



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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Decarbamylation 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 decarbamylation efficiency. Decarbamylation of *N*-*n*-butyloxy-*N*-(4-dimethylaminopyridin-1-ium-1-yl)urea chloride at 20 °C 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 °C, but it forms selectively 1-methoxyamino-4-dimethylaminopyridinium chloride at 82 °C in 1 h. *N*-Ethoxy-*N*-(4-dimethylaminopyridin-1-ium-1-yl)urea chloride is also stable in dimethylsulfoxide at 20 °C, but it converts into 1-ethoxyamino-4-dimethylaminopyridinium chloride at 100 °C under heating for 3 h.

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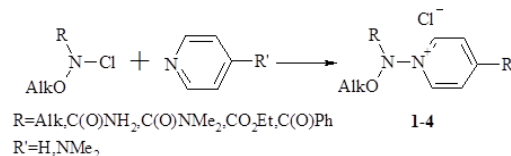
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Figure 1. The known types of 1-alkoxyaminopyridinium salts **1-5**

Compounds **1-4** were synthesized by the interaction of appropriate *N*-alkoxy-*N*-chloroamines and *N*-alkoxy-*N*-chloroamides with pyridines¹⁻⁹ (Figure 2).



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).

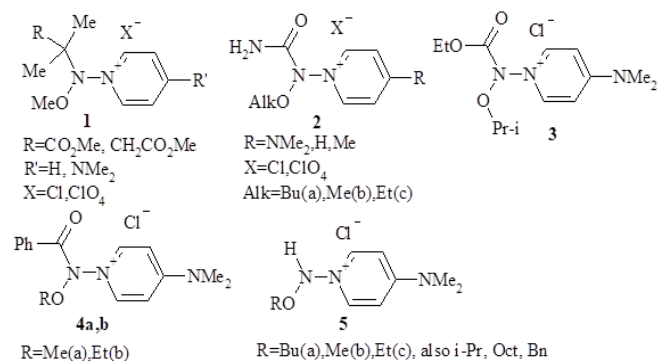


Figure 2. Synthesis of compounds **1-4**

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

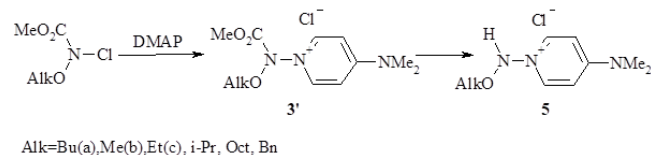


Figure 3. The most convenient synthesis of 1-alkoxyamino-4-dimethylaminopyridinium salts **5**.^{8,9}

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 fluoride⁹ or the reaction of AcONa and benzamide **4a**⁹ (Figure 4).

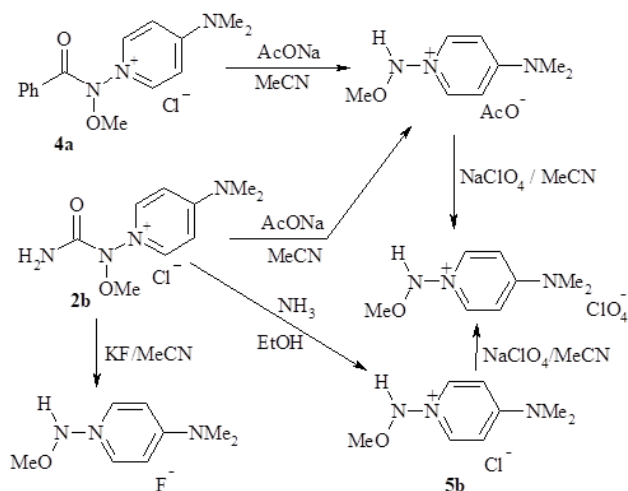


Figure 4. Other synthesis routes of 1-alkoxyaminopyridinium salts (**5**)

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)–NMe₂ bond is strongly shortened and is near to the length of a C=N double bond.

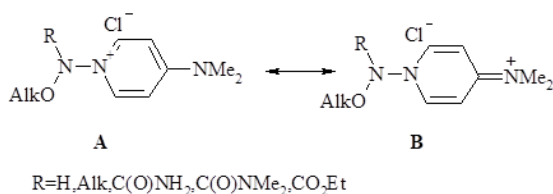


Figure 5. Quinonoid deformation of pyridine ring in 1-alkoxyamino-4-dimethylaminopyridinium salts

EXPERIMENTAL

300 MHz ¹H NMR spectra were recorded on a VARIAN VXR-300 spectrometer, 400 MHz ¹H NMR spectra were recorded on a VARIAN JEMINI 400 spectrometer with

Me₄Si 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-dimethylaminopyridin-1-ium-1-yl)urea chloride⁶ **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 CH₂Cl₂ (8 mL). The CH₂Cl₂-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 ¹H NMR spectra and mass spectrum.⁸

¹H NMR (400 MHz, CDCl₃) δ = 0.901 (3H, t, ³J = 7.4 Hz, NO(CH₂)₃Me), 1.340 (2H, sex, ³J = 7.4 Hz, NO(CH₂)₂CH₂Me), 1.573 (2H, quint, ³J = 7.4 Hz, NOCH₂CH₂CH₂Me), 3.302 (6H, s, NMe₂), 3.807–3.843 (2H, m, NOCH₂), 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). ¹H NMR (400 MHz, CD₃OD) δ = 0.858 (3H, t, ³J = 7.0 Hz, NO(CH₂)₃Me), 1.293 (2H, sex, ³J = 7.0 Hz, NO(CH₂)₂CH₂Me), 1.532 (2H, quint, ³J = 7.0 Hz, NOCH₂CH₂CH₂Me), 3.302 (6H, s, NMe₂), 3.807–3.895 (2H, m, NOCH₂), 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). ¹H NMR (300 MHz, (CD₃)₂SO) δ = 0.86 (3H, t, ³J = 7.5 Hz, NOCH₂CH₂CH₂Me), 1.27 (2H, sex, ³J = 7.5 Hz, NOCH₂CH₂CH₂Me), 1.51 (2H, quint, ³J = 7.5 Hz, NOCH₂CH₂CH₂Me), 3.25 (6H, s, NMe₂); 3.79 (2H, t, ³J = 6.3 Hz, NOCH₂); 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-dimethylaminopyridin-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 CH₂Cl₂ (4 mL), this CH₂Cl₂-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-aminopyridinium chloride (**5b**) (51.8 mg, 70 %), as colorless crystals, which were identified by ¹H NMR and mass spectra.⁸

¹H NMR (300 MHz, CDCl₃) δ=3.299 (6H, s, NMe₂), 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). ¹H NMR (300 MHz, CD₃OD) δ = 3.304 (6H, s, NMe₂), 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 ¹H NMR spectrum. ¹H NMR (300 MHz, CD₃OD) δ = 3.330 (6H, s, NMe₂), 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).

Decarbamylation 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 chloride⁶ (**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 ¹H NMR spectra. ¹H NMR (400 MHz, CD₃OD) δ= 1.313 (3H, t, ³J=7.0 Hz, NOCH₂Me), 3.334 (6H, s, NMe₂), 4.107 (2H, q, ³J=7.0 Hz, NOCH₂Me), 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). ¹H NMR (400 MHz, (CD₃)₂SO) δ = 1.218 (3H, t, ³J=7.0 Hz, NOCH₂Me), 3.268 (6H, s, NMe₂), 4.003 (2H, q, ³J=7.0 Hz, NOCH₂Me), 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 ¹H 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. ¹H NMR of compound **5c** (400 MHz,

(CD₃)₂SO)δ= 1.120 (3H, t, ³J=7.0 Hz, NOCH₂Me), 3.235 (6H, s, NMe₂), 3.819 (2H, q, ³J=7.0 Hz, NOCH₂Me), 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 ¹H 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 ¹H NMR spectrum of compound **2a** becomes similar to the spectrum of 1-*n*-butyloxyamino-4-dimethylaminopyridinium chloride **5a**. In ¹H 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 decarbamylation 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.

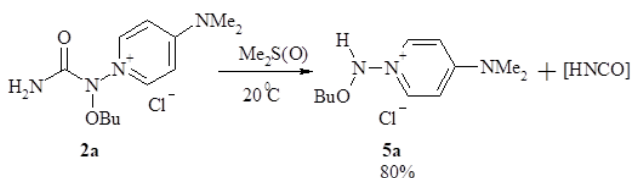


Figure 6. Decarbamylation of *N*-*n*-butyloxy-*N*-(4-dimethylaminopyridin-1-ium-1-yl)urea chloride **2a** in dimethylsulfoxide

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 °C for 1 h (Figure 7).

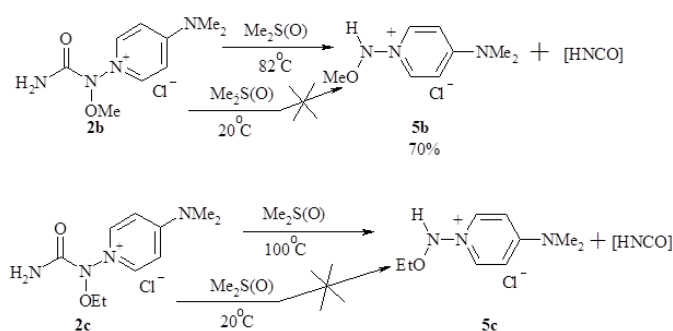


Figure 7. Decarbamylation of *N*-alkoxy-*N*-(4-dimethylaminopyridin-1-ium-1-yl)ureas chlorides **2b,c** in dimethylsulfoxide

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

Decarbamylation of compound **2c** at 62 °C occurred very slow. Heating at 100 °C for 1 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 °C 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 decarbamylation of *N*-alkoxy-*N*-(4-dimethylaminopyridin-1-ium-1-yl)ureas salts (**2**) in the presence of base⁹ is not known. It may be supposed, that dimethylsulfoxide as a weak base facilitates proton elimination at high temperatures (Figure 8).

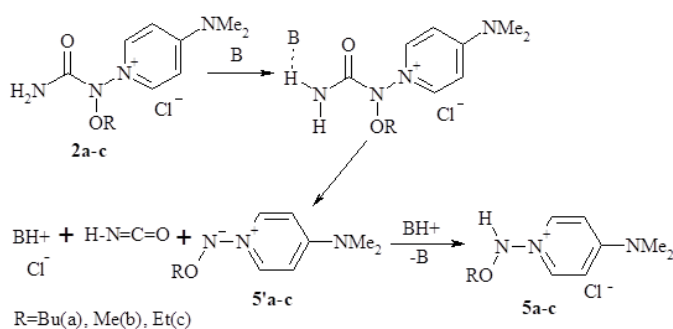


Figure 8. The possible mechanism of decarbamylation of ureas **2** by action base (AcO⁻, F⁻, NH₃) and DMSO

It is probable, that the differences of *N*-alkoxy-*N*-(4-dimethylaminopyridin-1-ium-1-yl)urea chlorides (**2**) activity in the decarbamylation processes may be caused by the different degree of pyramidalty 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 pyramidalty 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 pyramidalty of the central nitrogen atom of O–N–O geminal systems of *N*-(4-chlorbenzoyloxy)-*N*-alkoxyureas (**6a** and **6b**, R= BuⁿO(**a**), EtO (**b**)) (Figure 9) depends on the nature of *N*-alkoxy moiety.¹⁴ In *N*-(4-chlorbenzoyloxy)-*N*-*n*-butyloxyurea **6a**, the pyramidalty of the central nitrogen atom is such as great (sum of bond angles is 323.8°)⁵, as that was found in *N*-(4-chlorbenzoyloxy)-*N*-etoxyurea **6b** (sum of bond angles is 329.3°).¹⁴

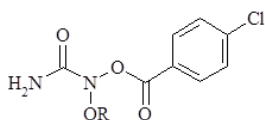


Figure 9. The family of *N*-(4-chlorbenzoyloxy)-*N*-alkoxyureas **6a,b**^{5,14}

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 **7b** (*N*-alkoxy group = BuⁿO (**a**), MeO(**b**)).¹⁵ In isopropanol, *N*-acetoxy-*N*-*n*-butyloxyurea **7a** selectively forms *N*-*n*-butyloxy-*N*-isopropoxyurea **8** at room temperature (Figure 10). At the same time, *N*-acetoxy-*N*-methoxyurea **7b** is stable towards isopropanolysis at room temperature. It was proposed¹⁵ that the nitrogen pyramidalty 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

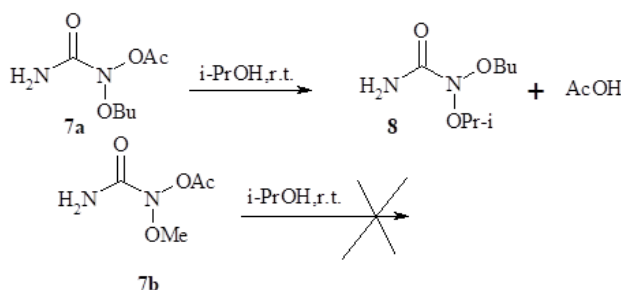


Figure 10. Isopropanolysis of *N*-acetoxy-*N*-alkoxyureas **7a,b** at room temperatures¹⁵

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 pyramidalty 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*-etoxyurea **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

Decarbamylation of *N*-alkoxy-*N*-(4-dimethylaminopyridin-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 decarbamylation reaction.

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