NUCLEOPHILIC SUBSTITUTION IN *N*-ALKOXY-*N*-CHLOROCARBAMATES AS A WAY TO *N*-ALKOXY-*N'*,*N'*,*N'*-TRIMETHYLHYDRAZINIUM CHLORIDES

Vasiliy G. Shtamburg[a]*, Victor V. Shtamburg[a], Evgeniy A. Klots[b], Andrey A. Anishchenko[c], Alexander V. Mazepa[d] and Svetlana V. Kravchenko[e]

Keywords: *N*-Alkoxy-*N*-chlorocarbamates, *N*-alkoxyhydrazines, *N*-alkoxy-*N'*,*N'*,*N'*-trimethylhydrazinium chlorides, synthesis, O-N-N geminal systems, nucleophilic substitution at nitrogen.

A series of *N*-alkoxy-*N*',*N*',*N*-trimethylhydrazinium chlorides by interaction of *N*-alkoxy-*N*-chlorocarbamates with trimethylamine could be prepared.

* Corresponding Authors
Phone: +380-97-651-61-72
E-Mail: stamburg@gmail.com
[a] 49005 Ukraine, Dnepr, Gagarina st., 8. Ukrainian State University of Chemical Technology.
[b] 25006 Ukraine, Kropyvnytskyi, Shevchenko st., 1. Volodymyr Vinnichenko Central Ukrainian State Pedagogical University.
[c] 49050 Ukraine, Dnepr, Nauchnaya st. 25. O. Gonchar Dnepropetrovsk National University.
[d] 65080 Odessa, Luystdorfskaya Doroga st., 86. A.V. Bogatsky Physico-Chemical Institute of NAS of Ukraine.
[e] 49600 Ukraine, Dnepr, Efremova st., 25. Dnipro State Agrarian and Ecomomic University.

INTRODUCTION

N-Alkoxy-*N*',*N*',*N*-trimethylhydrazinium salts (**1**) are stable[1,2] derivatives of unstable *N*-alkoxyhydrazines[3-10] and they have a unique structure. *N*-Methoxy-*N'*,*N'N'*-trimethylhydrazinium perchlorate has the longest N–N^+ bond [1.483(30Å][2] and a very short N–OMe bond [1.391(3) Å].[2]

Normally, some types of *N*-alkoxyhydrazines such as *N*-alkoxy-*N*-alkylamines[3,5] and *N*-alkoxy-*N*-aminoamides[4,6-10] are destabilized by the $n_{N'}\rightarrow\sigma^*_{N\text{-}O(R)}$ orbital interaction ("anomeric effect").[6-10] Usually, the *N*-alkoxy-*N*-chloro-*N*-t-alkylamines interaction with amines gives unstable *N*-alkoxyhydrazines which eliminate a molecule of alcohol yielding the proper diazenes[3] (Scheme 1). Only one single relatively stable *N*-alkoxyhydrazine (**2**) has been obtained but it is converted into diazene (**3**) by an action of methanol.[3]

N-Alkoxy-*N*-chloro derivatives of amines[3,5] and amides[1-4,11-15] selectively give stable *N*-alkoxyamino-pyridinium salts (**4**) by interacting with pyridines (Scheme 2). [3,5,11-17]

However the *N*-alkoxy-*N'*,*N'*,*N*-trialkylhydrazinium salts (**1**,**5**)[1,2] are formed only during the reaction of *N*-alkoxy-*N*-chloroureas with trimethylamine and 1,4-diazabicyclo[2.2.2]octane (Scheme 3). The stability of the *N*-alkoxy-*N'*,*N'*,*N*-trialkylhydrazinium salts (**1**,**5**)[1,2] as well as the 1-*N*-alkoxyamino-pyridinium salts (**4**)[3-5,11-17] is based on the inability of $n_{N'}\rightarrow\sigma^*_{N\text{-}O(R)}$ anomeric effect due to the absence of the lone electron pair in N' nitrogen atom. The mechanism of generation of *N*-alkoxy-*N'*,*N'*,*N*-trialkylhydrazinium salts (**1**,**5)** is unknown but it may be presumed that at the first stage the labile product of nucleophilic substitution at the nitrogen atom (**6**,**7)** is formed. Then, the intermediates **6**,**7** are decarbamoylated by the action of excess amine. In a similar way the decarbamoylation in the presence of bases of the *N*-alkoxyaminopyridinium salts (**4b**) (or *N*-alkoxy-*N*-(4-dimethylaminopyridin-1-ium-yl)urea chlorides) produces 1-alkoxyaminopyridinium chlorides.[14,17]

The aim of our investigation is to study the possibility of synthesis of *N*-alkoxy-*N'*,*N'*,*N*-trimethylhydrazinium chlorides (**1**) from methyl *N*-alkoxy-*N*-chlorocarbamates (**8a-f**) and ethyl *N*-chloro-*N*-methoxycarbamate (**9**).

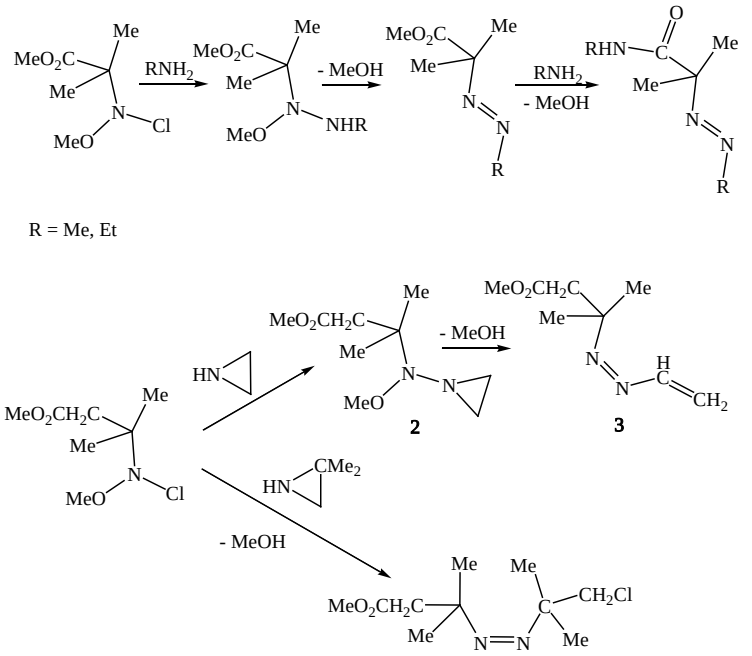
EXPERIMENTAL

^{1}H NMR spectra were recorded on the 300 MHz VARIAN VXR-300 and the 400 MHz VARIAN JEMINI 400 spectrometers. ^{13}C NMR spectra were recorded on a Varian VXP-300 spectrometer (75 MHz). ^{1}H NMR chemical shifts were reported relative to the residual solvent protons as an internal standard ($(CD_3)_2SO$: 2.50 ppm) or with Me_4Si as an internal standard (in $CDCl_3$). Solvent carbon atoms served as an internal standard for ^{13}C NMR spectra ($(CD_3)_2SO$: 39.52 ppm). Mass spectrum was recorded on VG 770-70EQ spectrometer in FAB regime. The solvents were purified and dried according to the standard procedures.

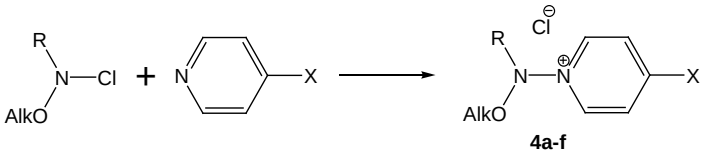
N-Methoxy-*N'*,*N'N'*-trimethylhydrazinium chloride (1a)

Method A: A solution of trimethylamine (3.735 mmol, 221 mg) in MeCN (3 mL) was added to a solution of methyl *N*-chloro-*N*-methoxycarbamate[18] (**8a,** 3.216 mmol, 449 mg) in MeCN (7 mL) at -29 °C, the reaction mixture was heated to 14 °C during 21 h, then the negligible precipitate formed was filtered off, the MeCN-filtrate was evaporated under vacuum (25 mm Hg), benzene (10 mL) was added, the mixture was kept at 5 °C for 4 days, then the benzene phase

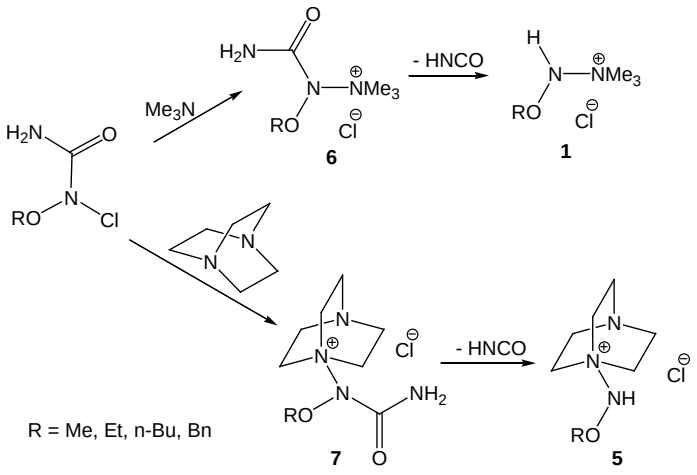
was decanted from obtained solid residue. The solid residue was washed by benzene (3mL), dried under vacuum 2 mm Hg, dissolved in MeCN and precipitated by EtOAc (2:1), dried under vacuum (2 mmHg), giving *N*-methoxy-*N'*,*N'N'*-trimethylhydrazinium chloride (**1a**) as colorless hygroscopic crystals (49 mg, 11 %). ^{1}H NMR (300 MHz, $(CD_3)_2SO$) δ =3.239 (9H, s, Me_3N^+), 3.740 (3H, s, NOMe), 10.404 (1H, s, NH). ^{13}C NMR (75 MHz, $(CD_3)_2SO$) δ = 50.39 (Me_3N^+), 64.71 (NOMe). MS (FAB, m/z, I_{rel}, (%)): 105 M^+ (65), 74 (100).



Scheme 1. The formation of diazenes as the result of *N*-alkoxy-*N*-chloro-*N-tert.*-alkylamines interaction with amines.



Scheme 2. The formation of *N*-alkoxyaminopyridinium salts (**4a-f**) from *N*-alkoxy-*N*-chloro compounds by an interaction with the pyridines.



Scheme 3. The earlier reported synthesis of the *N*-alkoxy-*N'*,*N'*,*N*-trialkylhydrazinium salts (**1**,**5**).

From MeCN–EtOAc phase after evaporation under vacuum and crystallization compound (**1a**) (199 mg, 44 %) was obtained additionally.

The benzene extract was evaporated under vacuum (20 mm Hg), the residue was maintained at 4 mm Hg giving *N,N'*-dimethoxy-*N,N'*-di(methoxycarbonyl)hydrazine (**10a**) as white crystals (51 mg, 15 %), mp 52–53°C (hexane), which was identified by ^{1}H NMR spectra and mass spectrum.[2,18] ^{1}H NMR (300 MHz, $CDCl_3$) δ = 3.891 (12H, s, NOMe, CO_2Me). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 3.902 (6H, s, NOMe), 3.916 (6H, s, CO_2Me). MS (FAB, KI, *m/z*, I_{rel}, (%)): 247 $[M+K]^+$ (100).

Method B: A solution of trimethylamine (4.284 mmol, 253 mg) in MeCN (5 mL) was added to a solution of ethyl *N*-chloro-*N*-methoxycarbamate[19] (**9**) (2.108 mmol, 324 mg) in MeCN (5 mL) at -30 °C, the reaction mixture was heated to 18 °C for 22 h, then the negligible precipitate formed was filtered off, the MeCN-filtrate was evaporated under vacuum (20 mm Hg), the residue was washed by Et_2O (10 mL), the residue was dissolved in MeCN (4 mL) and benzene (8 mL) was added. The precipitated viscous oil was separated from PhH–MeCN phase, dried under vacuum (2 mm Hg), giving *N*-methoxy-*N',N'N'*-trimethylhydrazinium chloride (**1a**) as colorless hygroscopic crystals (143 mg, 48 %) which was identified by ^{1}H and ^{13}C MR spectra, and MS spectrum.

The Et_2O-extact was evaporated under vacuum (20 mm Hg), the residue was washed by CCl_4 (5 mL) for 40 h, then it was separated and dried under vacuum (2 mm Hg), giving **1a** (125 mg, 42 %) additionally.

1-*N*-Ethoxy-*N',N'N'*-trimethylhydrazinium chloride (1b)

A solution of trimethylamine (2.487 mmol, 147 mg) in MeCN (2 mL) was added to a solution of methyl *N*-chloro-*N*-ethoxycarbamate[20] (**8b**) (1.370 mmol, 210 mg) in MeCN (5 mL) at -15 °C, the reaction mixture was kept at -15 °C for 2 h and at 5 °C for 20 h. The negligible precipitate was then filtered off, the MeCN-filtrate was evaporated under vacuum (15 mm Hg), the residue was washed by Et_2O (5 mL) and dried at 2 mm Hg, giving *N*-ethoxy-*N',N'N'*-trimethylhydrazinium chloride (**1b**) as white hygroscopic solid (209 mg, 98 %). ^{1}H NMR (300 MHz, $(CD_3)_2SO$) δ = 1.192 (3H, t, ^3J=6.9 Hz, $NOCH_2\underline{Me}$), 3.253 (9H, s, Me_3N^+), 3.900–4.050 (2H, m, $NO\underline{CH_2}Me$), 10.334 (1H, s, NHO). ^{13}C NMR (75 MHz, $(CD_3)_2SO$) δ = 13.76 (Me), 50.27 (Me_3N^+), 72.24 (OCH_2). MS (FAB, *m/z*, I_{rel}, (%)): 275 $[2M•Cl]^+$(6), 273 $[2M•Cl]^+$(18), 119 M^+ (100), 73(73).

***N-n*-Propyloxy-*N',N'N'*-trimethylhydrazinium chloride (1c)**

A solution of trimethylamine (2.739 mmol, 162 mg) in MeCN (2 mL) was added to a solution of methyl *N*-chloro-*N*-*n*-propyloxycarbamate (**8c**) (1.996 mmol, 336 mg) in MeCN (5 mL) at -25 °C, the reaction mixture was heated to -14 °C for 1 h, then it was maintained at 15 °C for 24 h and the negligible precipitate was filtered off. The MeCN-solution was evaporated under vacuum (20 mm Hg), the residue was dried at 2 mm Hg, washed by benzene (10 mL), dried under vacuum(2 mm Hg) and giving *N*-*n*-propyloxy-*N',N'N'*-trimethylhydrazinium chloride (**1c**) as white hygroscopic solid (178 mg, 53 %). ^{1}H NMR (400 MHz, $(CD_3)_2SO$) δ = 0.895 (3H, t, *J*=7.2 Hz, $NO(CH_2)_2\underline{Me}$), 1.499–1.613(2H, m, $NOCH_2\underline{CH_2}Me$), 3.252 (9H, s, Me_3N^+), 3.788–3.865 (1H, m, $NOCH_2$), 3.886–3.958 (1H, m, $NOCH_2$), 10.438 (1H, s, NHO). ^{13}C NMR (100 MHz, $(CD_3)_2SO$) δ=10.14 ($NO(CH_2)_2\underline{Me}$), 21.46 ($NOCH_2\underline{CH_2}Me$), 50.31 (Me_3N^+), 78.12 ($NOCH_2$). MS (FAB, *m/z*, I_{rel}, (%)): 303 $[2M^+•Cl^-]$ (4), 301 $[2M^+•Cl^-]$ (13), 133 M^+ (100), 73(35), 56(37).

***N-n*-Butyloxy-*N',N'N'*-trimethylhydrazinium chloride (1d)**

A solution of trimethylamine (2.490 mmol, 147 mg) in MeCN (3 mL) was added to a solution of methyl *N*-*n*-butyloxy-*N*-chlorocarbamate[20,21] (**8c**) (1.663 mmol, 302 mg) in MeCN (4 mL) at -30 °C, the reaction mixture was heated to 15 °C for 18 h and the negligible precipitate was filtered off. The MeCN-filtrate was evaporated under vacuum (20 mm Hg), the residue was washed by benzene (10 mL), dried under vacuum (4 mm Hg) and extracted by CH_2Cl_2 (10 mL). The CH_2Cl_2-extract was evaporated under vacuum (20 mm Hg), the residue was extracted by acetone (3 mL), $Me_2C(O)$-extract was evaporated under vacuum and dried at 4 mm Hg, giving *N*-*n*-butyloxy-*N',N'N'*-trimethylhydrazinium chloride (**1d**) as viscous yellowish oil (151 mg, 50 %). ^{1}H NMR (400 MHz, $(CD_3)_2SO$) δ = 0.899 (3H, t, ^3J=7.2 Hz, $OCH_2CH_2CH_2\underline{Me}$), 1.357 (2H, sex, ^3J=7.2 Hz, $OCH_2CH_2\underline{CH_2}Me$), 1.545 (2h, quint, ^3J=7.2 Hz, $OCH_2\underline{CH_2}CH_2Me$), 3.217 (9H, s, Me_3N^+), 3.781–3.913 (1H, m, $NOCH_2$), 3.950–4.035 (1H, m, $NOCH_2$), 10.129 (1H, s, NHO). ^{13}C NMR (75 MHz, $(CD_3)_2SO$) δ = 13.75 (Me), 18.48, 30.19 (CH_2), 50.41 (Me_3N^+), 76.53 ($NOCH_2$). MS (FAB, *m/z*, I_{rel}, (%)): 331 $[2M•Cl]^+$(1.5), 329 $[2M•Cl]^+$(5), 147 M^+ (100), 57 Bu^+ (48).

***N*-Benzyloxy-*N',N'N'*-trimethylhydrazinium chloride (1e)**

A solution of trimethylamine (2.856 mmol, 169 mg) in MeCN (2 mL) was added to a solution of methyl *N*-benzyloxy-*N*-chlorocarbamate[18] (**8e**) (1.454 mmol, 314 mg) in MeCN (5 mL) at -15 °C, the reaction mixture was heated to 5 °C for 2h, was kept at 5 °C for 20 h, then it was evaporated under vacuum (15 mm Hg), the residue washed by Et_2O (7 mL), dried at 2 mm Hg, giving *N*-benzyloxy-*N',N'N'*-trimethylhydrazinium chloride (**1e**) as hygroscopic white solid (256 mg, 86 %). ^{1}H NMR (300 MHz, $(CDCl_3)$ δ=3.409 (9H, s, Me_3N^+), 4.880 (1H, d, ^2J=10.5 Hz, $NO\underline{CH_2}Ph$), 4.943 (1H, d, ^2J=10.5 Hz, $NO\underline{CH_2}Ph$), 7.342 (5H, s, Ph); 10.963 (1H, s, NHO). ^{1}H NMR (300 MHz, $(CD_3)_2SO$) δ = 3.314 (9H, s, Me_3N^+), 4.86–5.14 (2H, m, $NO\underline{CH_2}Ph$), 7.31–7.45 (5H, m, Ph), 10.629 (1H, s, NHO). ^{13}C NMR (75 MHz, $(CD_3)_2SO$) δ = 50.52 (Me_3N^+), 78.34 ($NOCH_2$), 128.31 [C(4) Ph], 128.39, 128.41 [C(2,4) and C(3,5) Ph], 135.92 [C(1) Ph]. MS (FAB, *m/z*, I_{rel}, (%)):181 M^+ (100), 91(55), 74 (53).

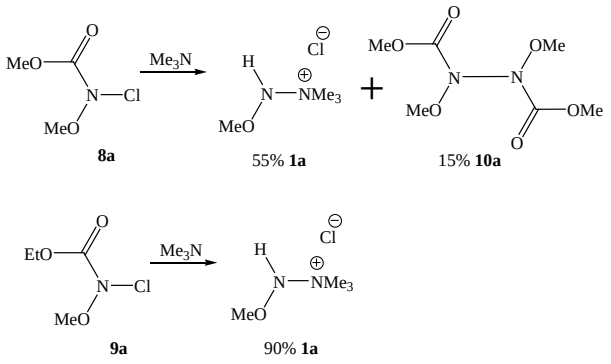
***N-n*-Octyloxy-*N',N'N'*-trimethylhydrazinium chloride (1f)**

A solution of trimethylamine (2.988 mmol, 177 mg) in MeCN (2 mL) was added to a solution of methyl *N*-chloro-*N*-*n*-octyloxycarbamate[19] (**8f**) (0.979 mmol, 233 mg) in MeCN (5 mL) at -17 °C, the reaction mixture was heated to 11 °C for 21 h, then it was evaporated under vacuum (15 Hg), the residue was extracted by CH_2Cl_2 (8 mL), the

negligible solid was filtered off. The CH_2Cl_2-extract was evaporated under vacuum (20 mm Hg), the residue was dissolved in benzene (6 mL), and hexane (12 mL) was added. The precipitated liquid phase was separated, washed by hexane (4 mL), dried under vacuum (2 mm Hg) giving *N*-*n*-octyloxy-*N',N'N'*-trimethylhydrazinium chloride (**1f**) as colorless hygroscopic solid (89 mg, 38 %). ^{1}H NMR (300 MHz, $CDCl_3$) δ = 0.855 (3H, t, *J*=6.9 Hz, $NO(CH_2)_7\underline{Me}$), 1.159–1.368 (10H, m, $NOCH_2CH_2(\underline{CH_2})_5Me$), 1.553–1.664 (2H, m, $NOCH_2\underline{CH_2}(CH_2)_5Me$), 3.494 (9H, s, Me_3N^+), 3.911 (2H, t, *J*=6.3 Hz, $NOCH_2$), 10.721 (1H, s, NHO). ^{1}H NMR (300 MHz, $(CD_3)_2SO$) δ = 0.850 (3H, t, *J*=6.3 Hz, $NO(CH_2)_7\underline{Me}$), 1.204–1.344 (10H, m, $NOCH_2CH_2(\underline{CH_2})_5Me$), 1.489–1.604 (2H, m, $NOCH_2\underline{CH_2}(CH_2)_5Me$), 3.248 (9H, s, Me_3N^+), 3.816–3.911 (1H, m, $NOCH_2$), 3.952–4.029 (1H, m, $NOCH_2$), 10.413 (1H, s, NHO). ^{13}C NMR (75 MHz, $(CD_3)_2SO$) δ = 13.90 (Me), 22.04, 25.17, 28.08, 28.58, 28.75, 31.19 (CH_2), 50.37 (Me_3N^+), 76.78 ($NOCH_2$). MS (FAB, *m/z*, I_{rel}, (%)): 443 $[2M^+•Cl^-]^+$ (2), 441 $[2M^+•Cl^-]^+$(6), 203 M^+ (100).

RESULTS AND DISCUSSION

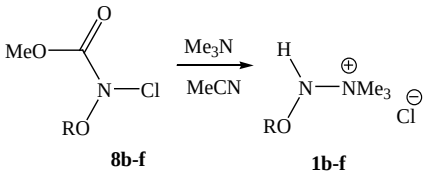
It has been found that methyl *N*-chloro-*N*-methoxycarbamate (**8a**) interacts with an excess of trimethylamine in MeCN forming of *N*-methoxy-*N',N'N'*-trimethylhydrazinium chloride (**1a**) as the main product (Scheme 4). Also, *N,N'*-dimethoxy-*N,N'*-di(methoxycarbonyl)hydrazine (**10a**) has been obtained as by-product in a relatively small yield. Ethyl *N*-chloro-*N*-methoxycarbamate (**9**) reacts with trimethylamine in MeCN producing *N*-methoxy-*N',N'N'*-trimethylhydrazinium chloride (**1a**) (Scheme 4).



Scheme 4. Synthesis of *N*-methoxy-*N',N'N'*-trimethylhydrazinium chloride **1a** from methyl (**8a**) and ethyl (**9**) *N*-chloro-*N*-methoxycarbamates.

In a similar manner methyl *N*-alkoxy-*N*-chlorocarbamates (**8b-f**) react with trimethylamine yielding *N*-alkoxy-*N',N'N'*-trimethylhydrazinium chlorides (**1b-f**) (Scheme 5).The structure of the synthesized *N*-alkoxy-*N',N'N'*-trimethylhydrazinium chlorides (**1a-f**) has been confirmed by data of ^{1}H and ^{13}C NMR spectra and mass spectra.

In ^{1}H NMR spectra of compounds **1a-f** the characteristic chemical shifts of hydrogen atoms of Me_3N^+ group are observed at 3.2 – 3.3 ppm, and protons of NHO group in a low field are observed at 10.1 – 10.6 ppm (Table 1).



R = Et (**b**), n-Pr (**c**), n-Bu (**d**), Bn (**e**), n-C_8H_{17} (**f**)

Scheme 5. Synthesis of *N*-alkoxy-*N',N'N'*-trimethylhydrazinium chlorides **1b-f.**

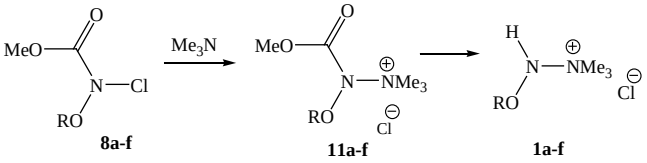
Table 1. The characteristic ^{1}H NMR chemical shifts of *N*-alkoxy-*N',N'N'*-trimethylhydrazinium chlorides (**1a-f**) in $(CD_3)_2SO$.

R	Resonance, σ, ppm	
	Me_3N^+	NHO
Me (**1a**)	3.239	10.404
Et (**1b**)	3.253	10.334
Pr (**1c**)	3.252	10.438
n-Bu (**1d**)	3.217	10.129
$PhCH_2$ (**1e**)	3.314	10.629
n-C_8H_{17} (**1f**)	3.248	10.413

Table 2. The characteristic ^{13}C NMR chemical shifts of *N*-alkoxy-*N',N'N'*-trimethylhydrazinium chlorides (**1a-f**) in $(CD_3)_2SO$

R	Resonance, σ ppm	
	Me_3N^+	$NOCH_2$
Me (**1a**)	50.39	64.71(Me)
Et (**1b**)	50.27	72.24
Pr (**1c**)	50.31	78.12
n-Bu (**1d**)	50.41	76.53
$PhCH_2$ (**1e**)	50.52	78.34
n-C_8H_{17} (**1f**)	50.37	76.78

In ^{13}C NMR spectra of compounds **1a-f** the characteristic chemical shifts of carbon atoms of Me_3N^+ group are observed at 50.3 – 50.5 ppm and $NOCH_2$ group at 72.2 – 78.3 ppm (Table 2). In the mass spectra the signals of M^+ ion are present. The signals of $[2M•Cl]^+$ ions are often observed as well. As the mechanism of compounds **1a-f** formation remains unclear, one may assume that it occurs in two stages (Scheme 6). At the first stage the unstable intermediates (**11a-f**) are formed by nucleophilic substitution at the nitrogen atom in *N*-alkoxy-*N*-chlorocarbamates **8**,**9** (Scheme 6). Then the intermediates **11a-f** produce *N*-alkoxy-*N',N'N'*-trimethylhydrazinium chlorides (**1a-f**) by the methoxycarbonyl group elimination.



R = Me (**a**), Et (**b**), n-Pr (**c**), n-Bu (**d**), Bn (**e**), n-C_8H_{17} (**f**)

Scheme 6. The possible route of *N*-alkoxy-*N',N'N'*-trimethylhydrazinium chlorides **1a-f** formation

This reaction is a new kind of the synthesis of *N*-alkoxy-*N'*,*N'N'*-trimethylhydrazinium chlorides **(1a-f)**, which confirms that this type of reactions can be performed.

CONCLUSIONS

It has been found that the synthesis of *N*-alkoxy-*N'*,*N'*,*N*-trimethylhydrazinium chlorides by the *N*-alkoxy-*N*-chlorocarbamates interaction with trimethylamine is possible.

REFERENCES

[1]Shtamburg, V. G., Tsygankov, A. V., Shishkin, O. V., Zubatyuk, R. I., Shtamburg, V. V., Gerasimenko, M. V., Mazepa, A. V., Kostyanovsky, R. G., 1-Alkoxyamino-4-dimethylaminopyridinium derivatives as new representatives of O-N-N$^+$ geminal systems and their structure, *Mendeleev Commun*., **2012**, *22(2)*, 92−94. https://doi.org/10.1016/j.men.com.2012.02.014

[2]Shtamburg, V. G., Shishkin, O. V., Zubatyuk, R. I., Shtamburg, V. V., Tsygankov, A. V., Mazepa, A. V., Kadorkina, G. K., Kostyanovsky, R. G., Synthesis and structure of *N*-alkoxyhydrazines and *N*-alkoxy-*N'*,*N'*,*N*-trialkylhydrazinium salts, *Mendeleev Commun*. **2013**, *23(5)*, 289−291. https://doi.org./10.1016/j.men.com.2013.09.018

[3]Shtamburg, V. G., Rudchenko, V. F., Nasibov, Sh. S., Chervin, I. I., Pleshkova, A.P., Kostyanovsky, R.G., Geminal Systems. Communication 16. Reactions of N-Chloro-N-alkoxyamines with Amines, *Bull. Acad. Sci. USSR. Div. Chem. Sci*., **1981**, *30(10)*, 1914−1920. https://doi.org/10.1007/BF00963422

[4]Rudchenko, V. F., Shevchenko, V. I., Kostyanovsky, R. G., Geminal systems. Communication 29. Reaction of N-Chloro-N-methoxy-N',N'-dimethylurea with N-Nucleophiles, *Bull.Acad.Sci.USSR.Div.Chem.Sci*., **1986**, *35(3)*, 551–554. https://doi.org/10.1007/BF00953223

[5]Rudchenko, V. F., Kostyanovsky, R. G., Geminal oxygen–nitrogen–halohen systems. *N*-Halohydroxylamine derivatives, *Russ. Chem. Rev.*, **1998**, *67(3)*, 179–192. . https://doi.org/10.1070/RC1998v067n03ABEH000351

[6]Glover, S. A., Anomeric Amides – Structure, Properties and Reactivity, *Tetrahedron*, **1998**, *54(26)*, 7229−7271. https://doi.org/10.1016/S0040-4020(98)00197-5

[7]Glover, S. A., Rauk, A., Conformational Stereochemistry of the HERON Amide, *N*-Methoxy-*N*-dimethylaminoformamide: A Theoretical Study, *J. Org. Chem.*, **1999**, *64(7)*, 2340–2345. https://doi.org/10.1021/jo982048p

[8]Glover, S. A., Chapter 18. N-Heteroatom-substituted hydroxamic esters, in *The Chemistry of Hydroxylamines, Oximes and Hydroxamic Acids*, Eds Rappoport, Z., Liebman, J. F., John Wiley and Sons, New York. **2009**, 839–923. https://doi.org/10.1002/9780470741962ch18

[9]Glover, S. A., White, J. M., Rosser, A. A., Digianantonio, K. M. Structure of N,N-Dialkoxyamides: Pyramidal Anomeric Amides with Low Amidicity, *J. Org. Chem.*, **2011**, *76*, 9757−9763. https://doi.org/10.1021/jo201856u

[10]Glover, S. A., Rosser, A. A., Heteroatom Substitution at Amide Nitrogen – Resonance Reduction and HERON Reactions of Anomeric Amides, *Molecules*, **2018**, *23(11)*, 2834. https://doi.org/10.3390/molecules23112834

[11]Shtamburg, V. G., Shishkin, O. V., Zubatyuk, R. I., Kravchenko, S. V., Shtamburg, V. V., Distanov, V. B., Tsygankov, A. V., Kostyanovsky, R. G., Synthesis, structure and properties of N-alkoxy-N-(1-pyridinium)urea salts, N-alkoxy-N-acyloxyureas and N,N-dialkoxyureas, *Mendeleev Commun*., **2007**, *17(3)*, 178–180. https://doi.org/10.1016/j.men.com.2007.05.016

[12]Shtamburg, V. G., Shtamburg, V. V., Tsygankov, A. V., Anishchenko, A. A., Zubatyuk, R. I., Shishkina, S. V., Mazepa, A. V., Klots, E. A., Synthesis and Structure of New *N*-Alkoxy-*N*-(1-pyridinium)urea Chlorides, *Eur. Chem. Bull.*, **2016**, *5(4)*, 142–146. https://doi.org/10.17628/ECB.2016.5.142

[13]Shtamburg, V. G., Shishkina, S. V., Shtamburg, V. V., Mazepa, A. V., Kadorkina, G. K., Kostyanovsky, R. G., 1-Alkoxyamino-4-dimethylaminopyridiniun Salts: Synthesis and Structure, *Mendeleev Commun*., **2016**, *26(2)*, 169–171. https://doi.org/10.1016/j.men.com.2016.03.030

[14]Shtamburg, V. G., Shtamburg, V. V., Kravchenko, S. V., Mazepa, A. V., Anishchenko, A. A., Posokhov, E. A., A New Synthesis of N-Alkoxyaminopyridinium Salts, *Bulletin of National University "KhPI". Series: New solutions in modern technology*, **2017***(7)*, 211−218. https://doi.org/10.20998/2413−4295.2017.07.30

[15]Shtamburg, V. G., Anishchenko, A. A., Shishkina, S. V. Konovalova, I. S., Shtamburg, V. V., Mazepa, A. V., Kravchenko, S. V., 1-(N-Ethoxycarbonyl-N-isopropyloxy)amino-dimethylaminopyridinium Chloride. Synthesis and Structure, *Eur. Chem. Bull.*, **2017**, *6(10)*, 470–474. https://doi.org/10.17628/ecb.2017.6.470-474

[16]Shtamburg, V. G., Tsygankov, A. V., Klots, E. A., Fedyanin, I. V., Lyssenko, K. A., Kostyanovsky, R. G., N,N-Dimethoxy-N-tert.-alkylamines: New Synthesis Methods and Crystal Structure of Precursor, *Mendeleev Commun.*, **2006**, *16(2)*, 84–85. https://doi.org/10.1070/MC2006v016n02ABEH002222

[17]Shtamburg, V. G., Shtamburg, V. V., Anishchenko, A. A., Kravchenko, S. V., Mazepa, A. V., Klots, E. A., Decarbamoylation of *N*-Alkoxy-*N*-(4-dimethylaminopyridin-1-ium-1-yl)urea Chlorides in Dimethylsulfoxide as A Route to 1-Alkoxyamino-4-dimethylaminopyridinium Chlorides, *Eur. Chem. Bull.*, **2018**, *7(9)*, 267–271. https://doi.org/10.17628/ecb.2018.7.267-271

[18]Shtamburg, V. G., Rudchenko, V. F., Nasibov, Sh. S., Chervin I. I., Kostyanovsky, R. G., *N*-Chloro-*N*-methoxyuretilane, *Russ. Chem. Bull., Int. Ed.*, **1981**, *30(2)*, 423−426. https://doi.org

[19]Shtamburg, V. G., Klots, E. A., Pleshkova, A. P., Avramenko, V. I., Ivonin, S. P., Tsygankov, A. V; Kostyanovsky, R. G., Geminal systems. 50. Synthesis and alcoholysis on *N*-acyloxy-*N*-alkoxy derivatives of ureas, carbamates and benzamide, *Russ. Chem. Bull., Int. Ed.*, **2003**, *52(10)*, 2251−2260. https://doi.org./10.1023/B:RUCB.0000011887.405.29.b0

[20]Shtamburg, V. G., Kostyanovsky, R. G., Tsygankov, A. V., Shtamburg, V. V., Shishkin, O. V., Zubatyuk, R. I., Mazepa, A. V., Kravchenko, S. V., Geminal Systems. Communication 64. *N*-Alkoxy-*N*-chloroureas and *N*,*N*-Dialkoxyureas, *Russ. Chem. Bulletin. Intern. Ed.*, **2015**, *64(1)*, 62–75. https://doi.org/10.1007/s11172-015-0822-9

[21]Shtamburg, V. G., Anishchenko, A. A., Shtamburg, V. V., Tsygankov, A. V; Kostyanovsky, R. G., Alcoholysis of *N*-Acetoxy-*N*-alkoxycarbamates. Synthesis of *NH*-*N*,*N*-Dialkoxyamines from *N*,*N*-Dialkoxycarbamates, *Eur. Chem. Bull.*, **2014**, *3(12)*, 1119–1125. https://doi.org/10.17628/ecb.2014.3.1119-1125

Received: 30.10.2019.
Accepted: 26.01.2020.