1.340 (2H, sex, ^3J=7.4 Hz, NO(CH$_2$)$_2$CH$_2$Me), 1.573 (2H, quint, ^3J=7.4 Hz, NOCH$_2$CH$_2$CH$_2$Me), 3.302 (6H, s, NMe$_2$), 3.807–3.843 (2H, m, NOCH$_2$), 6.877 (2H, d, ^3J=6.8 Hz, C(3,5)H Py), 8.530 (2H, d, ^3J= 6.8 Hz, C(2,6)H Py), 11.556 (1H, NH). ^{1}H NMR (400 MHz, CD$_3$OD) δ =0.858 (3H, t, ^3J=7.0 Hz, NO(CH$_2$)$_3$Me), 1.293 (2H, sex, ^3J=7.0 Hz, NO(CH$_2$)$_2$CH$_2$Me), 1.532 (2H, quint, ^3J=7.0 Hz, NOCH$_2$CH$_2$CH$_2$Me), 3.302 (6H, s, NMe$_2$), 3.807–3.895 (2H, m, NOCH$_2$), 7.017 (2H, d, ^3J=8.0 Hz, C(3,5)H Py), 8.312 (2H, d, ^3J=8.0 Hz, C(2,6)H Py). ^{1}H NMR (300 MHz, (CD$_3$)$_2$SO) δ = 0.86 (3H, t, ^3J=7.5 Hz, NOCH$_2$CH$_2$CH$_2$Me), 1.27 (2H, sex, ^3J=7.5 Hz, NOCH$_2$CH$_2$CH$_2$Me), 1.51 (2H, quint, ^3J=7.5 Hz, NOCH$_2$CH$_2$CH$_2$Me), 3.25 (6H, s, NMe$_2$); 3.79 (2H, t, ^3J=6.3 Hz, NOCH$_2$,); 7.05 (2H, d, ^3J=7.8 Hz, C(3,5)H Py); 8.46 (2H, d, ^3J=7.8 Hz, C(2,6)H Py), 11.00 (s, 1H, NHO). MS (FAB) *m/z* 210 M$^+$ (100), 152 (6), 137 (32), 123 (73).

b) The solution of *N*-*n*-butyloxy-*N*-(4-dimethyl-aminopyridin-1-ium-1-yl)urea chloride **2a** (0.242 mmol, 69.8 mg) in freshly distilled dimethylsulfoxide (2 mL) was kept at 80 °C for 30 min, then dimethylsulfoxide was distilled off at 70 °C and 2 Torr, then benzene (20 mL) was added to the obtained residue. The reaction mixture was kept under 6 °C for 20 h, and then, the benzene-phase (upper) was separated. The residue was dried at 20°C and 2 Torr for 4h, yielding compound **5a** (62.8 mg, 98%).

1-Methoxyamino-4-dimethylaminopyridinium chloride (5b).

a) The solution of *N*-methoxy-*N*-(4-dimethylaminopyridin-1-ium-1-yl)urea chloride[3,6] **(2b)** (0.361 mmol, 89.0 mg) in freshly distilled dimethylsulfoxide (5 mL) was kept at 82 °C for 1 h, then it was concentrated to a volume of 1 mL at 65–68 °C and 2 Torr. Benzene (20 mL) was added to the residue obtained. The reaction mixture was kept under 6 °C during 20 h, and then, the upper benzene-phase was separated. The lower liquid phase was extracted by benzene (2 mL) again, and the benzene-phase was separated, too. The lower liquid phase was dissolved in CH$_2$Cl$_2$ (4 mL), this CH$_2$Cl$_2$-solution was added to benzene (16 mL), this mixture was kept at 4 °C for 22 h. The obtained white precipitate was separated, dried *in vacuo* at 15 °C and 3 Torr for 5 h, yielding 1-methoxyamino-4-dimethyl-aminopyridium chloride **(5b)** (51.8 mg, 70 %), as colorless crystals, which were identified by ^{1}H NMR and mass spectra.[8]

^{1}H NMR (300 MHz, $CDCl_3$) δ=3.299 (6H, s, NMe_2), 3.599 (3H, s, NOMe), 6.923 (2H, d, ^3J= 8.1 Hz, C(3,5)H Py), 8.527 (2H, d, ^3J= 8.1 Hz, C(2,6)H Py), 11.669 (1H, NH). ^{1}H NMR (300 MHz, CD_3OD) δ = 3.304 (6H, s, NMe_2), 3.644 (3H, s, NOMe), 7.024 (2H, d, ^3J=8.1 Hz, C(3,5)H Py), 8.305 (2H, d, ^3J=8.1 Hz, C(2,6)H Py). MS (FAB) *m/z* 373 $2M^+$•Cl^- (1), 371 $2M^+$•Cl^- (4), 168 M^+ (100), 137 (41), 122 (22).

b) The solution of *N*-methoxy-*N*-(4-dimethylaminopyridin-1-ium-1-yl)urea chloride (**2b**) (0.147 mmol, 36.2 mg) in dimethylsulfoxide (2 mL) was kept at 19 °C for 22 h, then DMSO was distilled off at 65–68 °C and 2 Torr, then the obtained residue was washed twice by benzene (10 mL and 3 mL), yielding *N*-methoxy-*N*-(4-dimethyl-aminopyridin-1-ium-1-yl)urea chloride (**1b**) (34.0 mg, 92%) which was identified by its ^{1}H NMR spectrum. ^{1}H NMR (300 MHz, CD_3OD) δ =3.330 (6H, s, NMe_2), 3.892 (3H, s, NOMe), 7.074 (2H, d, ^3J= 6.6 Hz, C(3,5)H Py), 8.292 (2H, d, ^3J= 6.6 Hz, C(2,6)H Py).

Decarbamoylation of *N*-ethoxy-*N*-(4-dimethylaminopyridin-1-ium-1-yl)urea chloride (2c)

a) The solution of *N*-ethoxy-*N*-(4-dimethylaminopyridin-1-ium-1-yl)urea chloride[6] (**2c**) (0.1323 mmol, 34.5 mg) in dimethylsulfoxide (0.6 mL) was kept at 19 °C for 48 h, then benzene (20 mL) was added. The obtained white precipitate was filtered off, washed by benzene (5 ml), dried at 2 Torr, yielding *N*-ethoxy-*N*-(4-dimethylaminopyridin-1-ium-1-yl)-urea chloride (**2c**) (28,0 mg, 81%), which was identified by its ^{1}H NMR spectra. ^{1}H NMR (400 MHz, CD_3OD) δ= 1.313 (3H, t, ^3J=7.0 Hz, NOCH$_2$<u>Me</u>), 3.334 (6H, s, NMe_2), 4.107 (2H, q, ^3J=7.0 Hz, NO<u>CH$_2$</u>Me), 7.052 (2H, d, ^3J=8.0 Hz, C(3,5)H Py), 8.290 (2H, d, ^3J=8.0 Hz, C(2,6)H Py). ^{1}H NMR (400 MHz, $(CD_3)_2SO$) δ =1.218 (3H, t, ^3J=7.0 Hz, NOCH$_2$<u>Me</u>), 3.268 (6H, s, NMe_2), 4.003 (2H, q, ^3J=7.0 Hz, NO<u>CH$_2$</u>Me), 7.019 (2H, d, ^3J=7.2 Hz, C(3,5)H Py), 7.790 (1H, br. s, NH), 7.965 (1H, br. s, NH), 8.456 (2H, d, ^3J= 8.0 Hz, C(2,6)H Py).

b) The solution of *N*-ethoxy-*N*-(4-dimethylaminopyridin-1-ium-1-yl)urea chloride (**2c**) (0.1937 mmol, 50.5 mg) in dimethylsulfoxide (3 mL) was kept at 100 °C for 1 h, then DMSO was distilled off at 65 °C and 2 Torr, and benzene (10 mL) was added to the residue. The obtained white precipitate was filtered off, washed by benzene (3 mL), dried at 2 Torr, yielding 46.7 mg of mixture of unconverted *N*-ethoxy-*N*-(4-dimethylaminopyridin-1-ium-1-yl)urea chloride (**2c**) and 1-ethoxyamino-4-dimethylaminopyridinium chloride (**5c**)[8] in molar ratio 85:15 (according to ^{1}H NMR spectrum data).

c) The solution of *N*-ethoxy-*N*-(4-dimethylaminopyridin-1-ium-1-yl)urea chloride (**2c**) (0.2708 mmol, 70.6 mg) in DMSO (4 mL) was kept at 100 °C for 3 h, then DMSO was distilled off *in vacuo*, and purification following the emthdo given above yielded 67.7 mg of mixture of 1-ethoxyamino-4-dimethylaminopyridinium chloride (**5c**)[8] and 4-dimethylaminopyridine hydrochloride (DMAP•HCl) in molar ratio 75:25. ^{1}H NMR of compound **5c** (400 MHz, $(CD_3)_2SO$)δ= 1.120 (3H, t, ^3J=7.0 Hz, NOCH$_2$<u>Me</u>), 3.235 (6H, s, NMe_2), 3.819 (2H, q, ^3J=7.0 Hz, NO<u>CH$_2$</u>Me), 7.020 (2H, d, ^3J= 8.0 Hz, C(3,5)H Py), 8.432 (2H, d, ^3J= 8.0 Hz, C(2,6)H Py), 10.821 (1H, NHO).

RESULTS AND DISCUSSION

During registration of ^{1}H NMR spectrum of *N*-*n*-butyloxy-*N*-(4-dimethylaminopyridin-1-ium-1-yl)urea chloride (**2a**) in dimethylsulfoxide-d$_6$, a low field singlet peak appears nearby 11.00 ppm. After keeping the NMR sample in dimethylsulfoxide-d$_6$ for a longer time, the ^{1}H NMR spectrum of compound **2a** becomes similar to the spectrum of 1-*n*-butyloxyamino-4-dimethylaminopyridinium chloride **5a.** In ^{1}H NMR spectrum of compound **5a, a** low field singlet of NH-proton appears at 11.00 ppm.[8] The further study of **2a** decomposition in dimethylsulfoxide at room temperature during a long time has revealed that decarbamoylation of compound **2a** takes place with the selective forming of 1-*n*-butyloxyamino-4-dimethylaminopyridinium chloride **(5a)** (Figure 6). At 80°C, this reaction finishes in 30 min.

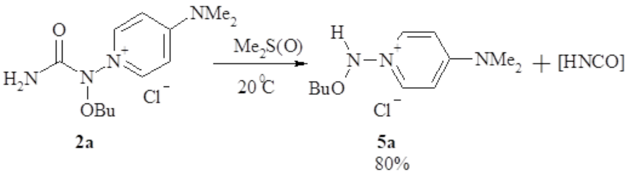

Figure 6. Decarbamoylation of *N*-*n*-butyloxy-*N*-(4-dimethylaminopyridin-1-ium-1-yl)urea chloride **2a** in dimethylsulphoxide

Contrary to the behavior of *N*-n-butyloxy-*N*-(4-dimethylaminopyridin-1-ium-1-yl)urea chloride **2a**, *N*-alkoxy-*N*-(4-dimethylaminopyridin-1-ium-1-yl)ureas salts **2b** and **2c** are stable in dimethylsulfoxide medium at room temperature. Compounds **2b** and **2c** could be recovered in unchanged form after keeping them in DMSO at room temperature. However, *N*-methoxy-*N*-(4-dimethylaminopyridin-1-ium-1-yl)urea chloride **2b,** has been converted in DMSO in 1-methoxy-4-dimethylaminopyridinium chloride (**5b**) on heating at 82 ºC for 1 h (Figure 7).

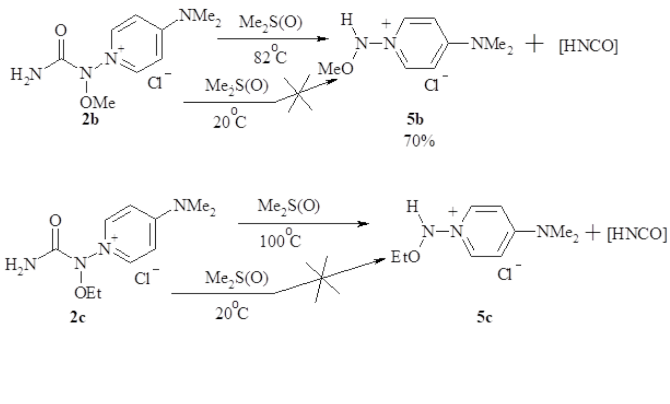

Figure 7. Decarbamoylation of *N*-alkoxy-*N*-(4-dimethylaminopyridin-1-ium-1-yl)ureas chlorides **2b**,**c** in dimethylsulfoxide

N-Ethoxy-*N*-(4-dimethylaminopyridin-1-ium-1-yl)urea chloride **2c** is more stable to decarbamoylation in DMSO solution.

Decarbamoylation of compound **2c** at6 82 °C occured very slow. Heating at 100 ºC for1 h with further DMSO removing yielded the mixture of compounds **2c** and **5c** in molar ratio 85:15. The heating of compound **2c** solution in DMSO at 100 ºC for 3 h yielded the mixture of compound **5c** and 4-dimethylaminopyridine hydrochloride (DMAP•HCl) in the molar ratio 3:1, the precursor **2c** was absent. Apparently, in this case, after the overall conversion of urea **2c**, the particular decomposition of product **5c** may be occurred.

Unfortunately, in our case, the mechanism of decarbamoylation of *N*-alkoxy-*N*-(4-dimethylaminopyridin-1-ium-1-yl)ureas salts (**2**) in the presence of base[9] is not known. It may be supposed, that dimethylsulfoxide as a weak base facilitates proton elimination at high temperatures (Figure 8).

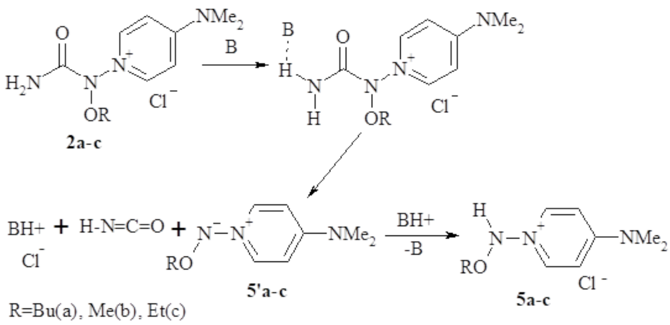

Figure 8. The possible mechanism of decarbamoylayion of ureas **2** by action base(AcO⁻, F⁻, NH₃) and DMSO

It is probable, that the differences of *N*-alkoxy-*N*-(4-dimethylaminopyridin-1-ium-1-yl)urea chlorides (**2**) activity in the decarbamoylation processes may be caused by the different degree of pyramidality of the central nitrogen atom of O–N–N⁺ geminal system. As it is known for compounds containing (R)O–N–O(Ac) geminal systems, the growth of pyramidality of central nitrogen atom facilitates to increasing of action of $n_{O(R)}\rightarrow\sigma^*_{N-O(Ac)}$ anomeric effect thus causes of N–O(Ac) bond weakening.[10-13]

The pyramidality of the central nitrogen atom of O–N–O geminal systems of *N*-(4-chlorbenzoyloxy)-*N*-alkoxyureas (**6a** and **6b**, R= Bu^{n}O(**a**), EtO (**b**)) (Figure 9) depends on the nature of *N*-alkoxy moiety.[14] In *N*-4-chlorbenzoyloxy-*N*-*n*-butyloxyurea **6a**, the pyramidality of the central nitrogen atom is such as great (sum of bond angles is 323.8º) [5], as that was found in *N*-4-chlorbenzoyloxy-*N*-etoxyurea **6b** (sum of bond angles is 329.3º).[14]

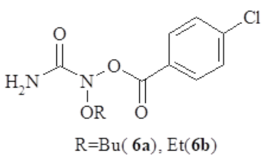

Figure 9. The family of *N*-4-chlorbenzoyloxy-*N*-alkoxyureas **6a**,**b**[5,14]

A similar influence of the nature of *N*-alkoxy substituent on the reactivity was found for the isopropanolysis of *N*-acetoxy-*N*-alkoxyureas **7a** and 7**b** (*N*-alkoxy group = Bu^{n}O (**a**), MeO(**b**)).[15] In isopropanol, *N*-acetoxy-*N*-*n*-butyloxyurea **7a** selectively forms *N*-*n*-butyloxy-*N*-isopropyloxyurea **8** at room temperature (Figure 10). At the same time, *N*-acetoxy-*N*-methoxyurea **7b** is stable towards isopropanolysis at room temperature. It was proposed[15] that the nitrogen pyramidality degree in *N*-acetoxy-*N*-*n*-butyloxyurea **7a** was higher than that in *N*-acetoxy-*N*-methoxyurea **7b** due to the influence of *N*-*n*-butyloxy moiety. Probably, this phenomenon facilitates the action of $n_{O(Bu)}\rightarrow\sigma^*_{N-OAc}$ anomeric effect and the more weakening of N−OAc bond. [15]

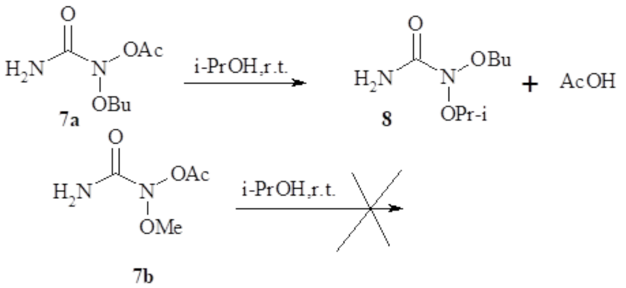

Figure 10. Isopropanolysis of *N*-acetoxy-*N*-alkoxyureas**7a**,**b** at room temperatures[15]

It may be proposed that similarly to *N*-alkoxy-*N*-(4-dimethylaminopyridin-1-ium-1-yl)urea salts **(2a-c),** compound **2a** has the largest nitrogen pyramidality degree which remains during forming intermediate **5a'** (Figure 8). Respectively, intermediate **5a'** may be more stable than intermediates **5b'** and **5c'**. It might cause the higher reactivity of *N*-*n*-butyloxyurea **2a** comparing to *N*-methoxyurea **2b** and *N*-ethoxyurea **2c**. But the structure parameters are known only for compound **2b**,[3] and further XRD study of the structure of compounds **2a** and **2c** is needed for correct mechanism proposition.

Conclusions

Decarbamoylation of *N*-alkoxy-*N*-(4-dimethylamino-pyridin-1-ium-1-yl)ureas chlorides in dimethylsulfoxide occurs with the formation of 1-alkoxyamino-4-dimethylaminopyridinium chlorides. The nature of *N*-alkoxy substituent's has a significant influence on easyness of the decarbamoylation reaction.

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