Geminal systems
50.* Synthesis and alcoholysis of *N*-acyloxy-*N*-alkoxy derivatives of ureas, carbamates, and benzamides

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Procedures were developed for the synthesis of *N*-acyloxy-*N*-alkoxy derivatives of ureas, carbamates, and benzamides by the reactions of the corresponding *N*-alkoxy-*N*-chloro derivatives with sodium carboxylates in MeCN. *N*-Chloro-*N*-ethoxy-*p*-toluenesulfonamide was inert in this reaction. Alcoholysis of *N*-acyloxy-*N*-alkoxy derivatives of ureas, carbamates, and *tert*-alkylamines afforded the corresponding *N*,*N*-dialkoxy derivatives, whereas alcoholysis of *N*-acetoxy-*N*-ethoxybenzamide gave rise to alkyl benzoates.

Key words: *N*-alkoxy-*N*-chloro derivatives of ureas, carbamates, benzamide, and *p*-toluenesulfonamide, sodium carboxylates, *N*-acyloxy-*N*-alkoxy derivatives of ureas, carbamates, and tertiary alkylamines, alcoholysis, ^{1}H NMR spectra, mass spectra, *N*,*N*-dialkoxyamino derivatives of ureas and carbamates.

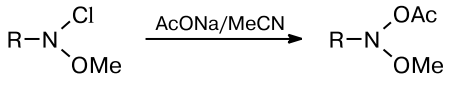
N-Alkoxy-*N*′,*N*′-dialkyl-*N*-chloroureas, *N*,*N*-dialkoxy-*N*-chloroamines, and *N*-alkoxy-*N*-chloro-*tert*-alkylamines, which are representatives of the O—N—Cl geminal system,[2a] are characterized by high anion mobility of Cl atoms and serve as precursors of important classes of compounds, such as dialkoxyamines[2b,c] and trialkoxyamines.[2b,d] However, these compounds are rather unstable.[2]

A comparison of their properties with those of the related N—C—X geminal system reveals the following features. In chloromethylamines, the C—Cl bond is completely ionized and these compounds exist as iminium salts $R_2N^+=CH_2Cl^-$, whereas the corresponding acetoxymethylamines exist in the covalent form $AcOCH_2NR_2$ as stable distillable compounds.[3] Hence, one would expect, on the one hand, an increase in stability of *N*-acyloxy-*N*-alkoxy derivatives of ureas, amines, and carbamates compared to *N*-chloro analogs and, on the other hand, the anion mobility of the *N*-acyloxy group, which provides an easy access to *N*,*N*-dialkoxy derivatives.

In this connection, we studied the synthesis of *N*-acyloxy-*N*-alkoxy derivatives of ureas and carbamates as well as their transformations under conditions of alcoholysis.*

Earlier, the only *N*-acyloxy-*N*-alkoxyamine **1** has been prepared (Scheme 1)[5].

Scheme 1



1

R = MeO(O)CC(Me)$_2$—

We found that *N*-alkoxy-*N*-chloroureas also reacted with sodium and potassium carboxylates in MeCN to form *N*-acyloxy-*N*-alkoxyureas (Scheme 2).

N-Alkoxy-*N*-chloroureas **10**—**15**, except for compound **9**,[6] have not been described earlier. We synthe-

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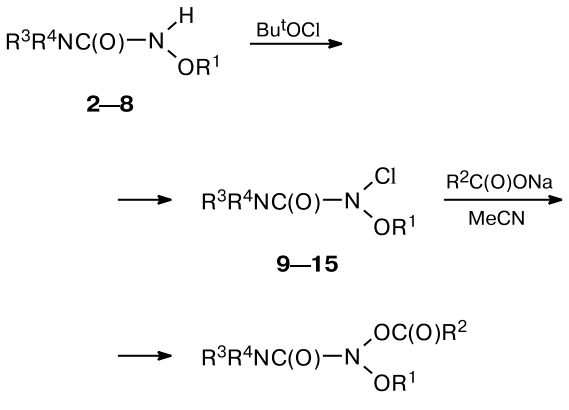
Scheme 2

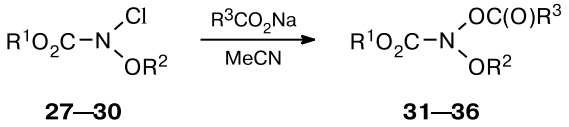


R^1 = Me (**2**, **9**, **16**—**19**), Pr^n (**3**, **4**, **10**, **11**, **20**—**22**), Et (**5**, **6**, **12**, **13**, **23**, **24**), Bu^n (**7**, **14**, **25**), *n*-$C_{12}H_{25}$ (**8**, **15**, **26**)
R^2 = Me (**16**, **20**, **21**, **23**—**26**), Et (**17** (from $EtCO_2K$)), Pr^i (**18**), Ph (**19**, **22**)
R^3 = Me (**2**—**4**, **9**—**11**, **16**—**22**), CH_2Nph-1 (**5**, **12**, **23**), H (**6**—**8**, **13**—**15**, **24**—**26**)
R^4 = Me (**2**, **3**, **9**, **10**, **16**—**20**), H (**4**—**8, 11**—**15, 21**—**26**)

sized these compounds, which are very unstable in pure form, by the reactions of *N*-alkoxyureas **3**—**8** with Bu^tOCl. *N*-Acyloxy-*N*-alkoxyureas **16**—**23** were prepared as yellowish liquids. *N*′-Unsubstituted *N*-acetoxy-*N*-alkoxyureas **24**—**26** represent colorless crystalline compounds. Most of these compounds are rather unstable at 20 °C. However, these compounds can be stored at −5 °C for up to 2 months.

In the earlier study of *N*-alkoxy-*N*-chlorocarbamates, attempts to carry out the nucleophilic replacement of the chlorine atom by an alkoxy group under conditions of alcoholysis in the presence of Et_3N failed.[7] In the present study, *N*-acyloxy-*N*-alkoxycarbamates **31**—**36** were synthesized for the first time in high yields by the reactions of *N*-alkoxy-*N*-chlorocarbamates **27**—**30** with Na(K) salts of carboxylic acids in MeCN (Scheme 3).

Scheme 3

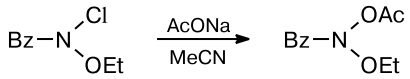


R^1 = Me (**27**, **28**, **31**—**33**), Et (**29**, **30**, **34**—**36**)
R^2 = Me (**27**, **29**, **31**, **32**, **34**, **35**), *n*-C_8H_{17} (**28**, **33**), Pr^i (**30**, **36**)
R^3 = Me (**31**, **33**, **34**, **36**), Et (**32** (from $EtCO_2K$)), Ph (**35**)

The resulting products are colorless liquids, which can be stored without noticeable decomposition at 20 °C for up to 2 days (except for compound **35**) or at −5 °C for 3—4 months. Compounds **31**, **32**, and **36** are distillable *in vacuo* (with partial decomposition).

The reactions of *N*-alkoxy-*N*-chlorobenzamides with AcONa in MeCN proved to be a convenient way of preparing *N*-acetoxy-*N*-alkoxybenzamides described earlier,[8—11] as exemplified by the synthesis of *N*-acetoxy-*N*-ethoxybenzamide (**38**) (Scheme 4).

Scheme 4



It is known that *N*-alkoxy-*N*-chlorosulfonamides remain intact under the action of MeONa/MeOH.[6] We demonstrated that *N*-chloro-*N*-ethoxytoluene-*p*-sulfonamide (**39**) also did not react with AcONa in MeCN. Therefore, it can be stated that the chlorine atom in *N*-alkoxy-*N*-chlorosulfonamides possesses no anion mobility.

The anion mobility of the acyloxy group in the resulting *N*-acyloxy-*N*-alkoxy derivatives of ureas and carbamates as well as in *N*-acyloxy-*N*-alkoxyamines was confirmed by the formation of the corresponding *N*,*N*-dialkoxyamino compounds upon alcoholysis.

Alcoholysis of *N*-acyloxy-*N*-alkoxyureas **16**—**26** with primary alcohols (methanol, ethanol, *n*-propanol) at 20—25 °C selectively afforded the corresponding *N*,*N*-di-

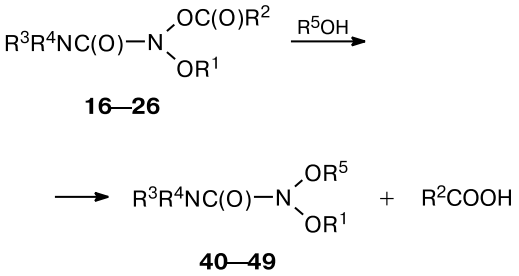
Table 1. *N*,*N*-Dialkoxyureas $R^3R^4NC(O)N(OR^1)OR^5$ **40**—**49** prepared by alcoholysis of *N*-acyloxy-*N*-alkoxyureas

Run	Starting compound	Alcohol	T^a/°C	Reaction time/h	Reaction product	Yield (%)
1	**16**	Pr^nOH	30	264	**40**	81.5
2	**20**	MeOH	20	55	**40**	80.1
3	**17**	EtOH	25—30	217	**41**	97.4
4	**18**	Pr^nOH	25—30	255	**40**	95.4
5	**21**	MeOH	25	169	**42**	92.2
6	**22**	MeOH	20	45	**42**	56.0
7	**23**	MeOH	22	92	**43**	99.5
8	**24**	MeOH	20	103	**44**	88.1
9	**25**	MeOH	30	30	**45**	92.2
10	**25**	EtOH	30	142	**46**	88.4
11	**26**	MeOH	20	960 (40 d)	**47**	95.2
12	**21**	Pr^iOH	20	450	**48**	71.0
13	**20**	Pr^iOH	20	527	**49**	75.4 [b]
14	**20**	Pr^iOH	20	1224 (51 d)	**49**	91.9
15	**20**	Pr^iOH	82	5	**49**	25.5

[a] Reaction temperature.
[b] With an admixture of the starting compound, the **49**/**20** ratio was ~3 (^{1}H NMR data).

alkoxyureas **40**—**47** (Table 1, runs *1*—*11*). In addition, alcoholysis gave rise to the corresponding carboxylic acid, which was identified by ^{1}H NMR spectroscopy of the reaction mixtures and by GLC (Scheme 5).

Scheme 5

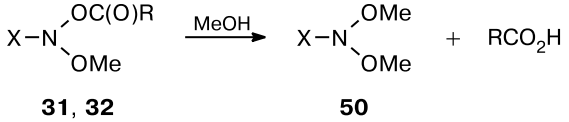


R^1 = Me (**40**, **41**), Et (**43**, **44**), Pr^n (**42**, **48**, **49**), Bu^n (**45**, **46**), *n*-$C_{12}H_{25}$ (**47**)
R^3 = H (**44**—**47**), Me (**40**—**42**, **48**, **49**), CH_2Nph-1 (**43**)
R^4 = H (**42**—**48**), Me (**40**, **41**, **49**)
R^5 = Me (**42**—**45**, **47**), Et (**41**, **46**), Pr^n (**40**), Pr^i (**48**, **49**)

Alcoholysis of *N*-acyloxy-*N*-alkoxyureas with propan-2-ol under standard conditions requires longer time. For example, *N*-acetoxy-*N*-*n*-propoxy-*N*′,*N*′-substituted ureas **20** and **21** reacted with propan-2-ol to give *N*-isopropoxy-*N*-*n*-propoxy-*N*′,*N*′-disubstituted ureas **48** and **49** in only 71—75% yields even after 22 days (see Table 1, runs *12* and *13*, respectively). The complete conversion was achieved only after 51 days (see Table 1, run *14*). Compound **20** was completely consumed upon refluxing in propan-2-ol for 5 h; however, product **49** was prepared in much lower yield (see Table 1, run *15*). Upon storage in *tert*-butyl alcohol for 70 h, *N*-acetoxy-*N*-*n*-propoxyurea **20** remained intact, its recovery was ~93%. An analogous steric hindrance to alcoholysis with *tert*-butyl alcohol was observed for *N*-alkoxy-*N*-chloroamines[2b] and *N*-alkoxy-*N*-chloro-*N*′,*N*′-dimethylureas.[6]

Alcoholysis of *N*-acyloxy-*N*-alkoxycarbamates is also accompanied by the replacement of the *N*-acyloxy group by the alkoxy group. Methanolysis of methyl *N*-acyloxy-*N*-methoxycarbamates **31** and **32** afforded methyl *N*,*N*-dimethoxycarbamate (**50**) in satisfactory yields (Scheme 6).

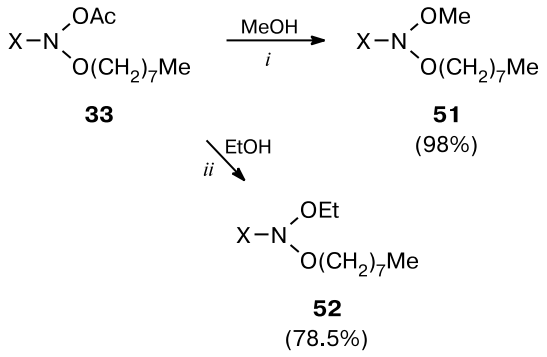
Scheme 6



X = MeOC(O)
R = Me (**31**), Et (**32**)

Methyl *N*-acetoxy-*N*-*n*-octyloxycarbamate (**33**) was transformed into the corresponding *N*-methoxy-*N*-*n*-octyloxycarbamate (**51**) upon methanolysis for 3 days (20 °C). Ethanolysis giving rise to methyl *N*,*N*-dialkoxycarbamate (**52**) was brought to completion within 120 days (Scheme 7).

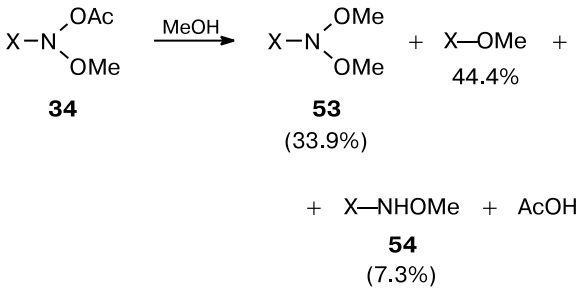
Scheme 7



X = MeOC(O)
i. 3 days. *ii*. 120 days.

Methanolysis of ethyl *N*-acetoxy-*N*-methoxycarbamate (**34**) afforded ethyl *N*,*N*-dimethoxycarbamate (**53**) along with ethyl methyl carbonate and ethyl *N*-methoxycarbamate (**54**) (Scheme 8).

Scheme 8

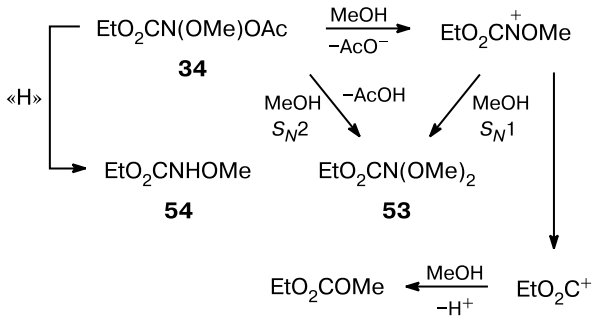


X = EtOC(O)

It should be noted that the nucleophilic substitution at the nitrogen atom to form *N*,*N*-dimethoxyurethane **53** is not dominant and proceeds, apparently, according to both the S_N1 and S_N2 mechanisms. Redox transformations giving rise to *N*-methoxyurethane **54** are not predominating reactions as well. Apparently, the main process involves the fragmentation of the nitrenium cation, which is generated from compound **34**, to produce the more stable ethoxycarbonyl cation (Scheme 9).

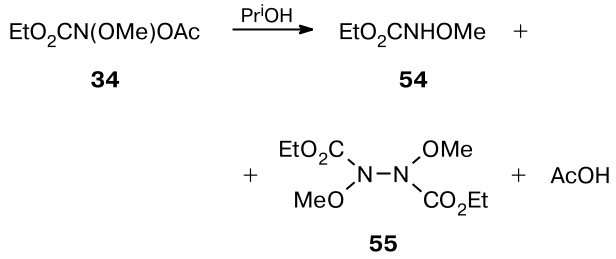
Storage of compounds **31** and **34** in *tert*-butyl alcohol did not afford *N*,*N*-dialkoxycarbamates. Storage of com-

Scheme 9



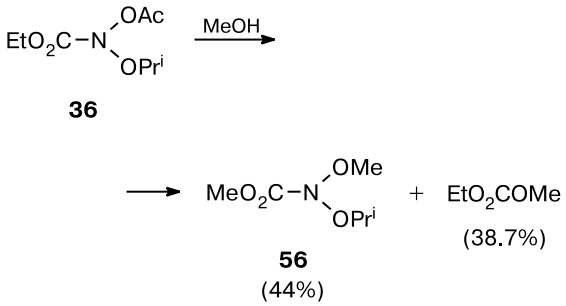
pound **34** in propan-2-ol gave rise to urethane **54** and hydrazine **55** (Scheme 10).

Scheme 10



Methanolysis of ethyl *N*-acetoxy-*N*-isopropoxycarbamate (**36**) produced ethyl *N*-isopropoxy-*N*-methoxycarbamate (**56**) and ethyl methyl carbonate in similar yields (Scheme 11).

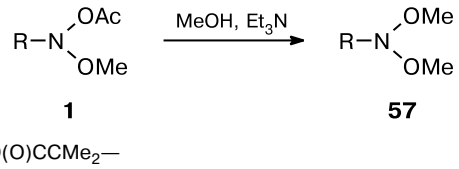
Scheme 11



Methanolysis of *N*-acetoxy-*N*-methoxyamine **1** gave rise to *N*,*N*-dimethoxyamine **57** (Scheme 12).

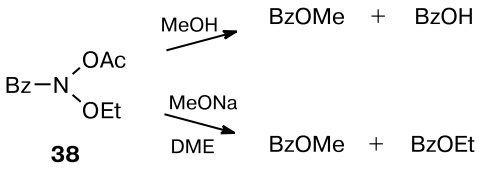
Unlike alcoholysis of *N*-acyloxy-*N*-alkoxy derivatives of ureas, carbamates, and amines, methanolysis of *N*-acetoxy-*N*-ethoxybenzamide **38** did not afford nucleophilic substitution products at the nitrogen atom at all and only methyl benzoate and benzoic acid were isolated. An attempt to replace the acetoxy group by the methoxy group

Scheme 12



in an aprotic medium also failed. Thus treatment of compound **38** with MeONa in DME gave rise to a mixture of methyl and ethyl benzoates (Scheme 13).

Scheme 13



Methyl benzoate was generated, apparently, as a result of the attack of MeO^- at the carbonyl fragment of the benzoyl group. Ethyl benzoate was produced due to migration of the benzoyl group from the nitrogen atom to the adjacent oxygen atom through the so-called Heteroatomic Rearrangement on Nitrogen (HERON) typical of *N*-acyloxy-*N*-alkoxybenzamides.[12]

Thus, a convenient procedure for the preparation of various *N*-acyloxy-*N*-alkoxy compounds involves the reactions of *N*-alkoxy-*N*-chloro compounds containing the anion-mobile chlorine atom with sodium carboxylates in MeCN. Alcoholysis of *N*-acyloxy-*N*-alkoxy compounds can involve the nucleophilic substitution at the nitrogen atom as well as redox processes and elimination depending on the nature of the third substituent at the nitrogen atom and the alcohol.

Experimental

The ^{1}H NMR spectra were recorded on a Varian VXP-300 spectrometer (300 MHz, Me_4Si as the internal standard) and a Tesla-567A spectrometer (100 MHz, $(Me_3Si)_2O$ as the internal standard); the chemical shifts are given in the δ scale; the spin-spin coupling constants are given in Hz. The IR spectra were measured on a UR-20 spectrometer in a thin layer. The mass spectra were obtained on a Kratos MS 890 instrument using chemical ionization (CI, isobutane as the reagent gas) and electron impact (EI, 70 eV). The GLC analysis was carried out on a Tsvet-5 chromatograph (flame ionization detector, 2400×3-mm glass column, 5% SE-30 on Chromaton N-AW). The solvents were purified according to standard procedures: MeCN was distilled from P_2O_5, Et_2O and PhH were distilled from Na, and MeOH and EtOH were distilled from Ca. Sodium carboxylates were dried *in vacuo* (1 Torr) at 100 °C.

Methyl 2-(*N*-acetoxy-*N*-methoxyamino)-2-methylpropionate (1) was prepared according to a known procedure.[5]

***N´*-Methoxy-*N,N*-dimethylurea (2)** and ***N*-chloro-*N*-methoxy-*N´,N´*-dimethylyurea (9)** were prepared according to procedures described earlier.[6]

***N,N*-Dimethyl-*N´*-*n*-propoxyurea (3)** was prepared from dimethylcarbamoyl chloride and propoxyamine analogously to compound **2** [6] in 67% yield as a colorless liquid, b.p. 117—118 °C (2 Torr), n_D^{20} 1.4650. ^{1}H NMR (300 MHz, $CDCl_3$): 0.95 (t, 3 H, $CH_2CH_2\underline{Me}$, J = 7.2 Hz); 1.67 (sext, 2 H, $CH_2C\underline{H}_2Me$, J = 7.2 Hz); 2.91 (s, 6 H, NMe_2); 3.81 (t, 2 H, $NOCH_2$, J = 7.2 Hz); 7.41 (s, 1 H, NHO). Found (%): C, 49.16; H, 9.72; N, 19.08. $C_6H_{14}N_2O_2$. Calculated (%): C, 49.30; H, 9.65; N, 19.16.

***N*-Methyl-*N´*-*n*-propoxyurea (4).** A solution of MeNCO (1.50 g, 26.3 mmol) in Et_2O (6 mL) was added dropwise to a solution of propoxyamine (1.98 g, 26.3 mmol) in Et_2O (10 mL) and the reaction mixture was kept at 20 °C for 6 days. The precipitate that formed was filtered off and the solution was concentrated *in vacuo* (10 Torr). Compound **4** was obtained in a yield of 3.15 g (90.5%) as a colorless liquid, n_D^{20} 1.4550. ^{1}H NMR (300 MHz, $CDCl_3$): 0.95 (t, 3 H, $CH_2CH_2\underline{Me}$, J = 7 Hz); 1.67 (sext, 2 H, $CH_2C\underline{H}_2Me$, J = 7 Hz); 2.86 (br.s, 3 H, NMe); 3.77 (t, 2 H, $NOCH_2$, J = 7 Hz); 5.73 (s, 1 H, NH); 7.61 (s, 1 H, NHO). Found (%): C, 45.67; H, 8.95; N, 21.46. $C_5H_{12}N_2O_2$. Calculated (%): C, 45.44; H, 9.15; N, 21.20.

***N*-Ethoxy-*N´*-(1-naphthyl)methylurea (5).** A solution of ethoxyamine (1.09 g, 17.8 mmol) in PhH (3 mL) was added to a solution of 1-naphthylmethyl isocyanate (2.11 g, 11.5 mmol) in PhH (11 mL) and the reaction mixture was kept at 20 °C for 2 days. The precipitate that formed was filtered off and washed with PhH (5 mL). Compound **5** was prepared in a yield of 2.09 g (74%) as colorless crystals, m.p. 145—146 °C. ^{1}H NMR (300 MHz, DMSO-d_6): 1.16 (t, 3 H, $OCH_2\underline{Me}$, J = 7 Hz); 3.75 (q, 2 H, $OC\underline{H}_2Me$, J = 7 Hz); 4.73 (d, 2 H, $C\underline{H}_2NH$, J = 6.3 Hz); 7.37—7.57 (m, 5 H, C(3)H, C(5)H, C(6)H, C(7)H, and NH); 7.83 (d, 1 H, C(4)H, J = 8.1 Hz); 7.93—7.96 (m, 1 H, C(2)H); 8.16—8.18 (m, 1 H, C(8)H); 9.14 (s, 1 H, NHO). Found (%): C, 68.73; H, 6.51; N, 11.38. $C_{14}H_{16}N_2O_2$. Calculated (%): C, 68.83; H, 6.60; N, 11.47.

***N*-*n*-Dodecyloxyurea (8).** Sodium cyanate (0.97 g, 18.9 mmol) was added portionwise with stirring to a solution of *n*-dodecyloxyamine (0.75 g, 3.7 mmol) in AcOH (8 mL). The reaction mixture was stirred for 2 h and kept for 10 h. Then AcOH was removed *in vacuo* (1 Torr), the residue was extracted with CH_2Cl_2 (50 mL), and CH_2Cl_2 (40 mL) was distilled off from the extract. The precipitate that formed was filtered off and washed with hexane (10 mL). Urea **8** was prepared in a yield of 0.61 g (67%) as colorless crystals, m.p. 124—125 °C. ^{1}H NMR (300 MHz, $CDCl_3$): 0.88 (t, 3 H, Me, J = 7.2 Hz); 1.23—1.40 (m, 18 H, $OCH_2CH_2(C\underline{H}_2)_9Me$); 1.64 (quint, 2 H, $OCH_2C\underline{H}_2$, J = 7.2 Hz); 3.84 (t, 2 H, OCH_2, J = 7.2 Hz); 5.56 (s, 2 H, NH_2); 7.66 (s, 1 H, NHO). Found (%): N, 11.51. $C_{13}H_{28}N_2O_2$. Calculated (%): N, 11.46. From the CH_2Cl_2 filtrate, urea **8** was additionally isolated in a yield of 0.28 g (30.7%) by precipitation with hexane.

***N*-Ethoxyurea (6)** was synthesized analogously to compound **8** from $EtONH_2$, NaOCN, and AcOH in a yield of 52% as colorless crystals, m.p. 85—86 °C. ^{1}H NMR (300 MHz, $CDCl_3$): 1.27 (t, 3 H, $OCH_2\underline{Me}$, J = 7 Hz); 3.93 (q, 2 H, $OC\underline{H}_2Me$, J = 7 Hz); 5.64 (s, 2 H, NH_2); 7.88 (s, 1 H, NHO). Found (%): N, 26.95. $C_3H_8N_2O_2$. Calculated (%): N, 26.91.

***N*-*n*-Butoxyurea (7)** was prepared analogously to compound **8** from Bu^nONH_2, NaOCN, and AcOH in a yield of 82% as colorless crystals, m.p. 109—111 °C ($CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): 0.94 (t, 3 H, $CH_2\underline{Me}$, J = 6.5 Hz); 1.39 (sext, 2 H, $CH_2\underline{CH}_2Me$, J = 6.5 Hz); 1.65 (quint, 2 H, $OCH_2C\underline{H}_2CH_2$, J = 6.5 Hz); 3.83 (t, 2 H, $OC\underline{H}_2CH_2$, J = 6.5 Hz); 5.72 (s, 2 H, NH_2); 8.00 (s, 1 H, NHO). Found (%): C, 45.19; H, 8.98; N, 21.06. $C_5H_{12}N_2O_2$. Calculated (%): C, 45.44; H, 9.15; N, 21.20.

Synthesis of *N*-alkoxy-*N*-chloroureas 10—15 (general procedure). A solution of Bu^tOCl (0.28 g, 2.6 mmol) in CH_2Cl_2 (3 mL) was added to a solution of *N*-alkoxyurea **3—8** (1.7 mmol) in CH_2Cl_2 (5 mL) at −30 °C. The reaction mixture was kept at 20 °C for 0.5 h, the solvent was removed *in vacuo*, and the residue was kept at 1 Torr to prepare compounds **10—15**.

***N*-Chloro-*N´,N´*-dimethyl-*N*-*n*-propoxyurea (10)**, yield 97.8%, yellow liquid, n_D^{25} 1.4680, unstable at 20 °C. ^{1}H NMR (100 MHz, CCl_4): 0.93 (t, 3 H, $OCH_2CH_2\underline{Me}$, J = 6.7 Hz); 1.69 (sext, 2 H, $OCH_2C\underline{H}_2Me$, J = 6.7 Hz); 3.00 (s, 6 H, NMe_2); 3.97 (t, 2 H, $OC\underline{H}_2CH_2Me$, J = 6.7 Hz). Found (%): Cl, 19.51. $C_6H_{13}ClN_2O_2$. Calculated (%): Cl, 19.63.

***N*-Chloro-*N´*-methyl-*N*-*n*-propoxyurea (11)**, yield 98.5%, yellow liquid, n_D^{20} 1.4720. ^{1}H NMR (100 MHz, CCl_4): 0.97 (t, 3 H, $CH_2CH_2\underline{Me}$, J = 7 Hz); 1.71 (sext, 2 H, $CH_2C\underline{H}_2Me$, J = 7 Hz); 2.85 (d, 3 H, MeN, J = 4.7 Hz); 3.93 (t, 2 H, $NOCH_2$, J = 7 Hz); 6.60 (br.s, 1 H, NH). Found (%): Cl, 21.08. $C_5H_{11}ClN_2O_2$. Calculated (%): Cl, 21.28.

***N*-Chloro-*N*-ethoxy-*N´*-(1-naphthyl)methylurea (12)**, yield 100%, yellowish viscous liquid. ^{1}H NMR (300 MHz, $CDCl_3$): 1.21 (t, 3 H, $OCH_2\underline{Me}$, J = 7 Hz); 4.04 (q, 2 H, $OC\underline{H}_2Me$, J = 7 Hz); 4.95 (d, 2 H, $C\underline{H}_2NH$, J = 5.7 Hz); 6.42 (br.s, 1 H, NH); 7.40—7.61 (m, 4 H, C(3)H, C(5)H, C(6)H, C(7)H); 7.83—7.93 (m, 2 H, C(2)H, C(4)H); 8.00 (d, 1 H, C(8)H, J = 8.1 Hz). Found (%): Cl, 12.43. $C_{14}H_{15}ClN_2O_2$. Calculated (%): Cl, 12.72.

***N*-Chloro-*N*-ethoxyurea (13)**, yield 98%, viscous colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$): 1.24 (t, 3 H, $OCH_2\underline{Me}$, J = 6.9 Hz); 4.11 (q, 2 H, $OC\underline{H}_2Me$, J = 6.9 Hz); 5.31 (s, 2 H, NH_2). Found (%): Cl, 25.20. $C_3H_7ClN_2O_2$. Calculated (%): Cl, 25.59.

***N*-*n*-Butoxy-*N*-chlorourea (14)**, yield 98%, colorless crystals, m.p. 24—26 °C (with decomp.). ^{1}H NMR (100 MHz, CCl_4): 0.96 (t, 3 H, $CH_2\underline{Me}$, J = 6.3 Hz); 1.1—1.8 (m, 4 H, $C\underline{H}_2C\underline{H}_2Me$); 3.96 (t, 2 H, $OC\underline{H}_2$, J = 6.3 Hz); 6.2 (s, 1 H, NH); 7.20 (s, 1 H, NH). Found (%): C, 35.82; H, 6.44; N, 16.81. $C_5H_{11}ClN_2O_2$. Calculated (%): C, 36.05; H, 6.65; N, 16.81.

***N*-Chloro-*N*-*n*-dodecyloxyurea (15)**, yield 100%, colorless solid, m.p. 69—72 °C. ^{1}H NMR (300 MHz, $CDCl_3$): 0.88 (t, 3 H, Me, J = 6.8 Hz); 1.14—1.47 (m, 18 H, $NOCH_2CH_2(C\underline{H}_2)_9Me$); 1.69 (quint, 2 H, $NOCH_2C\underline{H}_2$, J = 6.8 Hz); 4.04 (t, 2 H, $NOCH_2$, J = 6.8 Hz); 6.15 (br.s, 1 H, NH); 6.31 (br.s, 1 H, NH). Found (%): Cl, 12.59. $C_{13}H_{27}ClN_2O_2$. Calculated (%): Cl, 12.72.

Synthesis of *N*-acyloxy-*N*-alkoxyureas 16—26 (general procedure). A mixture of a solution of *N*-alkoxy-*N*-chlorourea **9—15** (8 mmol) and R^2COONa (20 mmol) in MeCN (20 mL) was stirred at 20 °C for 25 h (in the synthesis of compound **26**, for 58 h). The precipitate that formed was filtered off and washed with Et_2O. The filtrate was concentrated *in vacuo* (20 Torr) and the residue was extracted with benzene (15 mL). The benzene extract was concentrated *in vacuo* and the residue was kept at 20 °C and 2 Torr for 0.5 h.

***N*-Acetoxy-*N*-methoxy-*N′,N′*-dimethylurea (16)**, yield 87.0%, yellowish liquid, b.p. 64—65 °C (1 Torr) (with decomp.), n_D^{25} 1.4540. ^{1}H NMR (300 MHz, $CDCl_3$): 2.16 (s, 3 H, O_2CMe); 3.03 (s, 3 H, NMe_2); 3.85 (s, 3 H, NOMe). MS (CI), *m/z* (I_{rel} (%)): 175 $[M - H]^+$ (5.4); 162 (3.3); 161 (4.2); 160 (3.6); 149 (10.7); 146 (24.6); 133 (4.0); 132 (8.2); 130 (13.5); 129 (12.3); 119 (10.6); 118 (13.1); 117 (51.4); 104 (9.9); 89 (18.3); 88 (18.7); 85 (30.1); 72 (100); 61 (25.8); 45 (94.5). Found (%): C, 40.67; H, 6.83; N, 15.67. $C_6H_{12}N_2O_4$. Calculated (%): C, 40.91; H, 6.87; N, 15.90.

***N*-Methoxy-*N′,N′*-dimethyl-*N*-propionyloxyurea (17)**, yield 89.9%, yellowish liquid, b.p. 62 °C (2 Torr) (with decomp.), n_D^{20} 1.4529. ^{1}H NMR (300 MHz, $CDCl_3$): 1.21 (t, 3 H, $CH_2\underline{Me}$, *J* = 7.5 Hz); 2.45 (q, 2 H, $C\underline{H}_2Me$, *J* = 7.5 Hz); 3.04 (s, 6 H, NMe_2); 3.86 (s, 3 H, NOMe). MS (CI), *m/z* (I_{rel} (%)): 190 M^+ (12.0); 189 (6.6); 175 (5.3), 174 (3.5); 161 (5.6); 159 (3.7); 158 (5.5); 146 (21.5); 133 (5.7); 130 (11.0); 119 (14.5); 118 (13.6); 117 (61.0); 104 (10.4); 89 (14.0); 85 (23.7); 75 (19.0); 72 (100); 56 (17.3); 45 (87.9); Found (%): C, 44.38; H, 7.50; N, 14.44. $C_7H_{14}N_2O_4$. Calculated (%): C, 44.20; H, 7.42; N, 14.73.

***N*-Isobutyroyloxy-*N*-methoxy-*N′,N′*-dimethylyurea (18)** was prepared after additional purification by stirring a pentane solution with aqueous $NaHCO_3$, the yield was 78.3%, yellowish liquid, n_D^{20} 1.4462. ^{1}H NMR (300 MHz, $CDCl_3$): 1.24 (d, 6 H, $CH\underline{Me}_2$, *J* = 6.9 Hz); 2.69 (sept, 1 H, $C\underline{H}Me_2$, *J* = 6.9 Hz); 3.03 (s, 6 H, NMe_2); 3.85 (s, 3 H, NOMe). MS (EI, 70 eV), *m/z* (I_{rel} (%)): 204 $[M]^+$ (1.1); 189 (2.9); 173 (1.5); 73 (36.4); 72 (100); 71 (33.8); 44 (73.5); 43 (91.9). Found (%): C, 47.32; H, 7.98; N, 13.60. $C_8H_{16}N_2O_4$. Calculated (%): C, 47.05; H, 7.90; N, 13.72.

***N*-Benzoyloxy-*N*-methoxy-*N′,N′*-dimethylurea (19)**, yield 77.1%, colorless viscous liquid, n_D^{20} 1.5250. ^{1}H NMR (300 MHz, $CDCl_3$): 3.07 (br.s, 6 H, NMe_2); 3.96 (s, 3 H, NOMe); 7.47 (t, 2 H, C(3)H, C(5)H, *J* = 7.5 Hz); 7.61 (t, 1 H, C(4)H, *J* = 7.5 Hz); 8.09 (d, 2 H, C(2)H, C(6)H, *J* = 7.5 Hz). MS (EI, 70 eV), *m/z* (I_{rel} (%)): 238 $[M]^+$ (0.2); 208 (1.1); 192 (1.8); 149 (9.2); 148 (30.9); 106 (36.7); 105 (100); 77 (94.0); 72 (97.0). Found (%): C, 55.71; H, 6.01; N, 11.52. $C_{11}H_{14}N_2O_4$. Calculated (%): C, 55.46; H, 5.92; N, 11.76.

***N*-Acetoxy-*N′,N′*-dimethyl-*N*-*n*-propoxyurea (20)**, yield 90.9%, yellowish liquid, n_D^{20} 1.4561. ^{1}H NMR (300 MHz, $CDCl_3$): 0.95 (t, 3 H, $OCH_2CH_2\underline{Me}$, *J* = 7.2 Hz); 1.68 (sext, 2 H, $OCH_2C\underline{H}_2Me$, *J* = 7.2 Hz); 2.15 (s, 3 H, O_2CMe); 3.04 (s, 6 H, NMe_2); 4.04 (t, 2 H, $OC\underline{H}_2CH_2Me$, *J* = 7.2 Hz). IR, ν/cm^{-1}: 1784 (C=O), 1732 (C=O). MS (CI), *m/z* (I_{rel} (%)): 206 $[M + 2H]^+$ (17.3); 205 $[M + H]^+$ (100); 204 M^+ (19.4); 203 (11.9); 174 (15.3); 160 (16.0); 148 (10.8); 132 (25.8). Found (%): C, 47.12; H, 8.02; N, 13.65. $C_8H_{16}N_2O_4$. Calculated (%): C, 47.05; H, 7.90; N, 13.72.

***N*-Acetoxy-*N′*-methyl-*N*-*n*-propoxyurea (21)**, yield 92.0%, colorless liquid, n_D^{20} 1.4549. ^{1}H NMR (300 MHz, $CDCl_3$): 0.96 (t, 3 H, $OCH_2CH_2\underline{Me}$, *J* = 7.5 Hz); 1.71 (sext, 2 H, $OCH_2C\underline{H}_2Me$, *J* = 7.5 Hz); 2.18 (s, 3 H, O_2CMe); 2.90 (d, 3 H, $NH\underline{Me}$, *J* = 4.8 Hz); 4.04 (t, 2 H, $OC\underline{H}_2CH_2Me$, *J* = 7.5 Hz); 6.16 (s, 1 H, NH). IR, ν/cm^{-1}: 1795 (C=O), 1730 (C=O). MS (CI), *m/z* (I_{rel} (%)): 192 $[M + 2H]^+$ (8.1); 191 $[M + H]^+$ (82.4); 189 (0.6); 175 (3.0); 147 (11.2); 133 (83.8); 131 (100). Found (%): C, 44.34; H, 7.23; N, 14.61. $C_7H_{14}N_2O_4$. Calculated (%): C, 44.20; H, 7.42; N, 14.73.

***N*-Benzoyloxy-*N′*-methyl-*N*-*n*-propoxyurea (22)**, yield 86.2%, colorless viscous liquid, n_D^{20} 1.5171. ^{1}H NMR (300 MHz, $CDCl_3$): 0.95 (t, 3 H, $OCH_2CH_2\underline{Me}$, *J* = 7.2 Hz); 1.74 (sext, 2 H, $OCH_2C\underline{H}_2Me$, *J* = 7.2 Hz); 2.94 (d, 3 H, $NH\underline{Me}$, *J* = 5.1 Hz); 4.12 (t, 2 H, $OC\underline{H}_2CH_2Me$, *J* = 7.2 Hz); 6.23 (br.s, 1 H, NH); 7.47 (t, 2 H, C(3)H, C(5)H, *J* = 7.2 Hz); 7.61 (t, 1 H, C(4)H, *J* = 7.2 Hz); 8.07 (d, 2 H, C(2)H, C(6)H, *J* = 7.2 Hz). MS (CI), *m/z* (I_{rel} (%)): 253 $[M + H]^+$ (100); 252 M^+ (20.8); 106 (5.5); 105 (37.8); 90 (6.2); 78 (8.5). Found (%): C, 57.40; H, 6.55; N, 10.98. $C_{12}H_{16}N_2O_4$. Calculated (%): C, 57.13; H, 6.39; N, 11.10.

***N*-Acetoxy-*N*-ethoxy-*N′*-(1-naphthyl)methylurea (23)**, yield 98.1%, viscous yellowish liquid. ^{1}H NMR (300 MHz, $CDCl_3$): 1.20 (t, 3 H, $OCH_2\underline{Me}$, *J* = 7 Hz); 2.19 (s, 3 H, O_2CMe); 4.07 (q, 2 H, $OC\underline{H}_2Me$, *J* = 7 Hz); 4.91 (d, 2 H, $C\underline{H}_2NH$, *J* = 6.1 Hz); 6.41 (br.s, 1 H, NH); 7.25—7.70 (m, 4 H, C(3)H, C(5)H, C(6)H, C(7)H); 7.83—7.93 (m, 2 H, C(2)H, C(4)H); 7.99 (d, 1 H, C(8)H, *J* = 8 Hz). Found (%): C, 63.79; H, 6.21; N, 9.14. $C_{16}H_{18}N_2O_4$. Calculated (%): C, 63.57; H, 6.00; N, 9.27.

***N*-Acetoxy-*N*-ethoxyurea (24)**, yield 80.8%, colorless crystals, m.p. 93—95 °C. ^{1}H NMR (300 MHz, $CDCl_3$) 1.32 (t, 3 H, $OCH_2\underline{Me}$, *J* = 7 Hz); 2.18 (s, 3 H, O_2CMe); 4.14 (q, 2 H, $OC\underline{H}_2Me$, *J* = 7 Hz); 6.06 (br.s, 2 H, NH_2). Found (%): C, 37.30; H, 6.31; N, 17.15. $C_5H_{10}N_2O_4$. Calculated (%): C, 37.04; H, 6.22; N, 17.28.

***N*-Acetoxy-*N*-*n*-butoxyurea (25)**, yield 84.4%, colorless crystals, m.p. 53—55 °C (hexane). ^{1}H NMR (300 MHz, $CDCl_3$): 0.95 (t, 3 H, $CH_2\underline{Me}$, *J* = 7.5 Hz); 1.38 (sext, 2 H, $CH_2C\underline{H}_2Me$, *J* = 7.5 Hz); 1.67 (quint, 2 H, $OCH_2C\underline{H}_2CH_2Me$, *J* = 7.5 Hz); 2.19 (s, 3 H, O_2CMe); 4.09 (t, 2 H, $OC\underline{H}_2CH_2$, *J* = 7.5 Hz); 6.11 (br.s, 2 H, NH_2). IR, ν/cm^{-1}: 1790 (C=O); 1730 (C=O). MS (CI), *m/z* (I_{rel} (%)): 191 $[M + H]^+$ (11.2); 190 $[M]^+$ (100); 159 (7.7); 134 (21.5); 131 (5.0); 117 (15.2); 103 (51.4). Found (%): C, 44.93; H, 7.72; N, 14.60. $C_7H_{14}N_2O_4$. Calculated (%): C, 44.20; H, 7.42; N, 14.73.

***N*-Acetoxy-*N*-*n*-dodecyloxyurea (26)**, yield 84.5%, colorless crystals, m.p. 63—64 °C (hexane). ^{1}H NMR (300 MHz, $CDCl_3$): 0.88 (t, 3 H, Me, *J* = 6.9 Hz); 1.10—1.20 (m, 18 H, $NOCH_2CH_2(C\underline{H}_2)_9Me$); 1.68 (quint, 2 H, $NOCH_2C\underline{H}_2$, *J* = 6.9 Hz); 2.18 (s, 3 H, O_2CMe); 4.08 (t, 2 H, $NOC\underline{H}_2CH_2$, *J* = 6.9 Hz); 5.94 (s, 2 H, NH_2). Found (%): C, 59.65; H, 10.12; N, 9.07. $C_{15}H_{30}N_2O_4$. Calculated (%): C, 59.58; H, 10.00; N, 9.26.

Methyl *N*-chloro-*N*-methoxycarbamate (27) was synthesized according to a procedure described earlier.[7]

Synthesis of *N*-alkoxy-*N*-chlorocarbamates 28—30 (general procedure). A solution of Bu^tOCl (10 mmol) in CH_2Cl_2 (3 mL) was added to a solution of the corresponding *N*-alkoxycarbamate (5 mmol) in CH_2Cl_2 (6 mL) at −20 °C. The reaction mixture was kept at 20 °C for 0.5 h (in the case of **30**, for 2 h), concentrated *in vacuo* (10 Torr), and kept at 3 Torr for 10 min.

Methyl *N*-chloro-*N*-*n*-octyloxycarbamate (28), yellowish liquid, n_D^{20} 1.4520. ^{1}H NMR (100 MHz, CCl_4): 0.88 (t, 3 H, $(CH_2)_7\underline{Me}$, *J* = 7 Hz); 1.05—1.93 (m, 12 H, $OCH_2(C\underline{H}_2)_6Me$); 3.83 (s, 3 H, CO_2Me); 3.89 (t, 2 H, $NOCH_2$, *J* = 7 Hz). Found (%): Cl, 14.72. $C_{10}H_{20}ClNO_3$. Calculated (%): Cl, 14.91.

Ethyl *N*-chloro-*N*-methoxycarbamate (29), yellowish liquid, b.p. 45—46 °C (3 Torr), n_D^{24}1.4341. ^{1}H NMR (300 MHz, $CDCl_3$): 1.37 (t, 3 H, $CO_2CH_2\underline{Me}$, *J* = 7 Hz); 3.81 (s, 3 H, NOMe); 4.35 (q, 2 H, $CO_2C\underline{H}_2Me$, *J* = 7 Hz). Found (%): Cl, 22.80. $C_4H_8ClNO_3$. Calculated (%): Cl, 23.09.

Ethyl *N*-chloro-*N*-isopropoxycarbamate (30), yellowish liquid. ^{1}H NMR (300 Hz, $CDCl_3$): 1.28 (d, 6 H, $NOCH\underline{Me}_2$,

J = 6.3 Hz); 1.36 (t, 3 H, $CO_2CH_2\underline{Me}$, J = 7 Hz); 4.31 (sept, 1 H, $NOC\underline{H}Me_2$, J = 6.3 Hz); 4.33 (q, 2 H, $CO_2C\underline{H}_2Me$, J = 7 Hz). Found (%): Cl, 19.46. $C_6H_{12}ClNO_3$. Calculated (%): Cl, 19.52.

Synthesis of *N*-acyloxy-*N*-alkoxycarbamates 31—36 (general procedure). A solution of *N*-alkoxy-*N*-chlorocarbamate **28—30** (8 mmol) in MeCN (20 mL) was stirred with R^3COONa (26 mmol) at 20 °C for 25 h. The precipitate that formed was filtered off and washed with Et_2O. The filtrate was concentrated *in vacuo* (20 Torr). The residue was extracted with Et_2O (20 mL), the extract was concentrated *in vacuo*, and the residue was kept at 3 Torr and 20 °C for 0.5 h.

Methyl *N*-acetoxy-*N*-methoxycarbamate (31), yield 85.5%, colorless liquid, b.p. 69—70 °C (3 Torr), n_D^{22} 1.4213. ^{1}H NMR (300 MHz, C_6D_6): 1.59 (s, 3 H, CO_2Me); 3.30 (s, NOMe); 3.66 (s, 3 H, CO_2Me). ^{1}H NMR (300 MHz, $CDCl_3$): 2.19 (s, 3 H, O_2CMe); 3.89 (s, 6 H, CO_2Me and NOMe). IR, ν/cm^{-1}: 1805 (C=O); 1780 (C=O). MS (CI), m/z (I_{rel} (%)): 164 $[M + H]^+$ (3.5); 163 $[M]^+$ (9.8); 162 (8.5); 133 (9.9); 106 (7.9); 105 (100); 104 (16.0); 91 (11.3); 89 (13.2); 75 (7.1); 61 (29.6); 58 (48.5); 44 (89.5). Found (%): C, 36.95; H, 5.44; N, 8.53. $C_5H_9NO_5$. Calculated (%) : C, 36.81; H, 5.56; N, 8.59.

Methyl *N*-methoxy-*N*-propionyloxycarbamate (32), yield 74.2%, colorless liquid, b.p. 59—60 °C (1 Torr), n_D^{22} 1.4222. ^{1}H NMR (300 MHz, $CDCl_3$): 1.16 (t, 3 H, $CH_2\underline{Me}$, J = 7.5 Hz); 2.40 (q, 2 H, $C\underline{H}_2Me$, J = 7.5 Hz); 3.82 (s, 6 H, CO_2Me and NOMe). MS (CI), m/z (I_{rel} (%)): 178 $[M + H]^+$ (5.9); 177 $[M]^+$ (0.5); 176 (0.8); 106 (57.0); 105 (11.0); 104 (100). Found (%): C, 40.94; H, 6.30; N, 7.72. $C_6H_{11}NO_5$. Calculated (%): C, 40.68; H, 6.26; N, 7.91.

Methyl *N*-acetoxy-*N*-*n*-octyloxycarbamate (33), yield 93.4%, colorless liquid, n_D^{20} 1.4385. ^{1}H NMR (300 MHz, $CDCl_3$): 0.79 (t, 3 H, $(CH_2)_7\underline{Me}$, J = 7 Hz); 1.13—1.33 (m, 10 H, $OCH_2CH_2(C\underline{H}_2)_5Me$); 1.58 (quint, 2 H, $OCH_2C\underline{H}_2$, J = 7 Hz); 2.09 and 3.79 (both s, 3 H each, CO_2Me); 3.97 (t, 2 H, $NOCH_2$, J = 7 Hz). IR, ν/cm^{-1}: 1805 (C=O); 1780 (C=O). Found (%): C, 55.08; H, 8.95; N, 5.20. $C_{12}H_{23}NO_5$. Calculated (%): C, 55.16; H, 8.87; N, 5.36.

Ethyl *N*-acetoxy-*N*-methoxycarbamate (34), yield 92.3%, yellowish liquid, n_D^{22} 1.4232. ^{1}H NMR (300 MHz, $CDCl_3$): 1.35 (t, 3 H, $CO_2CH_2\underline{Me}$, J = 7 Hz); 2.19 (s, 3 H, O_2CMe); 3.89 (s, 3 H, NOMe); 4.32 (q, 2 H, $CO_2C\underline{H}_2Me$, J = 7 Hz). IR, ν/cm^{-1}: 1780 (C=O); 1755 (C=O). MS (EI, 70 eV), m/z (I_{rel} (%)): 177 $[M]^+$ (1.7); 146 (7.5); 119 (12.7); 118 (13.6); 90 (15.7); 75 (23.1); 74 (79.4); 73 (34.7); 72 (11.8); 59 (100); 58 (32.3); 46 (59.5); 45 (67.7); 43 (74.7). Found (%): C, 40.41; H, 6.31; N, 7.78. $C_6H_{11}NO_5$. Calculated (%): C, 40.68; H, 6.26; N, 7.91.

Ethyl *N*-benzoyloxy-*N*-methoxycarbamate (35), yield 60.5%, yellowish liquid, n_D^{22} 1.4879, can be stored at −5 °C for no more than one day. ^{1}H NMR (300 MHz, $CDCl_3$): 1.35 (t, 3 H, $CO_2CH_2\underline{Me}$, J = 7 Hz); 3.97 (s, 3 H, NOMe); 4.38 (q, 2 H, $CO_2C\underline{H}_2Me$, J = 7 Hz); 7.49 (t, 2 H, C(3)H, C(5)H, J = 6.9 Hz); 7.64 (t, 1 H, C(4)H, J = 6.9 Hz); 8.11 (d, 2 H, C(2)H, C(6)H, J = 6.9 Hz). Found (%): C, 55.04; H, 5.70; N, 5.47. $C_{11}H_{13}NO_5$. Calculated (%): C, 55.23; H, 5.48; N, 5.85.

Ethyl *N*-acetoxy-*N*-isopropoxycarbamate (36), yield 98.0%, yellowish liquid, n_D^{22} 1.4211. ^{1}H NMR (300 MHz, $CDCl_3$): 1.28 (d, 6 H, $OCH\underline{Me}_2$, J = 6.3 Hz); 1.33 (t, 3 H, $CO_2CH_2\underline{Me}$, J = 7.2 Hz); 2.17 (s, 3 H, O_2CMe); 4.30 (q, 2 H, $CO_2C\underline{H}_2Me$, J = 7.2 Hz); 4.33 (sept, 1 H, $NOC\underline{H}Me_2$, J = 6.3 Hz). Found (%): C, 46.61; H, 7.35; N 6.59. $C_8H_{15}NO_5$. Calculated (%): C, 46.82; H, 7.37; N, 6.83.

***N*-Chloro-*N*-ethoxybenzamide (37)** was synthesized as described earlier.[9]

***N*-Acetoxy-*N*-ethoxybenzamide (38).** A solution of compound **37** (0.505 g, 2.5 mmol) in MeCN (10 mL) was added with stirring to a solution of AcONa (0.52 g, 6.3 mmol) in MeCN (10 mL). The reaction mixture was stirred at 20 °C for 25 h. The precipitate that formed was filtered off and the filtrate was concentrated *in vacuo* (17 Torr). The residue was extracted with benzene (18 mL), the extract was concentrated *in vacuo* (17 Torr), and the residue was kept at 3 Torr. Compound **38** was prepared in a yield of 0.51 g (90.3%) as a yellowish liquid, n_D^{24} 1.5085. ^{1}H NMR (300 MHz, $CDCl_3$): 1.29 (t, 3 H, $OCH_2\underline{Me}$, J = 7 Hz); 2.11 (s, 3 H, O_2CMe); 4.24 (q, 2 H, $O\underline{CH}_2Me$, J = 7 Hz); 7.43 (t, 2 H, C(3)H, C(5)H, J = 6.9 Hz); 7.55 (t, 1 H, C(4)H, J = 6.9 Hz); 7.78 (d, 2 H, C(2)H, C(6)H, J = 6.9 Hz). This spectrum is identical with the ^{1}H NMR spectrum of the authentic sample.[8]

***N*-Chloro-*N*-ethoxytoluene-*p*-sulfonamide (39)** was prepared by chlorination of *N*-ethoxytoluene-*p*-sulfonamide[14] with *tert*-butyl hypochlorite in CH_2Cl_2 according to a known procedure,[6] yellowish liquid, n_D^{30} 1.5332. Found (%): C, 43.01; H, 4.95; Cl, 14.29. $C_9H_{12}ClNO_3S$. Calculated (%): C, 43.29; H, 4.84; Cl, 14.20.

Reaction of compound 39 with AcONa. A mixture of compound **39** (0.62 g, 2.5 mmol) and AcONa (1.42 g, 17.3 mmol) was stirred in MeCN (25 mL) at 20 °C for 20 h. The precipitate that formed was filtered off and the filtrate was concentrated *in vacuo* (20 Torr). The residue was extracted with benzene (13 mL). The extract was concentrated *in vacuo* and the residue was kept at 2 Torr. Unconsumed compound **39**, which was identified by ^{1}H NMR spectroscopy, was obtained in a yield of 0.55 g (88.7%).

Alcoholysis of *N*-acyloxy-*N*-alkoxyureas 16—18 and 20—26 (general procedure). *N*-Acyloxy-*N*-alkoxyurea (3 mmol) was dissolved in an alcohol (10—15 mL) and kept at 20—30 °C (see Table 1). Then the alcohol was removed *in vacuo*, the residue was extracted with ether (30 mL), and the extract was stirred with a solution of $NaHCO_3$ (1.3 g) in water (1 mL). The organic phase was separated and concentrated *in vacuo*. The residue was kept at 1 Torr and 25—30 °C for 20 min. The yields of products **40—47** are given in Table 1.

***N*-Methoxy-*N′*,*N′*-dimethyl-*N*-*n*-propoxyurea (40)** colorless liquid, b.p. 95—95.5 °C (1 Torr); n_D^{25} 1.4449. ^{1}H NMR (300 MHz, $CDCl_3$): 0.96 (t, 3 H, $CH_2CH_2\underline{Me}$, J = 7.1 Hz); 1.67 (sext, 2 H, $CH_2C\underline{H}_2Me$, J = 7.1 Hz); 3.00 (s, 6 H, NMe_2); 3.73 (s, 3 H, NOMe); 3.91 (t, 2 H, $NOCH_2$, J = 7.1 Hz). MS (CI), m/z (I_{rel} (%)): 177 $[M + H]^+$ (7.7); 175 (6.4); 174 (9.9); 161 (32.8); 160 (11.0); 146 (14.0); 145 (19.0); 133 (11.2); 118 (13.9); 117 (46.5); 116 (29.3); 105 (12.9); 104 (24.3); 103 (40.2); 90 (14.3); 89 (100); 73 (20.7); 72 (23.5). Found (%): C, 47.82; H, 9.17; N, 15.63. $C_7H_{16}N_2O_3$. Calculated (%): C, 47.71; H, 9.15; N, 15.90.

***N*-Ethoxy-*N*-methoxy-*N′*,*N′*-dimethylurea (41)** was identified by comparing its ^{1}H NMR spectrum with the spectrum of the authentic sample.[6]

***N*-Methoxy-*N′*-methyl-*N*-*n*-propoxyurea (42)**, colorless liquid, b.p. 91—92 °C (1 Torr), n_D^{20} 1.4491. ^{1}H NMR (300 MHz, $CDCl_3$): 0.98 (t, 3 H, $CH_2CH_2\underline{Me}$, J = 7.5 Hz); 1.72 (sext, 2 H,

$CH_2C\underline{H}_2Me$, J = 7.5 Hz); 2.87 (d, 3 H, NMe, J = 4.8 Hz); 3.82 (s, 3 H, NOMe); 4.00 (t, 2 H, $NOC\underline{H}_2$, J = 7.5 Hz); 6.15 (br.s, 1 H, NH). Found (%): C, 44.59; H, 8.86; N, 17.11. $C_6H_{14}N_2O_3$. Calculated (%): C, 44.43; H, 8.70; N, 17.27.

***N*-Ethoxy-*N*-methoxy-*N*′-(1-naphthyl)methylurea (43)**, viscous yellowish liquid. ^{1}H NMR (300 MHz, $CDCl_3$): 1.19 (t, 3 H, $OCH_2\underline{Me}$, J = 6.9 Hz); 3.73 (s, 3 H, NOMe); 4.02 (q, 2 H, $OC\underline{H}_2Me$, J = 6.9 Hz); 4.83 (d, 2 H, $C\underline{H}_2N$ H, J = 5.1 Hz); 6.31 (br.s, 1 H, NH); 7.26—7.63 (m, 4 H, C(3)H, C(5)H, C(6)H, C(7)H); 7.71—7.86 (m, 2 H, C(2)H, C(4)H); 7.95 (d, 1 H, C(8)H, J = 8 Hz). MS (EI, 70 eV), m/z (I_{rel} (%)): 274 $[M]^+$ (3.5), 243 $[M - MeO]^+$ (19.3), 229 $[M - EtO]^+$ (3.5), 201 (23.7), 200 (63.5), 182 (15.3), 156 (38.0), 155 (11.8), 154 (23.7), 142 (11.5), 141 (56.0), 129 (100), 128 (46.8), 127 (42.7). Found (%): N, 10.03. $C_{15}H_{18}N_2O_3$. Calculated (%): N, 10.21.

***N*-Ethoxy-*N*-methoxyurea (44)**, colorless liquid, n_D^{20} 1.4493. ^{1}H NMR (300 MHz, $CDCl_3$): 1.32 (t, 3 H, $OCH_2\underline{Me}$, J = 7 Hz); 3.83 (s, 3 H, NOMe); 4.12 (q, 2 H, $OC\underline{H}_2Me$, J = 7 Hz); 5.50 and 5.93 (both s, 1 H each, NH). Found (%): C, 35.93; H, 7.80; N, 20.69. $C_4H_{10}N_2O_3$. Calculated (%): C. 35.82; H, 7.51; N, 20.88.

***N*-*n*-Butoxy-*N*-methoxyurea (45)**, yellowish liquid, n_D^{25} 1.4495. ^{1}H NMR (300 MHz, $CDCl_3$): 0.95 (t, 3H, $CH_2\underline{Me}$, J = 7.5 Hz); 1.42 (sext, 2 H, $CH_2C\underline{H}_2Me$, J = 7.5 Hz); 1.67 (quint, 2 H, $OCH_2C\underline{H}_2CH_2$, J = 7.5 Hz); 3.81 (s, 3 H, NOMe); 4.04 (t, 2 H, $OC\underline{H}_2CH_2$, J = 7.5 Hz); 6.05 and 6.38 (both s, 1 H each, NH). MS (CI), m/z (I_{rel} (%)): 163 $[M + H]^+$ (5.9), 161 (3.0), 160 (3.0), 146 (3.2), 133 (12.7), 131 (15.4), 119 (6.0), 116 (9.4), 105 (4.6), 104 (21.5), 89 (56.4), 88 (91.1), 77 (42.7), 76.6 (11.1), 75 (48.1), 73 (10.0), 70 (46.4), 61 (56.5), 60 (48.6), 59 (100), 58 (36.6), 56 (70.1), 54 (15.1), 46 (16.0), 45 (57.2), 44 (54.4). Found (%): C, 44.21; H, 8.51; N, 17.38. $C_6H_{14}N_2O_3$. Calculated (%): C, 44.43; H, 8.70; N, 17.27.

***N*-*n*-Butoxy-*N*-ethoxyurea (46)**, yellowish liquid, b.p. 56—58 °C (1 Torr) (with decomp.), n_D^{25} 1.4465. ^{1}H NMR (300 MHz, $CDCl_3$): 0.91 (t, 3 H, $O(CH_2)_3\underline{Me}$, J = 7.5 Hz); 1.27 (t, 3 H, $OCH_2\underline{Me}$, J = 6.9 Hz); 1.38 (sext, 2 H, $OCH_2CH_2C\underline{H}_2Me$, J = 7.5 Hz); 1.63 (quint, 2 H, $OCH_2C\underline{H}_2CH_2$, J = 7.5 Hz); 3.99 (t, 2 H, $OC\underline{H}_2CH_2$, J = 7.5 Hz); 4.06 (q, 2 H, $OC\underline{H}_2Me$, J = 6.9 Hz); 6.01 (br.s, 2 H, NH_2). MS (CI), m/z (I_{rel} (%)): 178 $[M + 2 H]^+$ (10.5), 177 $[M + H]^+$ (100), 163 (12.4), 134 (10.1), 133 (37.0), 131 (25.9), 105 (27.9), 103 (43.7). Found (%): C, 47.54; H, 9.22; N, 15.50. $C_7H_{16}N_2O_3$. Calculated (%): C, 47.71; H, 9.15; N, 15.90.

***N*-*n*-Dodecyloxy-*N*-methoxyurea (47)**, colorless crystals, m.p. 46—49 °C. ^{1}H NMR (300 MHz, $CDCl_3$): 0.88 (t, 3 H, $O(CH_2)_{11}\underline{Me}$, J = 7 Hz); 1.20—1.40 (m, 18 H, $OCH_2CH_2(C\underline{H}_2)_9Me$); 1.66 (quint, 2 H, $NOCH_2C\underline{H}_2$, J = 7 Hz); 3.83 (s, 3 H, NOMe); 4.04 (t, 2 H, $NOC\underline{H}_2$, J = 7 Hz); 5.32 (br.s, 1 H, NH); 5.9 (br.s, 1 H, NH). IR, ν/cm^{-1}: 1708 (C=O). MS (EI, 70 eV), m/z (I_{rel} (%)): 274 $[M]^+$ (0.1), 259 $[M - Me]^+$ (0.1), 245 $[M - Et]^+$ (0.1), 113 (8.0), 111 (10.1), 99 (15.5); 86. (11.1), 85 (67.7), 84 (20.0), 71 (83.9), 70 (41.9), 69 (66.0), 68 (24.2), 67 (27.0), 63 (28.2), 58 (31.8), 57 (100), 56 (66.9), 55 (83.0), 54 (24.1). Found (%): C, 61.54; H, 10.95; N, 10.14. $C_{14}H_{30}N_2O_3$. Calculated (%): C, 61.28; H, 11.02; N, 10.21.

***N*-Isopropoxy-*N*′-methyl-*N*-propoxyurea (48)**, colorless liquid, n_D^{20} 1.4472. ^{1}H NMR (300 MHz, $CDCl_3$): 0.97 (t, 3 H, $OCH_2CH_2\underline{Me}$, J = 7.2 Hz); 1.28 (d, 6 H, $OCH\underline{Me}_2$, J = 6.3 Hz); 1.69 (sext, 2 H, $OCH_2C\underline{H}_2Me$, J = 7.2 Hz); 2.86 (d, 3 H, $NH\underline{Me}$, J = 4 Hz); 3.97 (t, 2 H, $OC\underline{H}_2CH_2Me$, J = 7.2 Hz); 4.30 (sept, 1 H, $OC\underline{H}Me_2$, J = 6.3 Hz); 6.13 (br.s, 1 H, NH). MS (EI, 70 eV), m/z (I_{rel} (%)): 190 M^+ (6.2); 189 (1.8); 188 (2.0); 133 (14.1); 132 (29.2); 131 (21.4); 130 (68.2); 118 (10.5); 90 (25.4); 89 (35.8); 88 (34.0); 73 (19.3); 59 (21.4); 58 (70.7); 43 (100). Found (%): C, 50.35; H, 9.42; N, 14.81. $C_8H_{18}N_2O_3$. Calculated (%): C, 50.51; H, 9.54; N, 14.72.

***N*-Isopropoxy-*N*′,*N*′-dimethyl-*N*-propoxyurea (49)**, colorless liquid, n_D^{20} 1.4460. ^{1}H NMR (300 MHz, $CDCl_3$): 0.95 (t, 3 H, $OCH_2CH_2\underline{Me}$, J = 7 Hz); 1.25 (d, 6 H, $OCH\underline{Me}_2$, J = 6.3 Hz); 1.63 (sext, 2 H, $OCH_2C\underline{H}_2Me$, J = 7 Hz); 3.01 (s, 6 H, NMe_2); 3.86 (t, 2 H, $OC\underline{H}_2CH_2Me$, J = 7 Hz); 4.21 (sept, 1 H, $OC\underline{H}Me_2$, J = 6.3 Hz). MS (EI, 70 eV), m/z (I_{rel} (%)): 204 M^+ (1.1); 146 (3.5); 144 (3.0); 104 (19.4); 101 (18.5); 73 (17.1); 72 (100); 59 (45.8); 57 (12.6); 45 (16.3); 44 (29.2); 43 (24.3). Found (%): C, 53.03; H, 9.94; N, 13.65. $C_9H_{20}N_2O_3$. Calculated (%): C, 52.92; H, 9.87; N, 13.71.

Methyl *N*,*N*-dimethoxycarbamate (50). ***A.*** A solution of methyl *N*-acetoxy-*N*-methoxycarbamate (**31**) (0.29 g, 1.8 mmol) in MeOH (2 mL) was kept at 20 °C for 8 days. Then MeOH was distilled off *in vacuo*, the residue was extracted with pentane, the extract was concentrated, and the residue was distilled *in vacuo*. Methyl *N*,*N*-dimethoxycarbamate (**50**) was prepared in a yield of 0.14 g (58.2%) as a colorless liquid, b.p. 52—55 °C (9 Torr). ^{1}H NMR (300 MHz, $CDCl_3$): 3.83 (s, 6 H, NOMe); 3.88 (s, 3 H, CO_2Me). MS (CI), m/z (I_{rel} (%)): 136 $[M + H]^+$ (2.2); 134 $[M - H]^+$ (5.6); 133 (5.8); 105 (43.8); 104 (32.0); 76 (96.4); 61 (56.0); 58 (47.2);46 (27.6); 45 (32.2); 44 (100). Found (%): C, 35.43; H, 6.81; N, 10.60. $C_4H_9NO_4$. Calculated (%): C, 35.56; H, 6.71; N, 10.37.

B. Methanolysis of methyl *N*-methoxy-*N*-propionyloxycarbamate (**32**) performed under analogous conditions afforded methyl *N*,*N*-dimethoxycarbamate (**50**) in 61.4% yield.

Methyl *N*-methoxy-*N*-*n*-octyloxycarbamate (51). A solution of methyl *N*-acetoxy-*N*-*n*-octyloxycarbamate (**33**) (0.28 g, 1.1 mmol) in MeOH (3 mL) was kept at 20 °C for 3 days. Then MeOH was evaporated *in vacuo*, the residue was treated with a mixture of hexane and aqueous $NaHCO_3$. The hexane extract was separated and concentrated *in vacuo*. The residue was kept at 20 °C and 2 Torr for 0.5 h. *N*-Methoxy-*N*-*n*-octyloxycarbamate **51** was prepared in a yield of 0.245 g (98%) as a colorless liquid, n_D^{20} 1.4345. ^{1}H NMR (300 MHz, $CDCl_3$): 0.88 (t, 3 H, $(CH_2)_7\underline{Me}$, J = 6.9 Hz); 1.24—1.43 (m, 10 H, $OCH_2CH_2(C\underline{H}_2)_5Me$); 1.67 (quint, 2 H, $OCH_2C\underline{H}_2$, J = 6.9 Hz); 3.80 (s, 3 H, NOMe); 3.87 (s, 3 H, CO_2Me); 4.00 (t, 2 H, $NOCH_2$, J = 6.9 Hz). MS (CI), m/z (I_{rel} (%)): 234 $[M + H]^+$ (3.8); 233 $[M]^+$ (0.6); 232 (0.6); 203 (13.3); 202 (100); 121 (10.9); 111 (37.5); 106 (19.7); 104 (16.2). Found (%): C, 56.51; H, 10.05; N, 5.82. $C_{11}H_{23}NO_4$. Calculated (%): C, 56.63; H, 9.94; N, 6.00.

Methyl *N*-ethoxy-*N*-*n*-octyloxycarbamate (52) was synthesized as described above by ethanolysis of methyl *N*-acetoxy-*N*-*n*-octyloxycarbamate (**33**) at 20 °C for 120 days. The yield was 78.5%, yellowish liquid, n_D^{20} 1.4348. ^{1}H NMR (300 MHz, $CDCl_3$): 0.88 (t, 3 H, $(CH_2)_7\underline{Me}$, J = 6.7 Hz); 1.24—1.36 (m, 10 H, $OCH_2CH_2(C\underline{H}_2)_5Me$); 1.29 (t, 3 H, $NOCH_2\underline{Me}$, J = 6.9 Hz); 1.66 (quint, 2 H, $OCH_2C\underline{H}_2$, J = 6.7 Hz); 3.85 (s, 3 H, CO_2Me); 3.99 (t, 2 H, $NOCH_2$, J = 6.7 Hz); 4.06 (q, 2 H, $NOC\underline{H}_2Me$, J = 6.9 Hz). MS (CI), m/z (I_{rel} (%)): 248 $[M + H]^+$

(10.3); 247 $[M]^+$ (6.3); 229 (4.3); 216 (1.3); 204 (8.2); 202 (31.4); 145 (9.8); 135 (69.2); 120 (51.8); 119 (11.1); 118 (100). Found (%): C, 58.10; H, 10.27; N, 5.51. $C_{12}H_{25}NO_4$. Calculated (%): C, 58.27; H, 10.19; N, 5.66.

Methanolysis of ethyl *N*-acetoxy-*N*-methoxycarbamate (34). A solution of ethyl *N*-acetoxy-*N*-methoxycarbamate (**34**) (1.10 g, 6.21 mmol) in MeOH (10 mL) was kept at 20 °C for 98 h. Then MeOH was distilled off *in vacuo* (17 Torr) into a cooled trap. The residue was extracted with pentane (25 mL). The extract was concentrated and the residue was distilled *in vacuo* (4 Torr). Ethyl *N*,*N*-dimethoxycarbamate (**53**) was prepared in a yield of 0.32 g (34%) as a colorless liquid, n_D^{25} 1.4200. ^{1}H NMR (300 MHz, $CDCl_3$): 1.36 (t, 3 H, $\underline{Me}CH_2$, ^2J = 7 Hz); 3.83 (s, 6 H, MeO); 4.32 (q, 2 H, $CO_2C\underline{H}_2Me$, ^2J = 7 Hz). MS (CI), *m*/*z* (I_{rel} (%)): 150 $[M + H]^+$ (0.5); 149 $[M]^+$ (4.1); 148 (62.4); 118 (44.6); 117 (19.6); 116 (100); 104 (10.2); 76 (9.5); 75 (20.4); 73 (9.0). Found (%): C, 40.35; H, 7.68; N, 9.20. $C_5H_{11}NO_4$. Calculated (%): C, 40.27; H, 7.43; N, 9.39.

After extraction with pentane, the residue was neutralized with $NaHCO_3$ and extracted with ether (15 mL). The ethereal extract was concentrated *in vacuo* to give ethyl *N*-methoxycarbamate (**54**) in a yield of 0.054 g (7.3%). Compound **54** was identified by comparing its ^{1}H NMR spectrum with the spectrum of the authentic sample.[13] In the MeOH condensate collected into a trap, ethyl methyl carbonate was detected (GLC) in a yield of 0.287 g (44.4%).

***tert*-Butanolysis of methyl *N*-acetoxy-*N*-methoxycarbamate (31).** A solution of compound **31** (0.135 g, 0.83 mmol) in Bu^tOH (3 mL) was kept at 28—30 °C for 7 days and then Bu^tOH was removed *in vacuo* (2 Torr, 30 °C). The starting compound **31**, which was identified by ^{1}H NMR spectroscopy, was obtained in a yield of 0.082 g.

Analogously, ethyl *N*-acetoxy-*N*-methoxycarbamate (**34**) was recovered in 82.7% yield after storage in Bu^tOH at 22 °C for 3 days.

Reduction of ethyl *N*-acetoxy-*N*-methoxycarbamate (34) in propan-2-ol. A solution of compound **34** (0.31 g, 1.73 mmol) in Pr^iOH (5 mL) was kept at 28 °C for 8 days. Then Pr^iOH was removed *in vacuo* (20 Torr) and the residue was chromatographed on a column (Al_2O_3, hexane—Et_2O as the eluent). Compound **55**, ethyl *N*-methoxycarbamate (**54**), and compound **34** were obtained in yields of 0.074 g (36.2%), 0.042 g (20.4%), and 0.02 g (6.5%), respectively. These compounds were identified by ^{1}H NMR spectroscopy. *N*,*N*′-Di(ethoxycarbonyl)-*N*,*N*′-dimethoxyhydrazine (**55**), colorless liquid, n_D^{20} 1.4330, was identified by comparing its ^{1}H NMR spectrum with the spectrum of the authentic sample[13] (300 MHz, $CDCl_3$): 1.35 (t, 6 H, $\underline{Me}CH_2$, J = 6.9 Hz); 3.89 (s, 6 H, MeO); 4.32 (q, 4 H, $C\underline{H}_2Me$, J = 6.9 Hz).

Methanolysis of ethyl *N*-acetoxy-*N*-isopropoxycarbamate (36). A solution of compound **36** (0.23 g, 1.1 mmol) in MeOH (2 mL) was kept at 20 °C for 120 h. Then MeOH was distilled off *in vacuo* (20 Torr) and collected in a trap. The residue was kept at 20 °C and 2 Torr for 1 h. Ethyl *N*-isopropoxy-*N*-methoxycarbamate (**56**) was prepared in a yield of 0.085 g (44%) as a colorless liquid, n_D^{23}1.4161. ^{1}H NMR (300 MHz, $CDCl_3$): 1.29 (d, 6 H, $\underline{Me}_2CH$, J = 6.3 Hz); 1.35 (t, 3 H, $\underline{Me}CH_2$, J = 7.2 Hz); 3.77 (s, 3 H, MeO); 4.26 (sept, 1 H, $C\underline{H}Me_2$, J = 6.3 Hz); 4.29 (q, 2 H, $\underline{CH}_2O$, J = 7.2 Hz). MS (EI, 70 eV), *m*/*z* (I_{rel} (%)): 177 $[M]^+$ (1.3); 133 (26.2); 88 (16.4); 75 (10.0); 74 (88.9); 61 (100); 60 (50.9); 59 (15.8); 58 (17.0); 56 (13.8); 46 (95.3); 45 (37.8); 43 (26.1); 42 (28.8). Found (%): C, 47.22; H, 8.70; N, 7.65. $C_7H_{15}NO_4$. Calculated (%): C, 47.45; H 8.53; N, 7.90.

Ethyl methyl carbonate was found (GLC) in the condensate in a yield of 0.044 g (38.7%).

Methanolysis of *N*-acetoxy-*N*-methoxyamine 1. A solution of compound **1** (0.48 g, 2.34 mmol) and triethylamine (0.3 g, 3 mmol) in MeOH (5 mL) was kept at 20 °C for 6 days. Then MeOH was removed *in vacuo*. The residue was extracted with Et_2O, washed with water, and dried over $MgSO_4$. Then Et_2O was removed *in vacuo* and the residue was distilled. Methyl 2-(*N*,*N*-dimethoxyamino)-2-methylpropionate (**57**) was prepared in a yield of 0.24 g (57.5%) and identified by comparing its ^{1}H NMR spectrum with the spectrum of the authentic sample.[2c]

Methanolysis of *N*-acetoxy-*N*-ethoxybenzamide (38). A solution of compound **38** (0.42 g, 1.9 mmol) in MeOH (4 mL) was kept at 20 °C for 6 days and then the methanol was removed *in vacuo* (17 Torr). The residue was fractionated *in vacuo*. Benzoic acid and methyl benzoate, which were identified by GLC and based on the ^{1}H NMR spectra, were obtained in yields of 0.048 g (20.7%) and 0.124 g (48%), respectively.

Reaction of *N*-acetoxy-*N*-ethoxybenzamide (38) with MeONa in dimethoxyethane. A mixture of compound **38** (1.26 g, 5.64 mmol), anhydrous DME (20 mL), and MeONa (0.34 g, 6.25 mmol) was stirred at 20 °C for 36 h and then CO_2 was passed through the reaction mixture. The precipitate that formed was filtered off, the filtrate was concentrated *in vacuo*, and the residue was extracted with Et_2O. The ethereal extract was concentrated *in vacuo* and the residue was chromatographed on a column (Al_2O_3, hexane—Et_2O as the eluent). Methyl and ethyl benzoates, which were identified by GLC and based on ^{1}H NMR spectra, were prepared in yields of 0.18 g (23.4%) and 0.26 g (30.6%), respectively.

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