



# ALCOHOLYSIS OF *N*-ACETOXY-*N*-ALKOXYCARBAMATES. SYNTHESIS OF *NH-N,N*-DIALKOXYAMINES FROM *N,N*- DIALKOXYCARBAMATES

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The alcoholysis of *N*-acetoxy-*N*-alkoxycarbamates by methanol or ethanol at 20 – 40 °C yields *N,N*-dialkoxy carbamates and acetic acid. At the lower temperature the competitive formation of *N,N'*-bis(alkoxycarbonyl)-*N,N'*-bis(alkoxy)hydrazines can occur. The alkaline hydrolysis of *N,N*-dialkoxy carbamates yields *NH-N,N*-dialkoxyamines.

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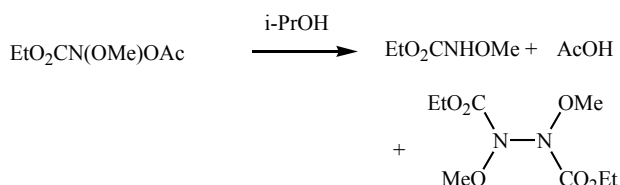
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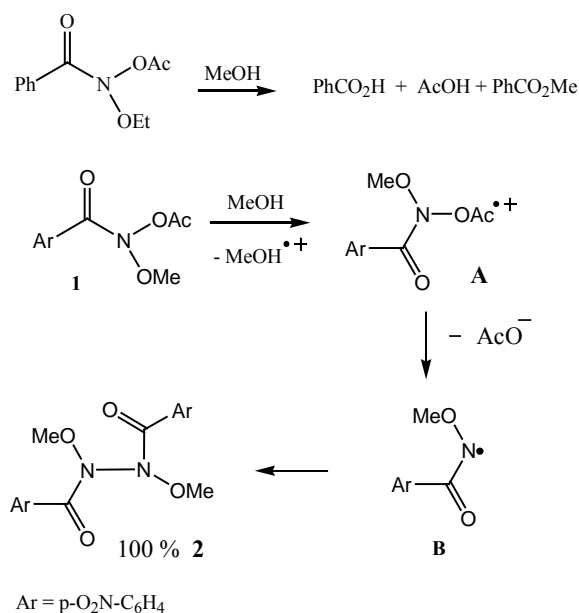
## INTRODUCTION

The nature of the products of the alcoholysis of *N*-acyloxy-*N*-alkoxyureas, *N*-acyloxy-*N*-alkoxycarbamates, *N*-acyloxy-*N*-alkoxybenzamides depends of the electronegativity of third substituent at nitrogen atom in the O-N-O geminal system. *N*-Acyloxy-*N*-alkoxyureas<sup>1-3</sup> and *N*-acyloxy-*N*-alkoxy-*N*-*tert*-alkylamines<sup>1</sup> yield respectively the *N,N*-dialkoxyureas and *N,N*-dialkoxy-*N*-*tert*-alkylamines by the alcoholysis. *N*-Acyloxy-*N*-alkoxycarbamates convert into *N,N*-dialkoxy carbamates only by the alcoholysis by primary alcohols.<sup>1</sup> The alcoholysis of *N*-acyloxy-*N*-alkoxycarbamates by *tert*-butanol does not take place, probably, due to sterical hindrances to S<sub>N</sub>2 nucleophilic substitution at the nitrogen.<sup>1</sup> Isopropanolysis of ethyl *N*-acetoxy-*N*-methoxycarbamate results in the formation of reduction products such as *N,N'*-bis(ethoxycarbonyl)-*N,N*-bis(methoxy)hydrazine and ethyl *N*-ethoxycarbamate<sup>[1]</sup> (Scheme 1).



Scheme 1

The nature of products of *N*-acyloxy-*N*-alkoxybenzamides alcoholysis is strongly depended by of the nature of *p*-substituent in the phenyl group. Thus, methanolysis of *N*-acetoxy-*N*-ethoxybenzamide yields the mixture of methyl benzoate, benzoic and acetic acid,<sup>1</sup> however, as we have found, the methanolysis<sup>4</sup> of *N*-acetoxy-*N*-methoxy-4-nitrobenzamide (**1**) yields only *N,N'*-bis(methoxy)-*N,N'*-bis(4-nitrobenzoyl)hydrazine (**2**). Probably, last reaction occurs by a SET mechanism with consecutive formation the anion-radical **A**, then radical **B** (Scheme 2).



Scheme 2.

*N*-acyloxy-*N*-alkoxybenzamides,<sup>5-9</sup> *N*-acyloxy-*N*-alkoxycarbamates<sup>1,10,11</sup> and *N*-acyloxy-*N*-alkoxyureas<sup>1,2,10,11</sup> are called “anomeric amides” due to nO(Alk)→σ\*N-OC(O)R anomeric effect domination. In RC(=O)O-N-O(Alk) group the amide nitrogen is sp<sup>3</sup> hybridized and has pyramidal configuration, (Alk)O-N

bond is shortened and N–OC(=O)R bond is elongated and destabilized.<sup>2,4,5,7,10,11</sup> Due to this N–OC(=O)R bond destabilization, the S<sub>N</sub>2 nucleophilic substitution at amide nitrogen atom or homolysis of this bond become possible.<sup>1,5,7</sup>

However, in the case of *N*-acyloxy-*N*-alkoxycarbamates, the influence of their structure on the nature of products of alcoholysis remains unknown. We cannot predict under which conditions the alcoholysis of *N*-acyloxy-*N*-alkoxycarbamates by primary alcohols will selectively yield *N,N*-dialkoxycarbamates, which are regarded as the potential sources of *NH-N,N*-dialkoxamines

## EXPERIMENTAL

### General

<sup>1</sup>H NMR spectra were recorded on a “Varian VXP-300” spectrometer (300 MHz), “Mercury-400” (400 MHz) and “Bruker Avance DRX 500” (500 MHz). Me<sub>4</sub>Si was used as an internal standard. Chemical shifts were measured in  $\sigma$ -scale (ppm) and coupling constants in Hz. <sup>13</sup>C NMR spectra were recorded on a “Varian VXP-300” spectrometer (75 MHz). IR spectra were recorded on “UR-20” spectrometer, in KBr or in the thin layer. Mass spectra were recorded on a “VG-70EQ 770” mass spectrometer in FAB mode (FAB) and on “Kratos MS 890” mass spectrometer, electron impact mode (EI) and chemical ionization mode (CI), gas-reagent was isobutane. MeOH and EtOH were dried by refluxing and distillation over metallic calcium.

### Metanolysis of *N*-acetoxy-*N*-methoxy-4-nitrobenzamide (1)

A solution of (1)<sup>4</sup> (0.06137 mmol, 0.0156 g) in MeOH (3 ml) was kept at 20 °C for 72 h, then methanol was evaporated *in vacuo* (5 Torr) yielding 0.0120 g (100%) of *N,N'*-bis(methoxy)-*N,N'*-bis(4-nitrobenzoyl)hydrazine (2) as yellowish white crystals, m.p. 86 – 88 °C (with decomp.). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 3.948 (s, 6H, NOME), 8.206 (d, 4H, H<sub>C6H4</sub><sup>2,6</sup>, <sup>3</sup>J = 9.2 Hz), 8.305 (d, 4H, H<sub>C6H4</sub><sup>3,5</sup>, <sup>3</sup>J = 9.2 Hz). <sup>1</sup>H NMR (400 MHz, (CD<sub>3</sub>)<sub>2</sub>SO): 3.948 (s, 6H, NOME), 8.206 (d, 4H, H<sub>C6H4</sub><sup>2,6</sup>, <sup>3</sup>J = 9.2 Hz), 8.329 (d, 4H, H<sub>C6H4</sub><sup>3,5</sup>, <sup>3</sup>J = 9.2 Hz). MS (FAB, *m/z*, I<sub>OTH</sub>, (%)): 391 [M+H]<sup>+</sup> (10), 307(88), 289(45), 155(90), 137(96), 79 (100). MS (FAB, Na<sup>+</sup>, *m/z*, I<sub>OTH</sub>, (%)): 413 [M+Na]<sup>+</sup> (10), 329 (100).

### Methyl *N*-ethoxycarbamate (3)

A solution of ethoxyamine (29.06 mmol, 1.78 g) in MeCN (7 ml) was added to the solution of MeO<sub>2</sub>CCl (37.77 mmol, 3.57 g) in MeCN (15 ml) at 10 °C, then K<sub>2</sub>CO<sub>3</sub> (43.59 mmol, 6.0 g) and 18-crown-6 (0.10 g) were added. The reaction mixture was stirred and heated to 20 °C for 3 h, then it was stored at 20 °C for another 24 h. After that the precipitate was filtered off, washed with CH<sub>2</sub>Cl<sub>2</sub>, and the combined filtrate was evaporated *in vacuo*. The residue was distilled *in vacuo* yielding 2.49 g (72 %) methyl *N*-ethoxycarbamate, colourless liquid, b.p. 74–79 °C (5 Torr), *n*<sub>D</sub><sup>21</sup> 1.4247 (cf. 1.4246<sup>12</sup>) identified by comparison its <sup>1</sup>H NMR spectra with that of an authentic sample.<sup>12</sup> <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):

1.18 (t, 3H, NOCH<sub>2</sub>Me, <sup>3</sup>J = 6.9 Hz), 3.69 (s, 3H, CO<sub>2</sub>Me), 3.85 (q, 2H, NOCH<sub>2</sub>Me, <sup>3</sup>J = 6.9 Hz), 7.40 (br. s, 1H, NH). IR ( $\nu$ , cm<sup>-1</sup>, KBr): 3430 (NH), 1740 (C=O).

Other *N*-alkoxycarbamates were synthesized in a similar manner.

**Methyl *N*-isopropoxy carbamate (4)**, yield 78%, colourless liquid, b.p. 87–88 °C (10 Torr), *n*<sub>D</sub><sup>27</sup> 1.4237. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): 1.15 (d, 6H, OCHMe<sub>2</sub>, <sup>3</sup>J = 6.3 Hz), 3.68 (s, 3H, CO<sub>2</sub>Me), 3.98 (sept, 1H, OCHMe<sub>2</sub>, <sup>3</sup>J = 6.3 Hz), 7.33 (br. s, 1H, NH). IR ( $\nu$ , cm<sup>-1</sup>, KBr): 3310 (NH), 1745 (C=O). Found (%): N 10.68. Calc. for C<sub>5</sub>H<sub>11</sub>NO<sub>3</sub> (%): N 10.52.

**Methyl *N*-*n*-butyloxy carbamate (5)**, yield 76 %, colourless liquid, b.p. 105–107 °C (5 Torr), *n*<sub>D</sub><sup>22</sup> 1.4312. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): 0.94 (t, 3H, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Me, <sup>3</sup>J = 7.2 Hz), 1.40 (sex, 2H, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Me, <sup>3</sup>J = 7.2 Hz), 1.63 (quint, 2H, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Me, <sup>3</sup>J = 7.2 Hz), 3.77 (s, 3H, CO<sub>2</sub>Me), 3.87 (t, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Me, <sup>3</sup>J = 7.2 Hz), 7.47 (br. s, 1H, NH). Found (%): N 9.31. Calc. for C<sub>6</sub>H<sub>13</sub>NO<sub>3</sub> (%): N 9.52.

**Ethyl *N*-isopropoxy carbamate (6)**, yield 67 %, colourless liquid, b.p. 68 °C (2 Torr), *n*<sub>D</sub><sup>20</sup> 1.4255. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): 1.22 (d, 6H, OCHMe<sub>2</sub>, <sup>3</sup>J = 6.3 Hz), 1.27 (t, 3H, CO<sub>2</sub>CH<sub>2</sub>Me, <sup>3</sup>J = 7.2 Hz), 4.05 (sept, 1H, OCHMe<sub>2</sub>, <sup>3</sup>J = 6.3 Hz), 4.19 (q, 2H, CO<sub>2</sub>CH<sub>2</sub>Me, <sup>3</sup>J = 7.2 Hz). Found (%): N 9.43. Calc. for C<sub>6</sub>H<sub>13</sub>NO<sub>3</sub> (%): N 9.52.

### General method for the synthesis of *N*-chloro-*N*-alkoxycarbamates

A solution of *t*-BuOCl (15 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (3 ml) was added to the solution of the alkyl *N*-alkoxycarbamate (5 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (6 ml) at -20 °C, the reaction solution was kept at 5 °C for 2 h, then it was evaporated *in vacuo* (10 Torr), the residue was kept at 3 Torr for 5 min. The yields were quantitative.

**Methyl *N*-chloro-*N*-ethoxycarbamate (7)**, yellowish oil. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): 1.31 (t, 3H, NOCH<sub>2</sub>Me, <sup>3</sup>J = 6.9 Hz), 3.92 (s, 3H, CO<sub>2</sub>Me), 4.07 (q, 2H, NOCH<sub>2</sub>Me, <sup>3</sup>J = 6.9 Hz). IR ( $\nu$ , cm<sup>-1</sup>, thin layer): 1795 (C=O). Found(%): Cl 22.85. Calc. for C<sub>4</sub>H<sub>8</sub>ClNO<sub>3</sub> (%): Cl 23.09.

**Methyl *N*-chloro-*N*-isopropoxy carbamate (8)**, yellow oil. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): 1.28 (d, 6H, NOCHMe<sub>2</sub>, <sup>3</sup>J = 6.3 Hz), 3.91 (s, 3H, CO<sub>2</sub>Me), 4.31 (sept, 1H, NOCHMe<sub>2</sub>, <sup>3</sup>J = 6.3 Hz). IR ( $\nu$ , cm<sup>-1</sup>, thin layer): 1780 (C=O). Found (%): Cl 21.04. Calc. for C<sub>5</sub>H<sub>10</sub>ClNO<sub>3</sub> (%): Cl 21.15

**Methyl *N*-chloro-*N*-*n*-butyloxy carbamate (9)**, yellowish oil, *n*<sub>D</sub><sup>25</sup> 1.4383. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): 0.95 (t, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Me, <sup>3</sup>J = 7.3 Hz), 1.45 (sex, 2H, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Me, <sup>3</sup>J = 7.3 Hz), 1.57 (quint, 2H, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Me, <sup>3</sup>J = 7.3 Hz), 3.90 (s, 3H, CO<sub>2</sub>Me), 3.97 (t, 2H, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Me, <sup>3</sup>J = 7.3 Hz). Found (%): Cl 19.16. Calc. for C<sub>6</sub>H<sub>12</sub>ClNO<sub>3</sub> (%): Cl 19.52.

**Ethyl *N*-chloro-*N*-isopropoxy carbamate (10)**, yellowish oil. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): 1.28 (d, 6H, NOCHMe<sub>2</sub>, <sup>3</sup>J = 6.3 Hz), 1.36 (t, 3H, CO<sub>2</sub>CH<sub>2</sub>Me, <sup>3</sup>J = 7.0

Hz), 4.31 (sept, 1H,  $\text{NOCHMe}_2$ ,  $^3J = 6.3$  Hz), 4.33 (q, 2H,  $\text{CO}_2\text{CH}_2\text{Me}$ ,  $^3J = 7.0$  Hz). Found (%): Cl 19.46. Calc. for  $\text{C}_6\text{H}_{12}\text{ClNO}_3$  (%): Cl 19.52.

#### General method for the synthesis of *N*-acetoxy-*N*-alkoxycarbamates

A mixture of the solution of *N*-chloro-*N*-alkoxycarbamate (8 mmol) in MeCN (20 ml) and AcONa (26 mmol) was stirred at 20 °C for 55 h, then  $\text{CH}_2\text{Cl}_2$  (10 ml) was added, the precipitate was filtered off, washed with  $\text{CH}_2\text{Cl}_2$ , the combined filtrate was evaporated *in vacuo* (20 Torr). The residue was extracted by  $\text{CH}_2\text{Cl}_2$  (20 ml), the extract was evaporated *in vacuo*, the residue was kept at 3 Torr and 20 °C for 30 min to yield the product.

**Methyl *N*-acetoxy-*N*-ethoxycarbamate (11)**, yield 87 %, colourless liquid,  $n_D^{19}$  1.4269.  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ ): 1.30 (t, 3H,  $\text{NOCH}_2\text{Me}$ ,  $^3J = 7.2$  Hz), 2.19 (s, 3H,  $\text{NOC(O)Me}$ ), 3.88 (s, 3H,  $\text{CO}_2\text{Me}$ ), 4.13 (q, 2H,  $\text{NOCH}_2\text{Me}$ ,  $^3J = 7.2$  Hz). IR ( $\nu$ ,  $\text{cm}^{-1}$ , thin layer): 1805 (C=O), 1780 (C=O). Found (%): C 40.41, H 6.31, N 7.78. Calc. for  $\text{C}_6\text{H}_{11}\text{NO}_5$  (%): C 40.68, H 6.26, N 7.91.

**Methyl *N*-acetoxy-*N*-isopropoxy carbamate (12)**, yield 96 %, yellowish liquid.  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ ): 1.28 (d, 6H,  $\text{OCHMe}_2$ ,  $^3J = 6.3$  Hz), 2.17 (s, 3H,  $\text{NOC(O)Me}$ ), 3.87 (s, 3H,  $\text{CO}_2\text{Me}$ ), 4.32 (sept, 1H,  $\text{OCHMe}_2$ ,  $^3J = 6.3$  Hz). IR ( $\nu$ ,  $\text{cm}^{-1}$ , thin layer): 1805 (C=O), 1780 (C=O). MS (CI,  $m/z$ ,  $I_{\text{rel}}$ , (%)): 192  $[\text{M}+\text{H}]^+$  (0.6), 191  $\text{M}^+$  (1.5), 148 (4.0), 132 (3.1), 59 (23.9), 45 (20.4), 43 (100). Found (%): C 43.81, H 6.82, N 7.18. Calc. for  $\text{C}_7\text{H}_{13}\text{NO}_5$  (%): C 43.98, H 6.85, N 7.33.

**Methyl *N*-acetoxy-*N*-*n*-butyloxycarbamate (13)**, yield 81 %, yellowish liquid.  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ ): 0.95 (t, 3H,  $\text{NO}(\text{CH}_2)_3\text{Me}$ ,  $^3J = 7.5$  Hz), 1.41 (sex, 2H,  $\text{NOCH}_2\text{CH}_2\text{CH}_2\text{Me}$ ,  $^3J = 7.5$  Hz), 1.66 (quint, 2H,  $\text{NOCH}_2\text{CH}_2\text{CH}_2\text{Me}$ ,  $^3J = 7.5$  Hz), 2.19 (s, 3H,  $\text{NOC(O)Me}$ ), 3.88 (s, 3H,  $\text{CO}_2\text{Me}$ ), 4.08 t (2H,  $\text{NOCH}_2\text{CH}_2\text{CH}_2\text{Me}$ ,  $^3J = 7.5$  Hz). IR ( $\nu$ ,  $\text{cm}^{-1}$ , thin layer): 1805 (C=O), 1780 (C=O). Found (%): C 46.68, H 7.34, N 6.79. Calc. for  $\text{C}_8\text{H}_{15}\text{NO}_5$  (%): C 46.83, H 7.38, N 6.83.

**Ethyl *N*-acetoxy-*N*-isopropoxy carbamate (14)**, yield 98 %, yellowish liquid,  $n_D^{22}$  1.4211.  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ ): 1.28 (d, 6H,  $\text{OCHMe}_2$ ,  $^3J = 6.3$  Hz), 1.33 (t, 3H,  $\text{CO}_2\text{CH}_2\text{Me}$ ,  $^3J = 7.2$  Hz), 2.17 (s, 3H,  $\text{NOC(O)Me}$ ), 4.30 (q, 2H,  $\text{CO}_2\text{CH}_2\text{Me}$ ,  $^3J = 7.2$  Hz), 4.33 (sept, 1H,  $\text{NOCHMe}_2$ ,  $^3J = 6.3$  Hz). MS (CI,  $m/z$ ,  $I_{\text{rel}}$ , (%)): 206  $[\text{M}+\text{H}]^+$  (2.0), 204 (0.6), 132 (100). Found (%): C 46.61, H 7.35, N 6.59. Calc. for  $\text{C}_8\text{H}_{15}\text{NO}_5$  (%): C 46.82, H 7.37, N 6.83.

**Methyl *N*-ethoxy-*N*-methoxycarbamate (15)**. Methyl *N*-acetoxy-*N*-ethoxycarbamate **11** (2.442 mmol, 0.432 g) was dissolved in MeOH (5 ml) at -12 °C, the solution was heated to 0 °C for 3 h, then it was kept at 24 °C for 44 h. Then it was evaporated *in vacuo* (2 Torr) yielding 0.248 g (68%) methyl *N*-ethoxy-*N*-methoxycarbamate (**15**), which was contaminated with some *N,N'*-bis(ethoxy)-*N,N'*-bis(methoxycarbonyl)hydrazine<sup>12</sup> (**16**) according to  $^1\text{H NMR}$ . After distillation *in vacuo* 0.080 g (22 %) pure (**15**) was obtained as colourless liquid.  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ ): 1.33 (t, 3H,  $\text{NOCH}_2\text{Me}$ ,  $^3J = 7.0$  Hz), 3.84 (s, 3H,  $\text{NOMe}$ ),

3.90 (s, 3H,  $\text{CO}_2\text{Me}$ ), 4.11 (q, 2H,  $\text{NOCH}_2\text{Me}$ ,  $^3J = 7.0$  Hz). Found (%): C 40.55, H 7.35. Calc. for  $\text{C}_5\text{H}_{11}\text{NO}_4$  (%): C 40.27, H 7.43.

**Ethanolysis of methyl *N*-acetoxy-*N*-ethoxycarbamate (11) at 4 °C**. Methyl *N*-acetoxy-*N*-ethoxycarbamate (**11**) (6.960 mmol, 1.232 g) was dissolved in EtOH (12 ml) at 4 °C, this solution was kept at 4 - 5 °C for 94 h, then it was evaporated *in vacuo*, yielding 1.1986 g of a yellowish liquid. According to  $^1\text{H NMR}$  this residue is a mixture of unreacted (**11**) and *N,N'*-bis(ethoxy)-*N,N'*-bis(methoxycarbonyl)hydrazine<sup>12</sup> (**16**) in molar ratio 97:3.  $^1\text{H NMR}$  of hydrazine (**16**) (300 MHz,  $\text{CDCl}_3$ ): 1.31 (t, 6H,  $\text{NOCH}_2\text{Me}$ ,  $^3J = 7.2$  Hz), 3.91 (s, 6H,  $\text{CO}_2\text{Me}$ ), 4.05 (q, 4H,  $\text{NOCH}_2\text{Me}$ ,  $^3J = 7.2$  Hz). On keeping of the solution of (**11**) in EtOH at 4 - 5 °C for 163 h, the ratio of compounds (**11**) and (**16**) became 63:37.

**Ethanolysis of methyl *N*-acetoxy-*N*-ethoxycarbamate (11) at 18 °C**. Methyl *N*-acetoxy-*N*-ethoxycarbamate (**11**) (6.766 mmol, 1.199 g) was dissolved in EtOH (12 ml) at 18 °C, this solution was kept at 17 - 18 °C for 219 h, then it was evaporated *in vacuo* (8 Torr), the residue was kept at 2 Torr and 20 °C yielding 0.563 g (51 %) methyl *N,N*-diethoxycarbamate (**17**), colourless liquid, b.p. 46-47 °C (2 Torr),  $n_D^{25}$  1.4139.  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ ): 1.30 (t, 6H,  $\text{NOCH}_2\text{Me}$ ,  $^3J = 7.2$  Hz), 3.87 (s, 3H,  $\text{CO}_2\text{Me}$ ), 4.07 (q, 4H,  $\text{NOCH}_2\text{Me}$ ,  $^3J = 7.2$  Hz).  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ ): 13.40 ( $\text{NOCH}_2\text{Me}$ ), 54.25 ( $\text{NOCH}_2\text{Me}$ ); 69.86 ( $\text{CO}_2\text{Me}$ ), 159.84 (C=O). MS (EI,  $m/z$ ,  $I_{\text{rel}}$ , (%)): 164  $[\text{M}+\text{H}]^+$  (0.4), 163  $\text{M}^+$  (2.0), 118 (1.7), 105 (3.1), 104 (2.7), 59 (59.8), 43 (100). Found (%): C 44.08, H 8.14, N 8.51. Calc. for  $\text{C}_6\text{H}_{13}\text{NO}_4$  (%): C 44.17, H, 8.03, N 8.58.

**Methyl *N*-isopropoxy-*N*-methoxycarbamate (18)**. Methyl *N*-acetoxy-*N*-isopropoxy carbamate (**12**) (8.68 mmol, 1.66 g) was dissolved in MeOH (21 ml) and kept at -32 °C, for 4 h, the solution was then heated to 20 °C and was kept at 20 °C for 7 days. The solution was then evaporated *in vacuo* (20 Torr). MeOH-condensate was trapped. The residue was distilled *in vacuo* yielding 0.86 g (60.4 %) methyl *N*-isopropoxy-*N*-methoxycarbamate (**18**), colourless liquid, b.p. 50-53 °C (3 Torr),  $n_D^{23}$  1.4168. IR ( $\nu$ ,  $\text{cm}^{-1}$ , thin layer): 1770 (C=O).  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ ): 1.29 (d, 6H,  $\text{OCHMe}_2$ ,  $^3J = 6.3$  Hz), 3.77 (s, 3H,  $\text{NOMe}$ ), 3.86 (s, 3H,  $\text{CO}_2\text{Me}$ ), 4.27 (sept, 1H,  $\text{OCHMe}_2$ ,  $^3J = 6.3$  Hz). MS (EI, 70 Ev,  $m/z$ ,  $I_{\text{rel}}$ , (%)): 163  $\text{M}^+$  (3.4), 105 (5.6), 91 (14.0), 60 (21.3), 59 (54.8), 58 (24.3), 46 (16.9), 45 (36.7), 44 (21.3), 43 (100). Found (%): C 44.23, H 8.17, N 8.42. Calc. for  $\text{C}_6\text{H}_{13}\text{NO}_4$  (%): C 44.17, H 8.03, N 8.58.

In the MeOH-condensate 0.076 g (9.7 %) of dimethylcarbonate was found by GLC.

**Methyl *N*-*n*-butyloxy-*N*-methoxycarbamate (19)**. Methyl *N*-acetoxy-*N*-*n*-butyloxycarbamate (**13**) (7.718 mmol, 1.584 g) was dissolved in MeOH (11 ml), the solution was kept at 18 °C for 148 h, then MeOH was evaporated *in vacuo* (20 Torr) and the MeOH-condensate was collected in a cold trap. The residue was kept at 20 °C and 3 Torr for 1 h yielding 1.122 g (82.3%) of methyl *N*-*n*-butyloxy-*N*-methoxycarbamate (**19**), colourless liquid,  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ ): 0.95 (t, 3H,  $\text{NO}(\text{CH}_2)_3\text{Me}$ ,  $^3J = 7.2$  Hz), 1.45 (sex, 2H,  $\text{NO}(\text{CH}_2)_2\text{CH}_2\text{Me}$ ,  $^3J = 7.2$  Hz), 1.66 (quint, 2H,  $\text{NOCH}_2\text{CH}_2\text{CH}_2\text{Me}$ ,  $^3J = 7.2$  Hz), 3.90 (s, 6H,

NOMe and CO<sub>2</sub>Me), 3.97 (t, 2H, NOCH<sub>2</sub>, <sup>3</sup>J = 7.2 Hz). IR (ν, cm<sup>-1</sup>, thin layer): 1780 (C=O). MS (EI, *m/z*, *I*<sub>rel</sub> (%)): 177 M<sup>+</sup> (3.8), 150 (76.7), 149 (87.6), 146 (40.9), 118 (14.6), 115 (9.7), 105 (29.1), 91 (57.5), 90 (52.1), 60 (64.9), 59 (100), 58 (22.1), 57 (76.5). Found (%): C 47.29, H 8.39, N 7.64. Calc. for C<sub>7</sub>H<sub>15</sub>NO<sub>4</sub> (%): C 47.45, H 8.53, N 7.90.

In the MeOH-condensate 0.0028 g (0.4 %) of dimethylcarbonate was found by GLC.

**Ethyl *N*-ethoxy-*N*-isopropylloxycarbamate (20).** A solution of ethyl *N*-acetoxy-*N*-isopropylloxycarbamate (14) (0.817 mmol, 0.168 g) in EtOH (2 ml) was kept at 20 °C for 66 h, then at 40 °C for 57 h. Then it was evaporated *in vacuo* (13 Torr) and EtOH-condensate was caught in a cold trap. The residue was kept at 20 °C and 2 Torr for 20 min yielding 0.097 g (62.2%) of ethyl *N*-ethoxy-*N*-isopropylloxycarbamate (20), colourless liquid, <sup>1</sup>HNMR (300 MHz, CDCl<sub>3</sub>): 1.276 (t, 3H, NOCH<sub>2</sub>Me, <sup>3</sup>J = 7.2 Hz), 1.278 (d, 6H, NOCHMe<sub>2</sub>, <sup>3</sup>J = 6.3 Hz), 1.34 (t, CO<sub>2</sub>CH<sub>2</sub>Me, <sup>3</sup>J = 7.2 Hz), 4.04 (q, 2H, NOCH<sub>2</sub>Me, <sup>3</sup>J = 7.2 Hz), 4.26 (sept, 1H, NOCHMe<sub>2</sub>, <sup>3</sup>J = 6.3 Hz), 4.27 (q, 2H, CO<sub>2</sub>CH<sub>2</sub>Me, <sup>3</sup>J = 7.2 Hz). MS (FAB, K<sup>+</sup>, *m/z*, *I*<sub>rel</sub> (%)): 230 [M+K]<sup>+</sup> (6), 215 (5), 192 [M+H]<sup>+</sup> (100), 176 (10). Found (%): N 7.05. Calc. for C<sub>8</sub>H<sub>17</sub>NO<sub>4</sub> (%): N 7.32.

In the EtOH-condensate 0.023 g (23.4 %) of diethylcarbonate was found by GLC.

***NH-N*-Methoxy-*N-n*-octyloxyamine (22).** A sodium methylate solution, prepared by dissolving Na (13.82 mmol, 0.318 g) in MeOH (20 ml) was added to the solution of methyl *N*-methoxy-*N-n*-octyloxyamine (21)<sup>1</sup> (6.910 mmol, 1.612 g) in MeOH (20 ml). The reaction mixture was kept at 18-20 °C for 7 h, then a solution of acetic acid (17.275 mmol, 1.04 g) in MeOH (7 ml) was added. The precipitate was filtered off, washed with MeOH, the combined MeOH-filtrate evaporated *in vacuo* (20 Torr). The residue was extracted by hexane (23 ml), the extract was evaporated *in vacuo* (20 Torr). The residue was kept at 20 °C and 2 Torr for 30 min yielding 1.148 g (94.8 %) *NH-N*-methoxy-*N-n*-octyloxyamine (22), colourless liquid, <sup>1</sup>HNMR (300 MHz, CDCl<sub>3</sub>): 0.82 (t, 3H, NO(CH<sub>2</sub>)<sub>7</sub>Me, <sup>3</sup>J = 6.9 Hz), 1.12-1.35 (m, 10H, NOCH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>5</sub>Me), 1.52 (quint, 2H, NOCH<sub>2</sub>CH<sub>2</sub>, <sup>3</sup>J = 6.9 Hz), 3.62 (s, 3H, NOMe), 3.80 (t, 2H, NOCH<sub>2</sub>, <sup>3</sup>J = 6.9 Hz), 7.80 (br. s, 1H, NH). Found (%): N 7.72. Calc. for C<sub>9</sub>H<sub>21</sub>NO<sub>2</sub> (%): N 7.99.

***NH-N-n*-Butyloxy-*N*-methoxyamine (23).** The mixture of a solution of methyl *N-n*-butyloxy-*N*-methoxycarbamate (19) (2.240 mmol, 0.397 g) in Et<sub>2</sub>O (4 ml) and a solution of NaOH (3.360 mmol, 0.134 g) in water (16 ml) was stirred at 20 °C for 1 h, then it was extracted by Et<sub>2</sub>O (25 ml). The extract was dried over MgSO<sub>4</sub> and after that it was evaporated *in vacuo*. The residue was kept at 5 Torr and 20 °C for 1 h to yield 0.253 g (94.5 %) *NH-N-n*-butyloxy-*N*-methoxyamine 23, colourless liquid, <sup>1</sup>HNMR (300 MHz, CDCl<sub>3</sub>): 0.95 (t, 3H, NO(CH<sub>2</sub>)<sub>3</sub>Me, <sup>3</sup>J = 7.2 Hz), 1.41 (sextett, 2H, NOCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Me, <sup>3</sup>J = 7.2 Hz), 1.63 (quint, 2H, NOCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Me, <sup>3</sup>J = 7.2 Hz), 3.78 (s, 3H, NOMe), 3.87 (t, 2H, NOCH<sub>2</sub>, <sup>3</sup>J = 7.2 Hz), 7.36 (br. s, 1H, NH). MS (EI, *m/z*, *I*<sub>rel</sub> (%)): 120 [M+H]<sup>+</sup> (1.2), 119 M<sup>+</sup> (6.1), 118 (1.9), 88 (2.1), 72 (14.7), 57 Bu<sup>+</sup> (81.2), 56 (53.4), 46 (21.7), 44 (31.2), 43 (100). Found (%): C 50.25, H 11.17, N 11.72. Calc. for C<sub>5</sub>H<sub>13</sub>NO<sub>2</sub> (%): C 50.40, H 11.00, N 11.75.

**Hydrolysis of methyl *N*-isopropylloxy-*N*-metoxycarbamate (18).** A mixture of a solution of methyl *N*-isopropylloxy-*N*-metoxycarbamate (18) (6.429 mmol, 1.049 g) in Et<sub>2</sub>O (7 ml) and that of NaOH (12.858 mmol, 0.51 g) and 15-crown-5 (0.15 g) in water (26 ml) was stirred at 25 °C for 1 h, and then Et<sub>2</sub>O (15 ml), acetic acid (11.66 mmol, 0.7 g) and water (2 ml) were added. The ether extract was separated, the aqueous phase was extracted with another 15 ml of Et<sub>2</sub>O. Combined ether extract was dried over MgSO<sub>4</sub>, and concentrated by removing of 3/4 of the ether (the bath temperature must be lower than 45 °C). The residue was condensed in two cold traps at different regime *in vacuo*:

(1) at 55 Torr and 35 °C to yield 0.176 g (26.0 %) *NH-N*-isopropylloxy-*N*-methoxyamine (24), colourless liquid. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): 1.21 (d, 6H, NOCHMe<sub>2</sub>, <sup>3</sup>J = 6.3 Hz), 3.66 (s, 3H, NOMe), 4.15 (centr, 1H, NOCHMe<sub>2</sub>, <sup>3</sup>J = 6.3 Hz), 7.87 (br. s, 1H, NH). Found (%): N 13.03. Calc. for C<sub>4</sub>H<sub>11</sub>NO<sub>2</sub> (%): N 13.32.

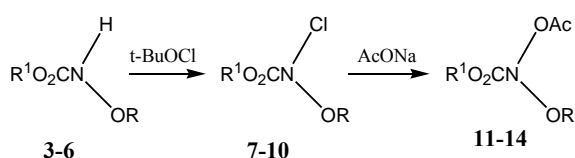
(2) at 3 Torr and 26 °C to yield 0.367 g (54.8 %) *N,N'*-bis(isopropylloxy)-*N,N'*-bis(methoxy)hydrazine (25), colourless liquid, <sup>1</sup>HNMR (300 MHz, CDCl<sub>3</sub>): 1.224 (d, 12H, NOCHMe<sub>2</sub>, <sup>3</sup>J = 6.3 Hz), 3.68 (s, 6H, NOMe), 4.17 (sept, 2H, NOCHMe<sub>2</sub>, <sup>3</sup>J = 6.3 Hz). MS (EI, *m/z*, *I*<sub>rel</sub> (%)): 209 [M+H]<sup>+</sup> (0.4), 208 M<sup>+</sup> (2.0), 207 (0.9), 177 (2.2), 105 (3.4), 104 (14.7), 60 (10.7), 59 (39.8), 58 (55.7), 46 (10.3), 45 (58.7), 44 (78.1), 43 (100). Found (%): N 13.34. Calc. for C<sub>8</sub>H<sub>20</sub>N<sub>2</sub>O<sub>4</sub> (%): N 13.45.

***NH-N,N*-diethoxyamine (26).** The mixture of a solution of methyl *N,N*-diethoxycarbamate (17) (2.542 mmol, 0.415 g) in Et<sub>2</sub>O (2 ml) and that of NaOH (7.62 mmol, 0.31 g) and 15-crown-5 (0.06 g) in water (5 ml) was stirred at 20 °C for 2 h, then a solution of acetic acid (7.62 mmol, 0.457 g) in Et<sub>2</sub>O (10 ml) was added. The ether layer was separated, the aqueous phase was extracted with Et<sub>2</sub>O (6 ml). The combined ether extract was dried over MgSO<sub>4</sub>. The extract was concentrated by evaporation (the bath temperature must be lower than 50 °C). The residue was recondensed in cold trap *in vacuo* (67 Torr) at 72 °C yielding 0.0141 g (5.2 %) *NH-N,N*-diethoxyamine (26), colourless liquid, <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): 1.23 (t, 6H, NOCH<sub>2</sub>Me, <sup>3</sup>J = 7.0 Hz), 3.93 (q, 4H, NOCH<sub>2</sub>Me, <sup>3</sup>J = 7.0 Hz), 7.95 (br. s, 1H, NH).

## RESULTS AND DISCUSSION

The major objective of this work was to study the alcoholysis of *N*-acetoxy-*N*-alkoxycarbamates and to explore of the possibility of synthesis of *NH-N,N*-dialkoxamines from methyl *NH-N,N*-dialkoxycarbamates. The last-named compounds may become useful synthones in organic synthesis but as of now only one method of their preparation is known.<sup>13,14</sup>

We have synthesized *N*-alkoxycarbamates (3-6) which were chlorinated to *N*-chloro-*N*-alkoxycarbamates (7-10) by *tert*-butyl hypochlorite in CH<sub>2</sub>Cl<sub>2</sub> solution (Scheme 3). *N*-Chloro-*N*-alkoxycarbamates react with anhydrous AcONa in MeCN selectively yielding *N*-acetoxy-*N*-alkoxycarbamates (11-14).

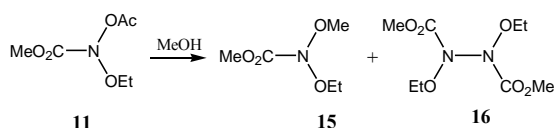


$R^1 = \text{Me}, R = \text{Et}$  (**3, 7, 11**),  $i\text{-Pr}$  (**4, 8, 12**),  $n\text{-Bu}$  (**5, 9, 13**)

$R^1 = \text{Et}, R = i\text{-Pr}$  (**6, 10, 14**)

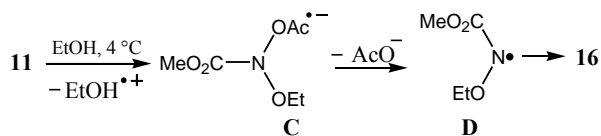
Scheme 3.

We found that methyl *N*-acetoxy-*N*-ethoxycarbamate, (**11**) is converted mainly to methyl *N*-ethoxy-*N*-methoxycarbamate (**15**) by the methanolysis at 24 °C. A by-product of this methanolysis is *N,N'*-bis(ethoxy)-*N,N'*-bis(methoxycarbonyl)hydrazine<sup>12</sup> (**16**) (Scheme 4).



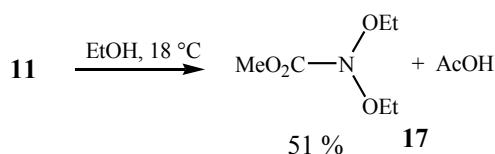
Scheme 4.

A study of ethanolysis of (**11**) showed that at 4 – 5 °C the nucleophilic substitution at nitrogen does not occur. On keeping of a solution of (**11**) in ethanol at 4 – 5 °C for 94 h, a mixture of unreacted (**11**) (main component, 97 mol. %) and *N,N'*-bis(ethoxy)-*N,N'*-bis(methoxycarbonyl)hydrazine (**16**) (3 mol. %) was obtained. On keeping the solution for 163 h, the ratio of unreacted (**11**) and the hydrazine (**16**) is 63:37 mol.%. The presence of methyl *N,N*-diethoxycarbamate (**17**) in reaction mixture was not detected. It may be supposed that at this temperature an  $S_N2$  nucleophilic substitution at nitrogen atom of (**11**) is impossible. But (**11**) is slowly reduced by ethanol to the anion-radical **C** by a SET mechanism (Scheme 5). Then the anion-radical **C** loses an acetate ion and forms radical **D** which couples to yield *N,N'*-bis(ethoxy)hydrazine (**16**).



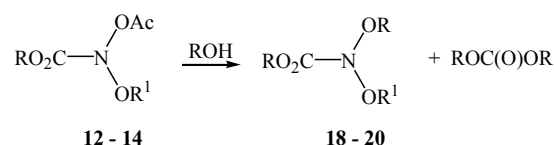
Scheme 5

But if ethanolysis of (**11**) is carried out at 17–18 °C, the  $S_N2$  nucleophilic substitution at nitrogen occurs yielding methyl *N,N*-diethoxycarbamate **17** (Scheme 6).



Scheme 6.

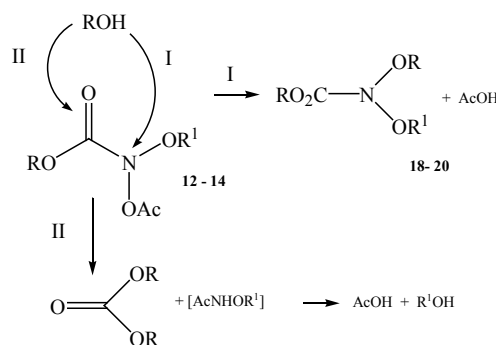
Methanolysis of *N*-acetoxy-*N*-alkoxycarbamate (**12,13**) at 20–23°C and of (**14**) at 40 °C yields alkyl *N,N*-dialkoxy-carbamates (**18–20**) and AcOH as main products (Scheme 7, Table 1). Dialkylcarbonates are by-products of these cases of alcoholysis.



Scheme 7.

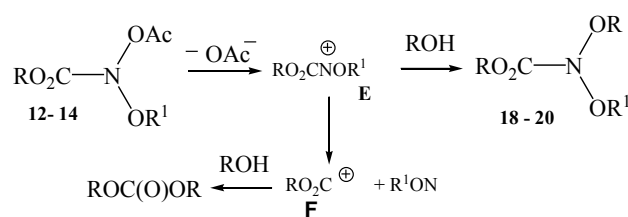
In the case of sterically hindered ethyl *N*-acetoxy-*N*-isopropoxycarbamate (**14**) the ethanolysis occurs more slowly than the methanolyses of *N*-acetoxy-*N*-alkoxycarbamates (**12, 13**).

On keeping of an ethanolic solution of (**14**) at 20 °C for 66 h, the molar ratio of unreacted (**14**) and product, *N*-ethoxy-*N*-isopropoxycarbamate (**20**) is 63:37. The complete alcoholysis take place only after keeping it at 40°C for additional 57 h yielding methyl *N*-ethoxy-*N*-isopropoxycarbamate (**20**) as main product (Table 1). The yield of by-product, diethylcarbonate is also quite high. Probably, the two competitive reactions take place simultaneously, the nucleophilic substitution at nitrogen by  $S_N2$  mechanism (route I) yielding *N,N*-dialkoxy-carbamates (**18–20**) and a nucleophilic attack of the alcohol on carbonyl group (route II) yielding dialkylcarbonate (Scheme 8).



Scheme 8

On other hand, the alcoholysis products formation may also arise through generation of *N*-alkoxyntrenium cation, **E** (Scheme 9), which reacts with alcohol yielding *N,N*-dialkoxy-carbamates (**18–20**). The further fragmentation caution **E** to more stable acyl cation **F**, which finally yields the dialkylcarbonate.

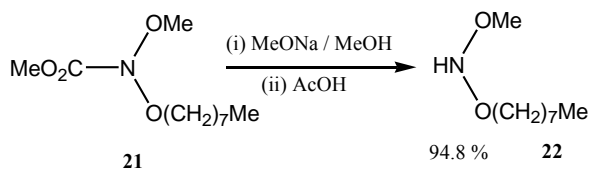


Scheme 9.

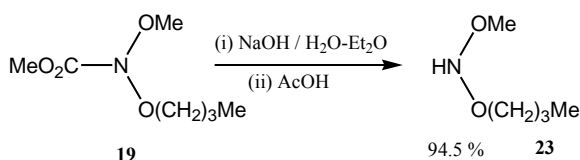
**Table 1.** Yields of products of alcoholysis of *N*-acetoxy-*N*-alkoxycarbamate **12-14**

No.	RO <sub>2</sub> CN(OR <sup>1</sup> )OAc		ROH	Temp., °C	Time, h	RO <sub>2</sub> CN(OR <sup>1</sup> )OR		ROC(O)OR
	R	R <sup>1</sup>				R	Yield, %	Yield, %
<b>12</b>	Me	<i>i</i> -Pr	MeOH	20	164	Me (18)	60.4	9.7
<b>13</b>	Me	<i>n</i> -Bu	MeOH	21-23	120	Me (19)	82.3	0.4
<b>14</b>	Et	<i>i</i> -Pr	EtOH	(a) 20 (b) 40	66 57	Et (20)	62.2	23.4

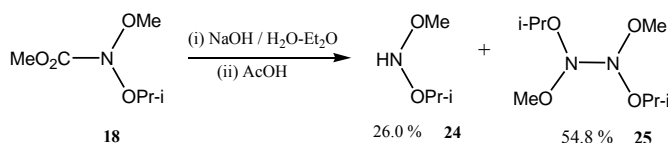
In methyl *N,N*-dialkoxy-carbamates, MeOC(O)-group can be easily eliminated by hydrolysis or alcoholysis in the presence of alkali to yield the particular *NH-N,N*-dialkoxyamines. But in every case the suitable reaction conditions must be carefully selected. Thus, methyl *N*-methoxy-*N-n*-octyloxycarbamate (**21**)<sup>1</sup> yields *NH-N*-methoxy-*N-n*-octyloxyamine (**22**) by treatment of MeONa solution in methanol then by action of acetic acid (Scheme 10).

**Scheme 10**

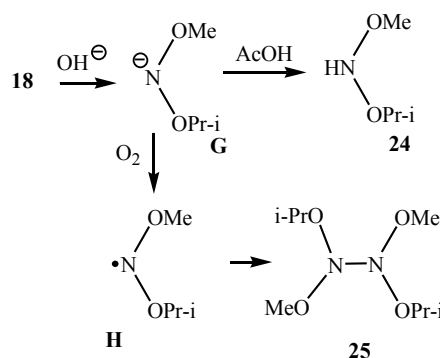
The hydrolysis of methyl *N-n*-butyloxy-*N*-methoxycarbamate (**19**) by 1.5 equivalent of NaOH in the water solution in the presence of ether (4:1) at 20° C for 1 h selectively yields *NH-N-n*-butyloxy-*N*-methoxyamine (**23**) (Scheme 11).

**Scheme 11**

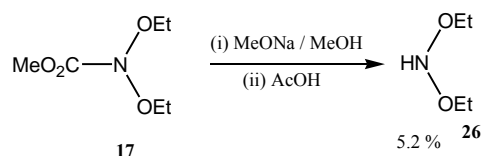
The alkaline hydrolysis of methyl *N*-isopropoxy-*N*-methoxycarbamate (**18**) occurs with the formation two main products, unstable *NH-N*-isopropoxy-*N*-methoxyamine (**24**) and *N,N'*-bis(isopropoxy)-*N,N'*-bis(methoxy)hydrazine (**25**) (Scheme 12).

**Scheme 12**

Probably, in this case (Scheme 13) the initially generated anion **G** may be protonated to unstable (**24**) or may undergo aerial oxidation to a relatively stable dialkoxyaminyl radical **H** which dimerises<sup>15</sup> to (**25**).

**Scheme 13**

*NH-N,N*-Diethoxyamine (**26**) was obtained in low yield by alkaline hydrolysis of methyl *N,N*-diethoxycarbamate (**17**) (Scheme 14). Probably the further rapid decomposition of (**17**) occurs in these reaction conditions.

**Scheme 14**

The structure of *NH-N,N*-dialkoxyamines (**22-24** and **26**) and *N,N,N',N'*-tetraalkoxyhydrazine (**25**) was confirmed by their <sup>1</sup>HNMR spectra, the structure of compounds (**23**) and (**25**) were confirmed by mass spectra also. In <sup>1</sup>HNMR spectra of (**22-24**) and (**26**), the characteristic signal of NH-proton as the broad singlet in field of 7.36 -7.95 ppm was observed.

Thus it was established that alcoholysis of *N*-acetoxy-*N*-alkoxycarbamates by methanol or ethanol at 20 – 40° C yields *N,N*-dialkoxy-carbamates and acetic acid. At the lower temperature the competitive formation of *N,N'*-dialkoxy-carbonyl-*N,N'*-dialkoxyhydrazines can occur. It was found that alkaline hydrolysis of *N,N*-dialkoxy-carbamates yields *NH-N,N*-dialkoxyamines.

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