GEMINAL SYSTEMS.

COMMUNICATION 28. ALCOHOLYSIS OF N-CHLORO-N-ALKOXYAMIDES AND SYNTHESIS OF N,N-DIALKOXYUREAS

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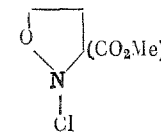
A limited number of compounds with the ONCl fragment are known: $SCF{-}\overset{\displaystyle O{-}NCl}{\overset{|}{C}}F{-}CF_2$, X = F, Cl [2]; RON(Cl)X, X = —CO [3]; $(EtO)_2PO$ [4]; $ArSO_2$ [5]; MeO_2C [6]; tert-alkyl [7];  [8].

The chemical properties of only N-chloro-N-alkoxy-N-tert-alkylamines were studied in detail [7], while N-chloro-N-alkoxyamides have virtually not been investigated. The chemical properties of these compounds are possibly determined by the following types of electronic interactions in the ONCl fragment: a) six-electron three-center destabilizing interaction, discussed in detail for the example of the isoelectronic ONO system [9]; b) interaction of highly nonbonding n orbitals of the O and Cl atoms with antibonding σ* orbitals of the N—Cl and N—O bonds. In this case, the $n_{\pi(O)} \rightarrow \sigma^*_{N-Cl}$ interaction is predominant, since the $n_{\pi(O)}$ orbital has a higher energy than $n_{\sigma(O)}$ and n_{Cl}, while σ^*_{N-Cl} has lower energy than σ^*_{N-O} [10]. In general, this interaction thermodynamically stabilizes the system. However, an increase in the population of the σ^*_{N-Cl} orbital kinetically destabilizes the N—Cl bond, polarizes it in the direction of Cl, and, in particular, favors a nucleophilic substitution of Cl. The limiting case of this interaction is the ionization of the N—Cl bonds.

$$RNCl \rightarrow RN{=}\overset{+}{O}RCl^-$$
$$\quad\;\; |$$
$$\quad\;\; OR$$

In fact, for N-chloro-N-alkoxy-N-tert-alkylamines [7] and N-chloroisoxazolidines [8], nucleophilic substitution reactions of Cl have been discovered, which are considered to occur with the intermediate formation of nitrenium-oxonium ions. Depending on the type of the substituents at the N and O atoms, the character of the electronic interactions differs substantially in the ONCl system, and correspondingly its chemical behavior. In the present work it was shown, by selecting the corresponding substituents, how it is possible to intentionally change the properties of N-chloro-N-alkoxyamides.

Introduction of an electronegative ligand to the N atom lowers the level of the n orbital, and thus decreases the six-electron destabilizing interaction. Thus, also the N—Cl bond becomes depolarized. Strongly electron-acceptor substituents may change the polarization of the N—Cl bond towards the N atom. In fact, N-chloro-N-benzyloxysulfonamide (II), which was obtained by us for the first time, is thermally stable, does not change by the action of MeONa in MeOH, and in the reaction with Et_3N in MeOH acts as a chlorinating agent:

$$Me_2NSO_2Cl \xrightarrow[Et_3N/Et_2O]{PhCH_2ONH_2} \underset{(I)}{Me_2NSO_2NHOCH_2Ph} \xrightarrow{t\text{-}BuOCl} \underset{(II)}{Me_2NSO_2N(Cl)OCH_2Ph} \xrightarrow{Et_3N/MeOH} (I)$$

The thermal addition of N-chloro-N-methoxyphosphamide ester (III) to styrene has been established to have a radical character [4]. However, in the reaction with Et_3N in MeOH, compound (III), similarly to (II), is a chlorinating agent:

*For Communication 27, see [1].

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$$\underset{\text{(III)}}{(EtO)_2P(O)N(Cl)OMe} \xrightarrow{Et_3N/MeOH} \underset{\text{(IV)}}{(EtO)_2P(O)NHOMe}$$

During the alcoholysis of (III) by the action of MeONa in MeOH, the attack of the nucleophile occurs at the phosphoryl group, with splitting of the pseudohalogen group MeONCl (compare with the pseudohalogen character of the NCl_2 group of dichloroamides [11])

$$\text{(III)} \xrightarrow{MeONa/MeOH} (EtO)_2P(O)OMe \quad \text{(V)}$$

It was assumed that with the decrease in the electron-acceptor character of the phosphoryl group in (VII), compared with (III), the character of the N—Cl bond would change. However, as the result of the reaction of (VIIa) with MeONa, only a product of the attack of the nucleophile at the phosphoryl group was isolated

$$\underset{\text{(VI)}}{(Me_2N)_2P(O)NHOR} \xrightarrow{t\text{-BuOCl}} \underset{\text{(VII)}}{(Me_2N)_2P(O)N(Cl)OR}$$

R = Me (a), $PhCH_2$(b).

$$\text{(VIIa)} \xrightarrow[DME]{MeONa} (Me_2N)_2P(O)OMe$$

The products of the reaction of (VII) with Et_3N in MeOH could not be identified, since, apparently, their acid-catalyzed decomposition takes place thereby.

The methanolysis of N-chloro-N-methoxyurethylane proceeds by a radical mechanism [6], i.e., in contrast to the above-discussed examples, the relatively weak electron-acceptor group MeO_2C decreases the polarization of the N—Cl bond, and thus, the $n-\sigma^*_{N-Cl}$ one-electron transfer becomes possible. This is favored by the capto-dative stabilization [12] of the N-alkoxyamidyl formed. As a result of the further decrease in the electron-acceptor ability of the substituent at the N atom, the properties of the ONCl fragment change substantially. We found that N-chloro-N-alkoxyureas (X) enter smoothly into nucleophilic substitution reaction of Cl, i.e., the anionic character of Cl is already sharply expressed in their case

$$Me_2NCOCl \xrightarrow{RONH_2} \underset{\text{(IX)}}{Me_2NCONHOR} \xrightarrow{t\text{-BuOCl}} \underset{\text{(X)}}{Me_2NCON(Cl)OR} \xrightarrow[B]{R'OH} \underset{\text{(XI)}}{Me_2NCON(OR')OR}$$

R = Me(a), *i*-Bu(b), CH_2=CH—CH_2 (c), $PhCH_2$ (d), MeO_2CCH_2 (e), $MeO_2CCH_2CH_2$ (f), MeO_2CCMe_2 (g)

R = Me; R′ = Me (a), Et (b), *i*-Bu (c), CH_2=CH—CH_2 (d);
R = *i*-Bu; R′ = Et (e), *i*-Bu (f), CF_3CH_2 (g);
R = CH_2 = CH—CH_2; R′ = Et (h), CF_3CH_2 (i);
R = $PhCH_2$; R′ = Me (j), Et (k), CF_3CH_2 (*l*);
R = $MeO_2CCH_2CH_2$; R′ = CF_3CH_2 (m);
R = MeO_2CCH_2; R′ = Me (n)

B = R′ONa, 2,4,6-trimethylpyridine.

The above-discussed examples clearly show how it is possible to intentionally change the properties of the ONCl fragment by introducing different kinds of substituents at the N atom. Another known example of the nucleophilic substitution reaction of the Cl atom in N-chloro-N-alkoxyamides is as follows [3]:

$$\underset{\substack{|\\OR}}{XNCl} + Na^+\underset{\substack{|\\OR}}{N^-}—X \rightarrow \underset{\substack{|\\RO}}{XN}—\underset{\substack{|\\OR}}{NX}$$

X = —CO, R = *t*-Bu.

N-Chloro-N-alkoxyureas and N,N-dialkoxyureas were prepared by us for the first time (preliminary communication [13]). Formerly, only one example of amides with the ONO fragment was known: N,N-bis(fluorosulfonyloxy)amides, which are slightly stable compounds obtained in a 25% yield according to the scheme [14]

$$RCONH_2 \xrightarrow{2(FSO_2O)_2} RCON(OSO_2F)_2$$

$$R = CF_3,\ C_3F_7,\ C_6F_{13}.$$

N-Chloro-N-alkoxyureas (X, a-d, f) are light-yellow, undistillable liquids; (X, e-g) are crystalline products. Compound (Xa) decomposes completely in CCl_4 after 25 days at 20°C to form N,N-dimethylcarbamoyl chloride (XII) and N,N-dimethylurethylane (XIII):

$$(Xa) \xrightarrow{CCl_4} \underset{(XII)}{Me_2NCOCl} + \underset{(XIII)}{Me_2NCO_2Me}$$

During the decomposition, the initial (Xa), MeOH, (XII), and (XIII) appear in the reaction mixture, whereby the content of MeOH and (XII) decreases with time, while that of (XIII) increases correspondingly. The decomposition of (Xa) can be represented either by the scheme

$$(Xa) \rightarrow [Me_2NCON{=}\overset{+}{O}MeCl^- \xrightarrow[-Me_2NCOCl]{} MeO\ddot{N}: \rightarrow MeON{=}NOMe \xrightarrow[-N_2]{} 2MeO\cdot \xrightarrow[-CH_2O]{} MeON] \xrightarrow{Me_2NCOCl} (XIII)$$

or by matched fragmentation.

Taking the alcoholysis of (Xe) as an example, we showed how the substituent at the O atom influences the properties of the ONCl fragment. In the reaction of (Xe) with MeONa in MeOH, the product of the nucleophilic substitution of Cl is formed in an inappreciable yield. This is fully understandable, since the increase in the electronegative character of the substituent at O lowers the $n_{\pi(O)}$ orbital level and decreases the $N{-}\sigma^*_{N-Cl}$ interaction and the polarization of the N–Cl bond. In this case the attack of the nucleophile at the carbonyl group becomes preferential:

$$(Xe) \xrightarrow{MeONa/MeOH} \begin{cases} \rightarrow Me_2NCON(OMe)OR\ (XIo) \\ \rightarrow Me_2NCO_2Me + [RO\ddot{N}Cl \xrightarrow[-Cl\ddot{N}:]{} R\bar{O}] \xrightarrow{H^+} ROH \end{cases}$$

$R = MeO_2CCH_2$.

The next limitation of the nucleophilic substitution reaction of Cl in N-chloro-N-alkoxyureas is the steric factor. Thus, it is impossible to carry out the nucleophilic substitution of Cl in the reaction of (Xa) with t-BuOH.

The nucleophilic substitution reaction of Cl in N-chloro-N-alkoxyureas that we have discovered uncovers possibilities for the synthesis of several new area derivatives with an ONX fragment, which is a pseudohalogen, readily leaving group. Thus, it was found that N,N-dialkoxyureas are readily hydrolyzed by aqueous alkali and undergo methanolysis by the action of MeONa in MeOH to form NH-dialkoxyamines (preliminary communication [13]).

EXPERIMENTAL

The PMR spectra were obtained on JNMC-C-60 HL (60 MHz) and Bruker WM-400 (400 MHz) spectrometers. The chemical shifts were measured in ppm with reference to HMDS; the spin-spin coupling constants J, in Hz.

$MeONH_2$, bp 49-50°C [15], i-$BuONH_2$, bp 106-107°C, $CH_2{=}CHCH_3$, bp 98-99°C, $PhCH_2ONH_2$, bp 70.5°C (2 mm), $MeO_2CCH_2ONH_2$, bp 66.5°C (11 mm), $MeO_2CCMe_2ONH_2$, bp 82-84°C (38 mm), were obtained according to [16]; $MeO_2CCH_2CH_2ONH_2$, bp 70°C (10 mm), was obtained according to [17]; $(EtO)_2P(O)NHOMe$, bp 83-84°C (0.4 mm), was obtained according to [4]; and $(Et_2O)_2P(O)N(Cl)OMe$ was obtained according to [4].

N,N-Dimethyl-N'-benzyloxysulfonamide (I). A solution of 1.44 g (10 mmoles) of Me_2NSO_2Cl [18] in 10 ml of absolute C_6H_6 was added to a solution of 1.23 g (10 mmoles) of $PhCH_2ONH_2$ and 1.01 g (10 mmoles) of Et_3N in 20 ml of absolute C_6H_6. The mixture was held for 7 days at 20°C, boiled for 8 h, and the precipitate was separated; the filtrate was evaporated in vacuo. The residue was crystallized from a CCl_4–pentane mixture to yield 1.12 g (48.6%) of (I), mp 65-70°C. PMR spectrum (60 MHz, $CDCl_3$): 2.88 (Me_2N), 4.85 (CH_2), 7.30 (Ph). Found: C 46.79; H 6.21; N 11.91%. $C_9H_{19}N_2O_3S$. Calculated: C 46.94; H 6.13; N 12.16%.

N,N-Dimethyl-N'-chloro-N'-benzyloxysulfonamide (II). A solution of 0.19 g (1.8 mmoles) of t-BuOCl in 10 ml of absolute MeOH was added at −78°C to a solution of 0.33 g (1.4 mmoles) of (I) in 10 ml of absolute MeOH. The solvent was evaporated in vacuo, and the residue was crystallized from a CCl_4–pentane mixture to yield 0.33 g (90.1%) of (II), mp 61-65°C. PMR spectrum (60 MHz, $CDCl_3$): 2.75 (Me_2N), 4.93 (CH_2), 7.35 (Ph). Found: C 40.75; H 4.99; N 10.52%. $C_9H_{18}N_2O_3SCl$. Calculated: C 40.83; H 4.95; N 10.58%.

Reaction of (II) with Et_3N in MeOH. A solution of 0.23 g (2.28 mmoles) of Et_3N in 10 ml of absolute MeOH was added at −78°C to a solution of 0.59 g (2.28 mmoles) of (II) in 15 ml of absolute MeOH. The mixture was held for 3 h at 0°C, the solvent was removed in vacuo, and the residue was extracted by C_6H_6. The extract was evaporated in vacuo, and the residue was crystallized from a benzene–ether mixture. Yield 0.40 g (76.5%) of (I), mp 65°C.

Reaction of (III) with Et_3N in MeOH. A solution of 0.10 g (1 mmole) of Et_3N in 10 ml of absolute MeOH was added at −78°C to a solution of 0.21 g (1 mmole) of (III) in 10 ml of absolute MeOH. The mixture was held at 0°C for 3 days, the solvent was removed in vacuo, and the residue was extracted by ether. The extract was evaporated in vacuo, and the residue was distilled to yield 0.13 g (70.6%) of diethyl-M-methoxyphosphamide, bp 83-84°C (0.4 mm) (cf. [4]).

Reaction of (III) with MeONa in MeOH. A solution of 0.63 g (11.4 mmoles) of MeONa in 15 ml of MeOH was added at −78°C to a solution of 2.37 g (11.4 mmoles) of (III) in 15 ml of absolute MeOH. The mixture was held for 1 h at 0°C, saturated with CO_2. MeOH was removed in vacuo, and the residue was extracted by ether. The extract was evaporated in vacuo, and the residue was distilled to yield 1.56 g (81.4%) of methyl diethyl phosphate, bp 56°C (1 mm). PMR spectrum (60 MHz, CCl_4): 1.30 4.00 (Et, J_{MeCH_2} = 6.8, $J_{P,H}$ = 9.0), 3.63 (MeO, $J_{P,H}$ = 11.3). Found: C 35.97; H 8.39%. $C_5H_{13}O_4P$. Calculated: C 35.72; H 7.79%.

N-Methoxyamide of Bis(dimethylamido)phosphoric Acid (VIa). A solution of 2.82 g (60 mmoles) of $MeONH_2$ and 5.13 g (30 mmoles) of $Me_2NP(O)Cl$ in 40 ml of absolute C_6H_6 was held for 6 days at 20°C. The precipitate was separated, and from the filtrate the solvent was removed in vacuo, and the residue distilled to yield 3.5 g (64.5%) of (VIa), bp 112°C (1 mm), mp 28-29°C. PMR spectrum (60 MHz, CCl_4): 2.65 (Me_2N, $J_{P,H}$ = 9.8), 3.55 (MeO), 8.63 (NH, $J_{P,H}$ = 11.3).

N-Benzyloxyamide of Bis(dimethylamido)phosphoric Acid (VIb). A solution of 2.94 g (17.1 mmoles) of $(Me_2N)_2P(O)Cl$, 2.12 g (17.19 mmoles) of $PhCH_2ONH_2$, and 1.74 g (17.1 mmoles) of Et_3N in 50 ml of absolute MeCN was held at 20°C for 16 h. The solvent was removed in vacuo, and the residue was extracted by CCl_4. The extract was evaporated in vacuo, and the residue was crystallized from a CCl_4–pentane mixture to yield 3.52 g (81.5%) of (VIb), mp. 66°C. PMR spectrum (60 MHz, CCl_4): 2.63 (Me_2N, $J_{P,H}$ = 9.8), 4.76 (CH_2), 7.38 (Ph), 8.0 (NH, $J_{P,H}$ = 11.3). Found: C 51.45; H 8.16; N 16.31%. $C_{11}H_{20}N_3O_2P$. Calculated: C 51.36; H 7.84; N 16.33].

N-Chloro-N-methoxyamide of Bis(dimethylamido)phosphoric Acid (VIIa) and N-Chloro-N-benzyloxyamide of Bis(dimethylamido)phosphoric Acid (VIIb). These compounds were obtained by chlorination of (VIa) and (VIb), respectively, by t-BuOCl in ether at −78°C. Yield quantitative. Oils decomposing at 20°C. PMR spectra (60 MHz, CCl_4) for (VII): 2.73 (Me_2N, $J_{P,H}$ = 9.8), 3.73 (MeO); for (VIIb): 2.85 (Me_2N, $J_{P,H}$ = 9.0), 4.81 (CH_2), 7.25 (Ph).

Reaction of (VIIa) with MeONa. A solution of 0.34 g (1.59 mmoles) of (VIIa) in 5 ml of DME was added at −78°C to a suspension of 0.097 g (1.8 mmoles) of MeONa in 5 ml of DME. The mixture was held at −8°C for 3 h, and then was saturated with CO_2. The solvent was removed in vacuo, and the residue was extracted by ether. The extract was evaporated in vacuo, and the residue was distilled to yield 0.11 g (41.6%) of methyl ester of bis(dimethylamido)phosphoric acid (VIII), bp 50°C (1 mm), bp 45-50°C (1 mm) [19]. PMR spectrum (60 MHz, CCl_4): 2.53 (Me_2N, $J_{P,H}$ = 8.3), 3.48 (MeO, $J_{P,H}$ = 10.5).

General Procedure for Synthesis of N,N-Dimethyl-N'-alkoxyureas (IX). A solution of equimolar amounts of $RONH_2$, Et_3N, and Me_2NCOCl in $RONH_2$ was held for 1 week at 20°C, then was boiled for 5 h and evaporated in vacuo. The residue was extracted by C_6H_6. The extract was evaporated in vacuo, and the residue was distilled in vacuo or crystallized from a suitable solvent (Table 1). For (IXe), the mixture was held for 6 days at 20°C and isolated without preliminary boiling.

General Procedure for the Synthesis of N,N-Dimethyl-N'-chloro-N'-alkoxyureas (X). An equimolar amount of t-BuOCl was added at −78°C to a suspension of (IX) in ether. The mixture

TABLE 1. N-Alkoxyureas $Me_2NCONHOR$ (IX)

Compound	R	Yield, %	bp, °C (p, mm Hg) mp, °C	PMR spectrum (60 MHz, CCl_4)			Found/Calculated, %		
				Me_2N	R	NH	C	H	N
(IXa)	Me	81,3	91–92(1), 37–38	2,85	3,56	8,35	40,78 / 40,67	8,53 / 8,53	23,60 / 23,71
(IXb)	*i*-Bu	79,8	109–110(1)	2,79	0,85(Me_2CH, J=6,8), 1,8(CH), 3,44(CH_2CH, J=6)	7,96	52,38 / 52,47	10,27 / 10,06	18,03 / 17,48
(IXc) *	$H_AH_BC{=}CH_CCH_2$	79,8	107(1)	2,85	4,26(OCH_2), 5,29(H_A), 5,21(H_B), 5,99(H_C), $J_{CH_2H_C}$=6,1, J_{AB}=1,45, J_{AC}=17,33, J_{BC} = 10,3, $J_{CH_2H_A} = J_{CH_2H_B} = 1,2$	8,12	49,99 / 49,98	8,38 / 8,38	19,71 / 19,43
(IXd)	$PhCH_2$	89,6	54–55 (CCl_4–hexane)	2,75	4,74(CH_2), 7,30(Ph)	7,96	61,53 / 61,84	7,44 / 7,26	14,18 / 14,42
(IXe)†	MeO_2CCH_2	48,7	63–65 (C_6H_6–ether)	2,84	3,70(MeO), 4,41(CH_2)	8,42	40,40 / 40,92	7,00 / 6,87	16,10 / 15,91
(IXf)	$MeO_2CCH_2CH_2$	77,6	152(1)	2,81	2,52(OCH_2CH_2, J=6) 3,60(MeO); 3,96(OCH_2)	8,65	44,62 / 44,21	7,37 / 7,42	14,68 / 14,73
(IXg)†	MeO_2CCMe_2	60,9	92–94(CCl_4)	2,80	1,42(Me_2C), 3,68(MeO)	7,60	46,95 / 46,82	7,79 / 7,85	13,41 / 13,64

*PMR spectrum (400 MHz) in CD_3OD

†PMR spectrum in $CDCl_3$.

TABLE 2. $Me_2NCON(OR)OR^1$ (XI)

Compound	R	R′	Yield, %	bp, °C (p, mm Hg)	PMR spectrum (60 MHz, CCl_4)			Found/Calculated, %		
					Me_2N	R	R′	C	H	N
(XIa)	Me	Me	84,5	61(1)	2,84	3,53	3,53	41,12 41,37	6,03 6,24	19,29 19,30
(XIb)	Me	Et	59,7	75(2)	2,93	3,57	1,2; 3,86(Et, J=7)	44,40 44,43	8,59 8,70	–
(XIc)	Me	*i*-Bu	50,7 [a]	97–98(2)	2,88	3,54	0.91($\underline{Me_2}$CH, J=6,8) 1,8(CH), 3,57($\underline{CH_2}$CH, J=6)	50,29 50,50	9,61 9,53	14,61 14,72
(XId)	Me	$H_AH_BC{=}CH_CCH_2$	47,6	84–85(2)	3,00 [б]	3,73	4,45(OCH_2, $J_{CH_2H_C}$=6,1, $J_{CH_2H_A} = J_{CH_2H_B} = 1,3$), 5,24($H_B$), 5,33($H_A$), 5,97($H_C$), J_{AB}=1,47, J_{AC}=17,14, J_{BC}=10,26	48,13 48,26	8,26 8,10	16,19 16,08
(XIe)	*i*-Bu	Et	74,2	82,5(1)	2,85	0,9($\underline{Me_2}$CH, J=6,8), 1,8(CH); 3,53($\underline{CH_2}$CH, J=6,0)	1,15; 3,80(Et, J=7,5)	52,95 52,92	9,89 9,87	13,81 13,71
(XIf)	*i*-Bu	*i*-Bu	45,5	91–92(1)	2,90	0,93($\underline{Me_2}$CH, J=6,8), 1,85(CH), 3,58($\underline{CH_2}$CH, J=6,0)		56,88 56,87	10,40 10,41	11,76 12,06
(XIg)	*i*-Bu	CF_3CH_2	83,0	– [в]	2,89	0,90($\underline{Me_2}$CH, J=6,8), 1,80(CH), 3,65($\underline{CH_2}$CH, J=6,0)	4,16($CF_3\underline{CH_2}$, $J_{F,H}$=9,0)	42,12 41,86	6,43 6,63	10,78 10,84

(XIh)	$H_AH_BC{=}CH_CCH_2$	Et	41,1	93(2)	2,52[d]	4,37(OCH_2, $J_{CH_2H_C}$=6,1, $J_{CH_2H_A} = J_{CH_2H_B}$ = =1,46, 5,0(H_B), 5,19(H_A), 5,88(H_C), J_{AB}=1,71, J_{BC}=10,5, J_{AC}=17,33	1,04; 3,85(Et, J=7,1)	51,44 51,04	8,41 8,56	15,09 14,88
(XIi)	$H_AH_BC{=}CH_CCH_2$	CF_3CH_2	61,6	80–82(1)	2,44[e]	4,23(OCH_2, $J_{CH_2H_C}$=6,1, $J_{CH_2H_A} = J_{CH_2H_B}$ = =1,22), 4,98(H_B), 5,09(H_A), 5,70(H_C), J_{AB}=1,46, J_{BC}=10,25, J_{AC}=17,09	4,08(CF_3CH_2, $J_{F,H}$=8,79)	51,62 51,88	6,99 7,07	14,85 15,12
(XIj)	$PhCH_2$	Me	79,6	–[c]	2,84	4,79(CH_2), 7,28(Ph)	3,55(MeO)	58,78 58,91	6,85 7,19	12,53 12,49
(XIk)	$PhCH_2$	Et	60,5	–[c]	2,93	4,84(CH_2), 7,30(Ph)	1,25; 3,90(Et, J=7,0)	60,49 60,84	7,61 7,86	11,75 11,60
(XIl)	$PhCH_2$	CF_3CH_2	68,8	–[c]	2,79	4,78(CH_2), 7,16(Ph)	4,13($CF_3\underline{CH_2}$, $J_{F,H}$=9,0)	49,11 49,31	5,02 5,17	9,63 9,58
(XIm)	$MeO_2CCH_2CH_2$	CF_3CH_2	76,3	–[c]	2,91	2,52($OCH_2\underline{CH_2}$, J=6), 3,61(MeO), 41,0(OCH_2)	4,20($CF_3\underline{CH_2}$, $J_{F,H}$=9,0)	37,41 37,50	5,01 5,24	9,53 9,71
(XIn)	MeO_2CCH_2	Me	14,1	–[f]	2,5[g]	3,29(MeO_2C), 4,39(CH_2)	3,57(MeO)	40,52 40,77	6,49 6,84	13,23 13,58

a) Yield of (XIc) 95.5%, based on (Xb).
b) PMR spectrum (400 Hz) in $CDCl_3$.
c) Purified by column chromatography (Al_2O_3, eluent – ether).
d) PMR spectrum (400 MHz) in C_6D_6.
e) PMR spectrum (400 MHz) in toluene-d_8.
f) Purified by precipitation by pentane from an ether solution.
g) PMR spectrum (80 MHz) in C_6D_6.

was held until the precipitate completely dissolved and the solvent was removed in vacuo. From the residue, compound (X) was obtained in a quantitative yield and was used without purification in further transformations. PMR spectra: (Xa) (60 MHz, CCl_4): 2.95 (Me_2N), 3.72 (MeO); (Xb) (60 MHz, CCl_4): 0.95 (Me_2C, J = 6.8), 1.9 (CH), 2.93 (Me_2N), 3.70 ($\underline{CH_2}CH$, J = 6); (Xc) (400 MHz, C_6D_6): 2.38 (Me_2N), 4.26 (OCH_2, J_{OCH_2HC} = 6.1, $J_{OCH_2H_A}$ = $J_{OCH_2H_B}$ = 1.22), 4.96 (H_B), 5.09 (H_A), 5.69 (H_C), J_{AB} = 1.2, J_{AC} = 17.2, J_{BC} = 10.5; (Xd) (60 MHz, CCl_4): 2.95 (Me_2N), 4.98 (CH_2), 7.45 (Ph); (Xe), mp 41-42°C (ether–pentane). PMR spectrum (60 MHz, $CDCl_3$): 3.0 (Me_2N), 3.90 (MeO), 4.55 (CH_2). Found: C 33.43; H 5.13; N 15.90%. $C_6H_{11}O_4N_2Cl_2$. Calculated: C 34.22; H 5.22; N 13.30%. (Xg), mp 34-35°C (ether–pentane), PMR spectrum (60 MHz, $CDCl_3$): 1.56 (Me_2C), 2.98 (Me_2N), 3.73 (MeO). Found: C 40.14; H 6.62; N 11.79%. $C_8H_{15}N_2O_4Cl$. Calculated: C 40.26; H 6.34; N 11.74%. (Xf) (60 MHz, CCl_4): 2.65 ($OCH_2\underline{CH_2}$, J = 6.8), 2.98 (Me_2N), 3.70 (MeO), 4.28 (OCH_2).

General Procedure for the Synthesis of N,N-Dimethyl-N',N'-dialkoxyurea (XI). A solution of an equimolar amount of the corresponding alcoholate in absolute ether was added at −78°C to freshly prepared (X). The mixture was held for 1 h at −8°C and for 30 min at 20°C. It was then saturated with CO_2, the alcohol was removed in vacuo, and the residue was extracted by ether. The extract was evaporated in vacuo, and the residue was distilled or chromatographed on a column (Table 2). For the preparation of (XIc, d, k) 2,4,6-trimethylpyridine was used instead of RONa.

Methanolysis of (Xe). A solution of 0.19 g (3.48 mmoles) of MeONa in 10 ml of absolute MeOH was added at −78°C to a solution of 0.73 g (3.48 mmoles) of (Xe) in 15 ml of absolute MeOH. The mixture was held for 45 min at 0°, saturated with CO_2, and the alcohol was removed in vacuo. The residue was extracted by ether, and the extract was evaporated in vacuo (30 mm). The volatile products from the residue were condensed in vacuo of 1 mm Hg. The yield of the mixture of Me_2NCO_2Me and MeO_2CCH_2OH (in a ratio of 1:2) was 0.097 g. The products were identified by comparison with known samples according to PMR and mass spectra. The residue was dissolved in ether and precipitated by heptane. Yield, 0.101 g (14.1%) of methyl ester of N-methoxy-N-dimethylcarbamoylaminoacetic acid (IXe) (see Table 2).

Thermal Decomposition of (Xa). A solution of 0.92 g (6.02 mmoles) of (Xa) in 20 ml of CCl_4 was held for 25 days at 20°C. According to the PMR spectrum, the mixture consisted of Me_2NCOCl and Me_2NCO_2Me in a 1:1 ratio (identified by adding authentic samples into the ampule of the NMR spectrometer). The solvent was removed in vacuo, and the residue was chromatographed on a column (silica gel 40/100, eluent – ether). Yield, 0.23 g (70%) of Me_2NOCl and 0.19 g (63.3%) of Me_2NCO_2Me.

CONCLUSIONS

1. N-Chloro-N-alkoxysulfonamides and N-chloro-N-alkoxyphosphoamides have chlorinating properties in the reaction with triethylamine in methanol.

2. N-Chloro-N-alkoxyureas were synthesized for the first time, and from them previously unknown N,N-dialkoxyureas were obtained by nucleophilic substitution reactions.

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GEMINAL SYSTEMS.

COMMUNICATION 29*. REACTIONS OF N-CHLORO-N-METHOXY-N',N'-DIMETHYLUREA WITH N-NUCLEOPHILES

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We have previously obtained N-chloro-N-alkoxy-N',N'-dimethylureas [1, 2], which, similarly to N-chloro-N-alkoxy-N-tert-alkylamines [3, 4] and N-chloro-N,N-dialkoxyamines [5], undergo by the action of alcohols, nucleophilic substitution to form N,N-dialkoxyureas [1, 2].

In the present work, we studied the reactions of N-chloro-N-methoxy-N',N'-dimethylurea (I) with N-nucleophiles to verify the possibility of synthesizing NH-alkoxyhydrazines as starting materials for the preparation of amido-esters of orthonitrous acid.

$$XN(Cl)OMe \xrightarrow{HNR_2} XN(NR_2)OR \xrightarrow{OH^-} HN(NR_2)OR \xrightarrow[-H^+]{Cl^+}$$
$$ClN(NR_2)OR \xrightarrow[-Cl^-]{OR^-} (RO)_2NNR_2 \qquad (1)$$
$$X = Me_2NCO.$$

This scheme has recently been applied in the successful synthesis of trialkoxyamines [5]. However, it was shown that in the reaction of (I) with secondary amines, as in the case of N-chloro-N-alkoxy-N-tert-alkylamines [6], the initially formed N-alkoxyhydrazines enter into further reactions under the reaction conditions. Thus, as a result of the reaction of (I) with an excess of Me_2NH, only products (II) and (III) could be isolated:

$$\underset{(I)}{XN(Cl)OMe} \xrightarrow[-HCl]{Me_2NH} \Big[XN(OMe)NMe_2 \xrightarrow[-MeOH]{H^+} XN{=}\overset{+}{N}Me_2 \xrightarrow[-H^+]{} \rightarrow X\bar{N}-\overset{+}{\underset{\underset{Me}{|}}{N}}{=}CH_2 \xrightarrow{Me_2NH} \underset{\underset{Me}{|}}{XNHNCH_2NMe_2} \Big] \xrightarrow{Me_2NH} \underset{(II)}{(Me_2N)_2CH_2} + \underset{(III)}{(Me_2N)_2CO} \qquad (2)$$

According to the data in [6], N-alkoxyhydrazine gives a diazenium salt, from which, as a result of a characteristic deprotonation, a dipole is generated, which adds Me_2NH to form an asymmetric aminal. The latter disproportionates to (II) under the action of Me_2NH. The formation of (III) can be attributed to the carbamoylation of Me_2NH by the action of (I) or one of the intermediate products.

*For Communication 28 see [1].

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