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


Keywords: Nucleophilic substitution at nitrogen, N-acyloxy-N-alkoxy carbamates, alcoholysis, N,N-dialkoxy carbamates, hydrolysis, NH-N,N-dialkoxyamines.

The alcoholysis of N-acetoxy-N-alkoxy carbamates 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(alkoxy carbonyl)-N,N′-bis(alkoxy) hydrazines can occur. The alkaline hydrolysis of N,N-dialkoxy carbamates yields NH-N,N-dialkoxyamines.

INTRODUCTION

The nature of the products of the alcoholysis of N-acyloxy-N-alkoxy ureas, N-acyloxy-N-alkoxy carbamates, N-acyloxy-N-alkoxy benzamides depends on the electronegativity of third substituent at nitrogen atom in the O-N-O geminal system. N-Acyloxy-N-alkoxy ureas1,3 and N-acyloxy-N-alkoxy-N-tert-alkylamines1 yield respectively the N,N-dialkonylureas and N,N-dialkonyl-N-tert-alkylamines by the alcoholysis. N-Acyloxy-N-alkoxy carbamates convert into N,N-dialkoxy carbamates only by the alcoholysis by primary alcohols.1 The alcoholysis of N-acyloxy-N-alkoxy carbamates by tert-butanol does not take place, probably, due to steric hindrances to Sx2 nucleophilic substitution at the nitrogen.1 Isopropanolysis of ethyl N-acyloxy-N-methoxy carbamate results in the formation of reduction products such as N,N′-bis(ethoxy carbonyl)-N,N′-bis(methoxy) hydrazine and ethyl N-ethoxy carbamate11 (Scheme 1).

EtO₂CN(OMe)OAc + i-PrOH → EtO₂CNHOMe + AcOH

Scheme 1

The nature of products of N-acyloxy-N-alkoxy benzamides alcoholysis is strongly depended by of the nature of p-substituent in the phenyl group. Thus, methanolysis of N-acyloxy-N-ethoxy benzamide yields the mixture of methyl benzoate, benzoic and acetic acid,1 however, as we have found, the methanolysis of N-acyloxy-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).

N-acyloxy-N-alkoxy benzamides,3-9 N-acyloxy-N-alkoxy carbamates1,10,11 and N-acyloxy-N-alkoxy ureas1,2,10,11 are called “anomeric amides” due to nO(Alk)→σ*N-OC(O)R anomeric effect domination. In R(C(=O)O–N–O(Alk) group the amide nitrogen is sp³ hybridized and has pyramidal configuration, (Alk)O–N
bond is shortened and N–OC(=O)R bond is elongated and destabilized. Due to this N–OC(=O)R bond destabilization, the S$_2$ nucleophilic substitution at amide nitrogen atom or homolysis of this bond become possible.

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-dialkoxymines

**EXPERIMENTAL**

**General**

$^1$HNMR spectra were recorded on a “Varian VXP-300” spectrometer (300 MHz), “Mercury-400” (400 MHz) and “Bruker Avance DRX 500” (500 MHz). Me$_2$Si was used as an internal standard. Chemical shifts were measured in ppm and coupling constants in Hz. $^1$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-reactent was isobutane. MeOH and EtOH were dried by refluxing and distillation over metallic calcium.

**Metanalysis of N-acycloxy-N-methoxy-4-nitrobenzamide (1)**

A solution of (1)$^9$ (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)hydrazide (2) as yellowish white crystals, m.p. 86 – 88 °C (with decomp.). $^1$HNMR (400 MHz, CDC$_3$): 3.948 (s, 6H, NOMe), 8.206 (d, 4H, H$_7$-Cl$_2$, J = 9.2 Hz), 8.305 (d, 4H, H$_7$-Cl$_2$, J = 9.2 Hz), 9.13 (br. s, 1H, NH). IR (ν, cm$^{-1}$, KBr): 3430 (NH), 1728 (C=O), 1603 (C=O). Found (%): N 9.43. Calc. for C$_6$H$_7$NClO$_4$: N 9.52.

**Methyl N-ethoxycarbamate (3)**

A solution of ethoxymine (29.06 mmol, 1.78 g) in MeCN (7 ml) was added to the solution of Me$_2$CCl (37.77 mmol, 3.57 g) in MeCN (15 ml) at 10 °C, then K$_2$CO$_3$ (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$_2$Cl$_2$ 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), $m_f^{25}$ 1.4247 (cf. 1.4246$^{15}$) identified by comparison its $^1$HNMR spectra with that of an authentic sample.$^{12}$ $^1$HNMR (300 MHz, CDC$_3$): 1.18 (t, 3H, NOCH$_3$Me, $^3$J = 6.9 Hz), 3.69 (s, 3H, CO$_2$Me), 3.85 (q, 2H, NOCH$_2$Me, $^3$J = 6.9 Hz), 7.40 (br. s, 1H, NH). IR (ν, cm$^{-1}$, KBr): 3430 (NH), 1740 (C=O).

**Methyl N-isopropylxycarbamate (4)**, yield 78%, colourless liquid, b.p. 87-88 °C (10 Torr), $m_f^{27} 1.4237$. $^1$HNMR (300 MHz, CDC$_3$): 1.15 (d, 6H, OCH$_3$Me, $^3$J = 6.3 Hz), 3.68 (s, 3H, CO$_2$Me), 3.98 (sept, 1H, OCHMe$_2$, $^3$J = 6.3 Hz), 7.33 (br. s, 1H, NH). IR (ν, cm$^{-1}$, KBr): 3310 (NH), 1745 (C=O). Found (%): N 10.68. Calc. for C$_3$H$_7$NO$_3$: N 10.52.

**Methyl N-n-butylxycarbamate (5)**, yield 76 %, colourless liquid, b.p. 105-107 °C (5 Torr), $m_f^{22} 1.4312$. $^1$HNMR (300 MHz, CDC$_3$): 0.94 (t, 3H, OCH$_2$CH$_3$CH$_2$Me, $^3$J = 7.2 Hz), 1.40 (ses, 2H, OCH$_2$CH$_2$Me, $^3$J = 7.2 Hz), 1.63 (quint, 2H, OCH$_2$CH$_2$CH$_2$Me, $^3$J = 7.2 Hz), 3.77 (s, 3H, CO$_2$Me), 3.87 (s, OCH$_2$CH$_2$CH$_2$Me, $^3$J = 7.2 Hz), 7.47 (br. s, 1H, NH). Found (%): N 9.31. Calc. for C$_8$H$_{13}$NO$_3$: N 9.52.

**Ethyl N-isopropylxycarbamate (6)**, yield 67 %, colourless liquid, b.p. 68°C (2 Torr), $m_f^{20} 1.4255$. $^1$HNMR (300 MHz, CDC$_3$): 1.22 (d, 6H, OCH$_3$Me, $^3$J = 6.3 Hz), 1.27 (t, 3H, CO$_2$CH$_2$Me, $^3$J = 7.2 Hz), 4.05 (sept, 1H, OCHMe$_2$, $^3$J = 6.3 Hz), 4.19 (q, 2H, CO$_2$CH$_2$Me, $^3$J = 7.2 Hz). Found (%): N 9.43. Calc. for C$_6$H$_9$NO$_3$: N 9.52.

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

A solution of t-BuOCl (15 mmol) in CH$_2$Cl$_2$ (3 ml) was added to the solution of the alky1 N-alkoxycarbamate (5 mmol) in CH$_2$Cl$_2$ (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. $^1$HNMR (300 MHz, CDC$_3$): 1.31 (t, 3H, NOCH$_2$Me, $^3$J = 6.9 Hz), 3.92 (s, 3H, CO$_2$Me), 4.07 (q, 2H, NOCH$_2$Me, $^3$J = 6.9 Hz). IR (ν, cm$^{-1}$, thin layer): 1795 (C=O). Found (%): Cl 22.85. Calc. for C$_3$H$_7$ClNO: Cl 22.69.

**Methyl N-chloro-N-isopropylxycarbamate (8)**, yellow oil. $^1$HNMR (300 MHz, CDC$_3$): 1.28 (d, 6H, OCH$_3$Me, $^3$J = 6.3 Hz), 3.91 (s, 3H, CO$_2$Me), 4.31 (sept, 1H, OCH$_2$Me, $^3$J = 6.3 Hz). IR (ν, cm$^{-1}$, thin layer): 1780 (C=O). Found (%): Cl 21.04. Calc. for C$_8$H$_{13}$ClNO: Cl 21.15.

**Methyl N-chloro-N-n-butylxycarbamate (9)**, yellow oil. $m_f^{25} 1.4383$. $^1$HNMR (300 MHz, CDC$_3$): 0.95 (t, OCH$_2$CH$_2$CH$_2$Me, $^3$J = 7.3 Hz), 1.45 (ses, 2H, OCH$_2$CH$_2$CH$_2$Me, $^3$J = 7.3 Hz), 1.57 (quint, 2H, OCH$_2$CH$_2$CH$_2$Me, $^3$J = 7.3 Hz), 3.90 (s, 3H, CO$_2$Me), 3.97 (t, 2H, OCH$_2$CH$_2$CH$_2$Me, $^3$J = 7.3 Hz). Found (%): Cl 19.16. Calc. for C$_{18}$H$_{25}$ClNO: Cl 19.52.

**Ethyl N-chloro-N-isopropylxycarbamate (10)**, yellowish oil. $^1$HNMR (300 MHz, CDC$_3$): 1.28 (d, 6H, NOCH$_2$Me, $^3$J = 6.3 Hz), 1.36 (t, 3H, CO$_2$CH$_2$Me, $^3$J = 7.0 Hz), 1.54 (t, 3H, CO$_2$CH$_2$Me, $^3$J = 7.0 Hz), 3.93 (s, 3H, CO$_2$Me), 4.31 (sept, 1H, OCH$_2$Me, $^3$J = 6.3 Hz). IR (ν, cm$^{-1}$, thin layer): 1780 (C=O). Found (%): Cl 21.04. Calc. for C$_{18}$H$_{25}$ClNO: Cl 21.15.
Hz), 4.31 (sept, 1H, NOCHMe₂, \(J = 6.3\) Hz), 4.33 (q, 2H, CO₂C₆H₄₂Me, \(J = 7.0\) Hz). Found (%): C 19.46. Calc. C₈H₅Cl₃NO₃ (%): C 19.52.

General method for the synthesis of N-acetoxy-N-alkoxy carbamates

A mixture of the solution of N-chloro-N-alkoxy carbamate (8 mmol) in MeCN (20 ml) and AcONa (26 mmol) was stirred at 20 °C for 55 h, then CH₃Cl (10 ml) was added, the precipitate was filtered off, washed with CH₂Cl₂, the combined filtrate was evaporated in vacuo (20 Torr). The residue was extracted by CH₃Cl (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-ethoxy carbamate (11), yield 87 %, colourless liquid, \(n_\text{D} = 1.4269\). \[^1\text{H}NMR\] (300 MHz, CDCl₃): 1.30 (t, 3H, NOCH₂Me, \(J = 7.2\) Hz), 2.19 (s, 3H, NOC(O)Me), 3.88 (s, 3H, CO₂Me), 4.13 (q, 2H, NOCH₂Me, \(J = 7.2\) Hz). IR (cm⁻¹, thin layer): 1805 (C=O), 1780 (C=O). Found (%): C 40.41, H 6.31, N 7.78. Calc. for C₇H₁₃NO₃ (%): C 40.68, H 6.26, N 7.91.

Methyl N-acetoxy-N-isopropoxycarbamate (12), yield 96 %, yellowish liquid. \[^1\text{H}NMR\] (300 MHz, CDCl₃): 1.28 (d, 6H, OCH₂CH₃, \(J = 6.3\) Hz), 2.17 (s, 3H, NOC(O)Me), 3.87 (s, 3H, CO₂Me), 4.32 (sept, 1H, OCH₂Me, \(J = 6.3\) Hz). IR (cm⁻¹, thin layer): 1805 (C=O), 1780 (C=O). MS (CI, m/z, \(I_\text{rel}\), %): 192 [M+H]⁺ (0.6), 191 M⁺ (1.5), 148 (4.0), 132 (3.1), 59 (23.9), 45 (5.4), 40 (13). Found (%): C 43.81, H 6.82, N 7.18. Calc for C₇H₁₈NO₂ (%): C 43.98, H 6.85, N 7.33.

Methyl N-acetoxy-N-n-butyloxy carbamate (13), yield 81 %, yellowish liquid. \[^1\text{H}NMR\] (300 MHz, CDCl₃): 0.95 (t, 3H, NO(CH₂)₂Me, \(J = 7.5\) Hz), 1.41 (sex, 2H, NOCH₂CH₂CH₃, \(J = 7.5\) Hz), 1.66 (quint, 2H, NOCH₂CH₂CH₃, \(J = 7.5\) Hz), 3.90 (s, 3H, CO₂Me), 4.11 (q, 2H, NOCH₂Me, \(J = 7.0\) Hz). Found (%): C 40.55, H 7.35. Calc. for C₈H₁₃NO₄ (%): C 40.27, H 7.43.

Ethanolysis of methyl N-acetoxy-N-ethoxy carbamate (11) at 4°C. Methyl N-acetoxy-N-ethoxy carbamate (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 1.1896 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 (16) in molar ratio 97:3. \[^1\text{H}NMR\] of hydrazine (16) (300 MHz, CDCl₃): 1.31 (t, 6H, NOCH₂Me, \(J = 7.2\) Hz), 3.91 (3H, CO₂Me), 4.05 (4H, NOCH₂Me, \(J = 7.2\) 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-ethoxy carbamate (11) at 18 °C. Methyl N-acetoxy-N-ethoxy carbamate (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), \(n_\text{D} = 1.4139\). \[^1\text{H}NMR\] (300 MHz, CDCl₃): 1.30 (t, 6H, NOCH₂Me, \(J = 7.2\) Hz), 3.87 (s, 3H, CO₂Me), 4.07 (q, 4H, NOCH₂Me, \(J = 7.2\) Hz). \[^13\text{C}NMR\] (75 MHz, CDCl₃): 13.40 (NOCH₂Me), 54.25 (NOCH₂Me), 69.86 (CO₂Me), 159.84 (C=O). MS (EI, m/z, \(I_\text{rel}\), %): 164 [M+H]⁺ (0.4), 163 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 C₉H₁₉NO₃ (%): C 44.17, H 8.03, N 8.58.

Methyl N-isopropoxy-N-methoxy carbamate (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 then was 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-methoxy carbamate (18), colourless liquid, b.p. 50-53 °C (3 Torr), \(n_\text{D} = 1.4168\) IR (cm⁻¹, thin layer): 1770 (C=O). \[^1\text{H}NMR\] (300 MHz, CDCl₃): 1.29 (t, 6H, OCH₂Me, \(J = 6.3\) Hz), 3.77 (s, 3H, NOME), 3.86 (s, 3H, CO₂Me), 4.27 (sept, 1H, OCH₂Me, \(J = 6.3\) Hz). MS (EI, 70 Ev, m/z, \(I_\text{rel}\), %): 163 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 C₉H₁₉NO₃ (%): C 44.17, H 8.03, N 8.58.

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

Ethyl N-n-butyloxy-N-methoxy carbamate (19). Methyl N-acetoxy-N-n-butyloxy carbamate (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-methoxy carbamate (19), colourless liquid, b.p. 46-47 °C (2 Torr), \(n_\text{D} = 1.4139\). \[^1\text{H}NMR\] (300 MHz, CDCl₃): 0.95 (t, 3H, NO(CH₂)₂Me, \(J = 7.2\) Hz), 1.45 (sex, 2H, NO(CH₂)₂CH₂Me, \(J = 7.2\) Hz), 1.66 (quint, 2H, NOCH₂CH₂CH₂Me, \(J = 7.2\) Hz), 3.90 (s, 6H, CO₂Me), 4.11 (q, 2H, NOCH₂Me, \(J = 7.0\) Hz). Found (%): C 40.55, H 7.35. Calc. for C₈H₁₃NO₄ (%): C 40.27, H 7.43.
Hydrolysis of methyl N-isopropoxy-N-metoxycarbamate (18). A mixture of a solution of methyl N-isopropoxy-N-metoxycarbamate (18) (6.429 mmol, 1.049 g) in Et₂O (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 Et₂O (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 Et₂O. Combined ether extract was dried over MgSO₄, 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-isopropoxy-N-methoxymine (24), colourless liquid. ¹H NMR (300 MHz, CDCl₃): 1.21 (d, 6H, NOCH₃, J = 6.3 Hz), 3.66 (s, 3H, NOMe), 4.15 (sept, 1H, NOCH₂, J = 6.3 Hz), 7.87 (br. s, 1H, NH). Found (%): N 13.05. Calc. for C₈H₈NO₂ (%): N 13.32.

(2) at 3 Torr and 26 °C to yield 0.367 g (54.8 %) N,N'-bis(isopropoxy)-N,N'-bis(methoxy)hydrazine (25), colourless liquid, ¹H NMR (300 MHz, CDCl₃): 1.224 (d, 12H, NOCH₃, J = 6.3 Hz), 3.68 (s, 6H, NOMe), 4.17 (sept, 2H, NOCH₂, J = 6.3 Hz). MS (EI, m/z, Irel (%)): 209 [M+H⁺]⁺ (64), 208 M⁺ (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 C₂H₁₃NO₄ (25): N 13.45.

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-dialkoxymamines from methyl NH-N,N-dialkoxycarbamates. The last-named compounds may become useful syntheses in organic synthesis but as of now only one method of their preparation is known.¹³,¹⁴

We have synthesized N-alkoxycarbamates (3-6) which were chlorinated to N-chloro-N-alkoxycarbamates (7-10) by tert-butyl hypochlorite in CH₂Cl₂ solution (Scheme 3). N-Chloro-N-alkoxycarbamates react with anhydrous AcONa in MeCN selectively yielding N-acetoxy-N-alkoxycarbamates (11-14).
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).

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 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(methoxy carbonyl)hydrazine (12) (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).

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

Scheme 7.

In the case of sterically hindered ethyl N-acetoxy-N-isopropoxycarbamate (14) the ethanolysis occurs more slowly than the methanolysies 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-dialkoxycarbamates (18-20) and a nucleophilic attack of the alcohol on carbonyl group (route II) yielding dialkylcarbonate (Scheme 8).

Scheme 8.

On other hand, the alcohololysis products formation may also arises through generation of N-alkoxycarnetium cation, E (Scheme 9), which reacts with alcohol yielding N,N-dialkoxycarbamates (18-20). The further fragmentation caution E to more stable acyl cation F, which finally yields the dialkylcarbonate.
The structure of compounds (22-24) and \( N,N,N',N' \)-tetraalkoxyhydrazine (25) was confirmed by their \(^1\)H NMR spectra, the structure of compounds (23) and (25) were confirmed by mass spectra also. In \(^1\)H NMR 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-dialkoxy carbamates 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-\( N,N' \)-dialkoxy hydrazines can occur. It was found that alkaline hydrolysis of \( N,N \)-dialkoxy carbamates yields \( NH-N,N \)-dialkoxyamines.
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