ASYMMETRIC NITROGEN.

COMMUNICATION 48.* GEMINAL SYSTEMS. COMMUNICATION 32.* NH-DIALKOXYAMINES: SYNTHESIS, HYDROXY- AND AMINOMETHYLATION, NMR SPECTRA, AND CONFIGURATIONAL STABILITY

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The following acyclic N,N-dialkoxyamines are known: perfluorinated N-alkyl-N,N-dialkoxyamines [2] and N-tert-alkyl- [3] and N-dimethylcarbamoyl-N,N-dialkoxyamines [4, 5]. The data on cyclic and bicyclic dialkoxyamines are summarized in [6].

We have prepared NH-dialkoxyamines (I) by alkaline hydrolysis of methanolysis of N,N-dialkoxyureas [4, 5] and have studied some of their properties:

$$Me_2NCON(OR)OR' \xrightarrow[\text{б) MeONa/MeOH}]{\text{а) KOH/H}_2\text{O, Cat}} \underset{\text{(I)}}{RONHOR'}$$

R = Me, R′ = Me(a), Et(b), *i*-Bu(c), $PhCH_2$(d);
R = Et, R′ = *i*-Bu(e), $PhCH_2$(f); R = $PhCH_2$, R′ = CF_3CH_2(g).

Cat = $Et_3\overset{+}{N}CH_2PhCl^-$

Compounds (I) are colorless distillable liquids (Table 1) that decompose explosively when pyrolyzed or treated with mineral acid. They are orthoesters of nitrosyl hydride (nitroxyl) HNO, an unstable compound that decomposes at −95° [7]. The intermediate formation and conversion of nitrosyl hydrate $HN(OH)_2$ have been described in [8], and its quantum-chemical calculation in [9].

It is known that hydroxylamines and monoalkoxyamines are more reactive than ordinary amines, e.g., toward carbonyl compounds [10]. Dialkoxyphosphines are more reactive than phosphines in reactions with aldehydes [11]. The reaction of difluoroamine with carbonyl compounds is catalyzed by acids and does not proceed under neutral conditions [12]. In essence this is alkylation of the weakly nucleophilic difluoroamine by an α-hydroxyalkylcarbenium ion. We have established that NH-dialkoxyamines (Ia, d) react smoothly with CH_2O to form the stable N,N-dialkoxyaminocarbinols (IIa, d) (Table 2):

$$(Ia, d) \xrightarrow[20°]{CH_2O/MeOH} \underset{(IIa,d)}{MeO(RO)NCH_2OH}$$

R = Me(a), $PhCH_2$ (d)

In this reaction (in CD_3OD at 20°) N,N-dimethoxyamines (Ia) are less reactive than MeONHMe, which is completely converted to the respective carbinol [13] in 15 min, whereas (Ia) is ~5% converted to (IIa) in that time, and ~85% after 3.5 h. Thus, the introduction of the second alkoxy substituent into the N atom decreases its nucleophilicity. This agrees with the calculations of [10]. It should be especially noted that when (Ia, d) react with CH_2O the respective methylenebisamines do not form; the latter form easily from ordinary secondary amines and monoalkoxyamines [13]. This is typical of secondary amines with an N atom of weakened M-capability, viz., aziridines and diaziridines.

The study of N nucleophilicity in the N,N-dialkoxyamines of interest consists of a comparison of the properties of the carbinols (II) with related compounds, in particular ethylenediamine derivatives. The chemical behavior of (II) should be determined mainly by the n_N–σ^*_{C-O}

*For preceding communications, see [1].

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TABLE 1. NH-Dialkoxyamines, RONHOR'

Compound	R	R'	Yield, %	bp, °C (p, mm Hg)	PMR spectrum (60 MHz, CCl_4) δ, ppm J, Hz			Found/Calculated, %		
					R	R'	NH	C	H	N
(Ia)[a]	Me	Me	61,5	83,5(760)	3,59	3,59	7,74	30,99 / 31,16	9,11 / 9,15	17,80 / 18,17
(Ib)	Me	Et	41,7	95–97(760)	3,54	1,15, 3,79(Et; J=6,8)	7,63	39,47 / 39,55	9,96 / 9,96	15,08 / 15,37
(Ic)[b]	Me	*t*-Bu	72,2	65(40)	3,42	0,84, 0,85 (Me_2CH; J=6,84), 1,81(CH), 3,43, 3,62(CH_2CH; J_{AB}=9,28, J_{CH^3CH}=6,59)	7,67	50,11 / 50,39	11,33 / 10,99	12,18 / 11,75
(Id)[c]	Me	$PhCH_2$	66,7	–d	3,57	4,8(CH_2), 7,29(Ph)	7,73	65,13 / 65,28	7,38 / 7,23	9,08 / 9,14
(Ie)[e]	Et	*i*-Bu	74,4	74(30)	1,06, 3,68 3,88(Et, J_{AB}=9,52, J=7,08)	0,84, 0,85(Me_2CH; J=6,84), 1,84(CH), 3,47, 3,68(CH_2CH; J_{AB}=9,28, J_{CH_2CH}=6,8)	7,57	53,88 / 54,11	11,38 / 11,35	10,53 / 10,52
(If)	Et	$PhCH_2$	61,0	–d	1,13, 3,75(Et, J=6,8)	4,73(CH_2), 7,20(Ph)	7,68	64,31 / 64,65	7,92 / 7,83	8,23 / 8,37
(Ig)	$PhCH_2$	CF_3CH_2	25,2	–d	4,70(CH_2), 7,15(Ph)	3,93(CH_2, $J_{F,H}$=8,5)	8,05	48,55 / 48,87	4,38 / 4,55	6,71 / 6,33

a) ^{13}C NMR ($C_6D_5CD_3$): 60.14 ($^1J_{CH}$ = 142.21, $^3J_{CONH}$ = 4.88); ^{15}N NMR (40.53 MHz, δ from $Na^{15}NO_3$, D_2O): 120.46 ($^1J_{^{15}N,H}$ = 65.92, $^3J^{15}N$, Me = 3.7). S Character of NH bond is 22.35% (calculated according to [21]). For comparison, ^{15}N NMR spectrum of $MeONHCMe_2CH_2CO_2Me$: δ^{15}_N = 150.24, $^1J_{^{15}N,H}$ = 58.59, $^3J_{^{15}N,Me}$ = 3.6, S character of NH bond is 19.2%.

b) PMR spectrum (400 MHz, $C_6D_5CD_3$); ^{13}C NMR spectrum (100.61 MHz, C_6D_6): 19.46 (Me_2C, $^1J_{C,H}$ = 125.5, $^2J_{C,H}$ = 4.62), 28.11 (CH, $^1J_{C,H}$ = 12.69,, $^2J_{C,H}$ = 3.7), 79.88 (CH_2O, $^1J_{C,H}$ = 141.49, $^2J_{C,H}$ = 4.6, $^3J_{CONH}$ = 4.62), 59.93 (MeO, $^1J_{C,H}$ = 142.42, $^2J_{CONH}$ = 5.55).

c) ^{13}C NMR spectrum (C_6D_6): 74.18 (CH_2O, $^1J_{C,H}$ = 144.04,' $^3J_{CONH}$ = 4.81, 59.87 (MeO, $^1J_{C,H}$ = 142.82, $^3J_{CONH}$ = 5.0), 129.3 (Ph).

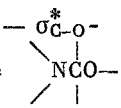
d) Purified by column chromatography (Al_2O_3, C_6H_6 eluent).

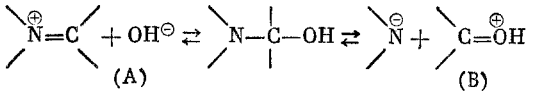
e) PMR spectrum (400 MHz, C_6D_6).

TABLE 2. N-Hydroxymethyl- and N-Aminomethyl-N,N-dialkoxyamines $RO(R'O)NCH_2X$ and $RO(R'O)NCH_2N(CH_2CH_2OCH_2 \cdot CH_2OCH_2CH_2)_2NCH_2N(OR')OR$ (Va, d)

Compound	R	R′	X	Yield, %	bp, °C (p, mm Hg)	PMR spectrum (400 MHz)		Found/Calculated, %		
						solvent	δ, ppm, J, Hz	C	H	N
(IIa)	Me	Me	HO	79,0	66,5(30)	CCl_4 *	2,23(OH, J_{CHOH}=8,25), 3,53(MeO), 3,98(CH_2)	33,69 33,64	8,80 8,47	13,04 13,08
(IId)	Me	$PhCH_2$	HO	93,5	86,5(1)	DMSO-d_6	3,59(MeO), 4,14(CH_2O, J_{AB}=11,0), 4,87, 4,92($PhCH_2$, J_{AB}=11,72), 7,33(Ph)	59,05 59,00	7,10 7,15	7,77 7,65
(III)	Me	Me	$MeCO_2$	37,5	73,5(30)	CCl_4 *	2,00(MeCO), 3,63(MeO), 4,73(CH_2)	40,11 40,27	7,23 7,43	9,34 9,39
(IVc)	Me	*i*-Bu	$O(CH_2CH_2)_2N$	70,1	83(2)	$C_6D_5CD_3$	0,87, 0,90(Me_2C, J_{MeCH}=6,84), 1,85(CH), 2,54(NCH_2), 3,53(OCH_2, $J_{CH_2CH_2}$=4,64), 3,62, 3,67(OCH_2CH, J_{AB}=9,28, J_{CH_2CH}=6,6), 3,65(NCH_2N), 3,52(MeO)	55,06 55,02	9,92 10,15	12,71 12,83
(IVd)	Me	$PhCH_2$	$O(CH_2CH_2)_2N$	62,1	113–118(1)	DMSO-d_6	3,56(MeO), 3,59(NCH_2N), 4,83, 4,89 ($PhCH_2$, J_{AB}=11,47), 7,31(Ph)	61,88 61,89	7,86 7,99	11,02 11,10
(Va)	Me	Me	–	100	–	$CDCl_3$	2,99(NCH_2, $J_{CH_2CH_2}$=6,1), 3,57(OCH_2), 3,59(OCH_2CH_2O), 3,67(MeO), 3,74(NCH_2N)	49,21 49,07	9,31 9,15	12,70 12,72
(Vd)	Me	$PhCH_2$	–	92,6	–	DMSO-d_6	2,84(NCH_2), 3,42(OCH_2, $J_{CH_2CH_2}$=5,71), 3,45(OCH_2CH_2O), 3,56(MeO), 3,68, 3,72(NCH_2N, J_{AB}=12,94), 4,82, 4,87 ($PhCH_2$, J_{AB}=11,23), 7,34(Ph)	60,81 60,79	8,25 8,16	9,47 9,45
(VIa)	Me	Me	Me_2N	57,4	53–54(50)	CCl_4 *	2,28(Me_2N), 3,43(NCH_2N), 3,53(MeO)	44,46 44,76	10,83 10,52	20,60 20,88
(VId)	Me	$PhCH_2$	Me_2N	56,2	69(1)	DMSO-d_6	2,28(Me_2N), 3,53(NCH_2N, J_{AB}=11,9), 3,56(MeO), 4,88, 4,82($PhCH_2$, J_{AB}=11,23), 7,34(Ph)	62,23 62,83	8,66 8,63	13,97 13,32
(VIIa)	Me	Me	Me_3N	72,8	T. пл. 155–157	$CDCl_3$	3,53(Me_3N), 3,80(MeO), 4,81(NCH_2N)	26,05 26,10	6,07 6,21	10,10 10,15
(VIId)	Me	$PhCH_2$	Me_3N	65,1	T. пл. 115–117	DMSO-d_6	3,07(Me_3N), 3,71(MeO), 4,58(NCH_2N) 4,99($PhCH_2$, J_{AB}=12,0), 7,41(Ph)	41,00 40,92	6,11 6,01	7,83 7,95

*PMR spectrum, 60 MHz.

and $n_{\pi}(O)-\sigma^{*}_{C-N}$ orbital interactions in the  segment [9], which are represented in the limiting structures A and B, respectively:

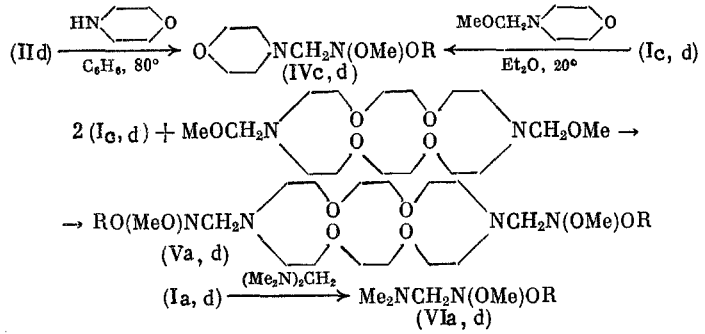


Electrophile attack can take place either at N or O. This is determined by the relative nucleophilicity of these atoms and by the thermodynamic stability of the reaction products. In most of the examples of aminocarbinol reactions with acid chlorides the attack takes place at O, thereby splitting the NCO segment [14]. For methoxymethylethyleneimine the reaction with Ac_2O goes by two competing routes [15]. The contributions of structures A and B to (IIa) are so trivial that its reaction with MeCOCl proceeds just as with an ordinary alcohol without fragmentation of the molecule:

$$(IIa) \xrightarrow[Et_3N]{MeCOCl} (MeO)_2NCH_2OCOMe \quad (III)$$

This example graphically illustrates the decrease of N nucleophilicity in N,N-dialkoxyamines and the decrease of $n_N-\sigma^{*}_{C-O}$ interaction in (II). The difluoroaminocarbonols have analogous properties [12].

The reaction of (II) with nucleophiles can take place by two mechanisms: a) aminomethylation, with participation of structure A, and b) peroxymethylation. The latter mechanism is presumed for the reaction of ethyleneiminocarbinol with amines [16] which goes smoothly at 20°. Carbinol (IId) does not react with Me_2NH under these conditions. The corresponding aminomethyldialkoxyamines are formed when the reaction is carried out under more severe conditions (boiling in C_6H_6 and azeotropic removal of H_2O), or by the reaction of (I) with methoxymethylamines or bis(dimethylamino) methanes:



R = Me (a), *i*-Bu (c), $PhCH_2$ (d).

The properties of the aminomethyl derivatives of N,N-dialkoxyamines (IV)-(VI) should also be determined by the $n_N-\sigma^{*}_{C-N}$ orbital interaction. For aminals, reactions with electrophiles involving their fragmentation are typical [14]. In the case of unsymmetrical aminals, e.g., in the reaction of N,N'-ethyleneiminomethylamines with Ac_2O, electrophile attack takes place at the less basic N atom [17]. When the basicity of one of the N atoms is decreased further, the reaction path changes. Thus, when acylamidomethylamines react with acyl chlorides, acylamidomethyl chlorides form [14]. We have established that just as in the reaction of (VIa) with MeCOCl the electrophile attack is directed at the more nucleophilic N atom:

$$(VIa) \xrightarrow{MeCOCl} Me_2NCOMe + Me_2NCOMe \cdot HCl$$

The formation of dimethylacetamide hydrochloride is apparently due to dehydrochlorination of the intermediate N-chloromethyl-N,N-dialkoxyamine.

In the reaction of (VIa, d) with MeI, the corresponding quaternary ammonium salts (VIIa, d) form; they cannot be made to react in dialkoxyaminomethylation with MeONa (MeOH, 48 h, 20°) or NaCN (MeCN, 72 h, 20°):

TABLE 3. Energy Parameters of N Inversion in N,N-Dialkoxyamines RO(R'O)NX and Aziridines $R_2CCH_2NCH_2X$ (VIIIa, b) and (IXa, b)

Compound	R	R′	X	Solvent	Group observed	$\Delta\nu$, Hz (J_{AB}, Hz)	T_s, °C	k, sec^{-1}	$\Delta G^{\neq}_{T_s}$ kcal/mole	$\Delta G^{\neq}_{25°}$ kcal/mole
(Ic)	Me	*i*-Bu	H	$C_6D_5CD_3$	Me_2C	2,5	92	5,6	20,3	20,4
(Ie)	Et	*i*-Bu	H	$C_6D_5CD_3$	Me_2C	1,8	80	4,0	19,9	20,0
(IId)	Me	$PhCH_2$	$HOCH_2$	DMSO-d_6	$PhCH_2$	8,8(11,72)	130	66,6	20,5	20,7
(IVd)	Me	$PhCH_2$	$O(CH_2CH_2)_2NCH_2$	DMSO-d_6	$PhCH_2$	6,6(11,47)	133	64,1	20,6	20,9
(VId)	Me	$PhCH_2$	Me_2NCH_2	DMSO-d_6	$PhCH_2$	7,3(11,23)	139	63,2	21,0	21,2
(VIId)	Me	$PhCH_2$	$Me_3\overset{+}{N}CH_2$	DMSO-d_6	NCH_2N	7,2(12,0)	32	67,0	15,3	15,4
(VIIIa)	H	–	Me_2N	$CDCl_3$	ring CH_2	49	94	108,8	18,2	18,3
(VIIIb)	Me	–	Me_2N	$CDCl_3$	NCH_2N	10,5(10,5)	40	61,7	15,8	15,8
(IXa)	H	–	$Me_3\overset{+}{N}$	$CDCl_3$	ring CH_2	4,5	0	9,9	14,7	14,6
(IXb)	Me	–	$Me_3\overset{+}{N}$	$CDCl_3$	NCH_2N	5,0(11)	33	60,8	15,4	15,4

$$(\text{VIa., d}) \xrightarrow{\text{MeI}} \underset{(\text{VIIa, d})}{Me_3\overset{\oplus}{N}CH_2(NOMe)ORI^{\ominus}}$$

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

On the other hand, similar ethyleneimine derivatives take part in ethyleneiminomethylation with MeONa (e.g., (IXa), which we prepared for comparative studies from (VIIIa) [16, 18]). This result is also evidence of the weakening of the n_N–σ^*C-N interaction in (VIIa, d) as compared with the corresponding ethyleneimine derivatives:

$$\underset{(\text{VIIIa, b})}{Me_2NCH_2NCH_2CR_2} \xrightarrow[Et_2O]{\text{MeI}} \underset{(\text{IXa., b})}{Me_3\overset{\oplus}{N}CH_2NCH_2CR_2I^{\ominus}}$$

R = H(a), Me(b)

Thus, the chemical behavior of N-hydroxymethyl- and N-aminomethyl-N,N-dialkoxyamines points to the weakening therein of the n_N–σ^*C-X orbital interaction as compared with analogous systems, particularly the corresponding ethylene imine derivatives. This should also affect the structural properties of these molecules. It has already been shown for the X–C–N geminal carbon system [19] that n_N–σ^*C-X interaction decreases the N inversion barrier because of stabilization of the planar transitional state of inversion. With increase of electronegativity of substituent X the σ^*C-X orbital level decreases, the n_N–σ^*C-X interaction increases, and the N inversion barrier decreases. We have determined the N inversion barriers in NH-dialkoxyamines and their hydroxymethyl and aminomethyl derivatives, and in model aziridines (VIIIa, b) and (IXa, b) (Table 3). The indication that the measured barriers in the case of (Ic, e) are related to N inversion, and not to N–H exchange, is the presence in the ^{13}C NMR spectrum of (Ic) of the $^3J_{^{13}C,NH}$ constant (see Table 1) at the merging temperature of the indicator group signals in the PMR spectrum. In contrast to the ethyleneimine derivatives [19], in going from (Ic, e) to (IId), (IVd), and (VId), the N inversion barrier increases. This increase is apparently due to the following. The presence at N of a CH_2X group (where X = O, N) that is more electronegative than H increases the configurational stability of the N atom [20]. But this effect of the electronegative substituent is leveled by the n_N–σ^*C-X interaction thereby produced, that flattens the pyramid of the N atom. The proportions of these factors should determine the configurational stability of the N-hydroxymethyl- or N-aminomethyl-N,N-dialkoxyamines. Comparison of the SSCC $^1J_{^{15}N,H}$ in mono- and dialkoxyamines shows that in this series the S character of the NH bond increases (see Table 1); this is indirect evidence of the increased S character of the orbital of the unshared electron pair of N. In agreement herewith, a significant increase of N inversion barrier in dialkoxyamines [3] over that in monoalkoxyamines [3] and aziridines [21] has been found. The decrease in n_N orbital level in dialkoxyamines causes a decrease in n_N–σ^*C-X orbital interaction in (II) and (IV)-(VI), and it has an insignificant effect on the configurational stability of N. But the effect undoubtedly exists, as evidenced by the regular change of N inversion barrier in going from (IId) to (IVd) and (VId). This is also confirmed by the sharp decrease of $\Delta G^{\neq}$ for (VIId). An analogous change in N inversion barriers takes place in going from aziridine (VIIIa) to aziridinomethylammonium salt (IXa). It is of interest that in going from (VIIIb) to (IXb) the N inversion barrier is practically unchanged, because the n_N–σ^*C-N^+ interaction is sterically suppressed, due to steric hindrance to the achievement of the necessary antiperiplanar orientation of the N unshared electron pair and the C–N^+ σ bond.

EXPERIMENTAL

The NMR spectra were obtained on JNM-C-60HL (60 MHz relative to HMDS) and Bruker WM-400 (400 MHz relative to TMS) spectrometers. N,N-Dialkoxy-N',N'-dimethylureas were obtained according to [5].

GENERAL PROCEDURE FOR SYNTHESIS OF NH-DIALKOXYAMINES (I)

Method a. A mixture of equimolar amounts of N,N-dialkoxy-N',N'-dimethylurea and KOH and catalytic amounts of $Et_3\overset{+}{N}CH_2PhCl^-$ in water were stirred for 4 h at 20°, saturated with NaCl, and extracted with ether [(Ia) and (Ib) were extracted with EtCl]. The extract was dried with $MgSO_4$ and evaporated in the vacuum of a water aspirator [for (Ia) and (Ib), spontaneous evaporation of EtCl]. The residue was distilled or chromatographed on a column (see Table 1).

Method b [for synthesis of (If) or (Ig)]. A solution of equimolar amounts of N,N-dialkoxy-N',N'-dimethylurea in MeONa (or KOH) in absolute MeOH was held at 20° for 1 day. The mixture was saturated with CO_2, and MeOH was removed in vacuum, and the residue was extracted with ether. The extract was evaporated in vacuum, and the residue was chromatographed on a column (see Table 1).

N,N-Dimethoxyaminocarbinol (IIa). A solution of 0.10 g (1.29 mmoles) of (Ia), 0.04 g (1.33 mmoles) of CH_2O, and catalytic amounts of KOH in 4 ml of absolute MeOH was held at 20° for 1 day. MeOH was removed in vacuum, and the residue was distilled to yield 0.11 g of (IIa) (see Table 2).

N-Methoxy-N-benzyloxyaminocarbinol (IId). Under the conditions of the preceding experiment, from 0.25 g (1.63 mmoles) of (Id) and 0.06 g (2 mmoles) of CH_2O in 10 ml of absolute MeOH there was obtained 0.28 g of (IId) (see Table 2).

N-Acetoxymethyl-N,N-dimethoxyamine (III). To a solution of 0.23 g (2.15 mmoles) of (IIa) and 0.22 g (2.15 mmoles) of Et_3N in 8 ml of absolute ether was added at −78° a solution of 0.17 g (2.15 mmoles) of MeCOCl in 2 ml of absolute ether. The mixture was kept for 1 h at −78° and overnight at −8°. The precipitate was separated. From the filtrate the solvent was removed in vacuum, and the residue was chromatographed on a column (Al_2O_3 with ether eluent) and then distilled. There was obtained 0.12 g of (III) (see Table 2).

N-Morpholinomethyl-N-methoxy-N-isobutoxyamine (IVc). A mixture of 0.35 g (2.94 mmoles) of (Ic) and 0.39 g (2.94 mmoles) of N-methoxymethylmorpholine was kept at 20° for 2 days, then vacuum-distilled to yield 0.45 g of (IVc) (see Table 2).

N-Morpholinomethyl-N-methoxy-N-benzyloxyamine (IVd). a) A solution of 0.62 g (3.38 mmoles) of (IId) and 0.29 g (3.38 mmoles) of morpholine in 15 ml of C_6H_6 was boiled for 6 h with constant removal of benzene and readdition to the reaction mixture. C_6H_6 was removed in vacuum, and the residue was distilled to yield 0.53 g of (IVd) (see Table 2).

b) A solution of 0.05 g (0.33 mmole) of (Id) and 0.043 g (0.33 mmole) of N-methoxymethylmorpholine in 2 ml of absolute ether was held at 20° for 1 day. The ether was evaporated in vacuum, and the residue was distilled to yield 0.05 g (60.6%) of (IVd).

N,N'-Bis(dimethoxyaminomethyl)diaza-18-crown-6 (Va). A solution of 0.7 g (2 mmoles) of N,N'-bis(methoxymethyl)diaza-18-crown-6 [22] and 0.34 g (4.4 mmoles) of (Ia) in 15 ml of absolute ether was boiled for 5 h, and the solvent was removed in vacuum. The residue yielded 0.94 g of (Va) (see Table 2).

N,N'-bis(benzyloxymethoxyaminomethyl)diaza-18-crown-6 (Vd) was obtained analogously (see Table 2).

N-Dimethylaminomethyl-N,N-dimethoxyamine (VIa). A mixture of 0.6 g (7.79 mmoles) of (Ia) and 0.87 g (8.57 mmoles) of bis(dimethylamino)methane was heated for 9 h at 90°, then distilled. There was obtained 0.6 g of (VIa) (see Table 2).

N-Dimethylaminomethyl-N-methoxy-N-benzyloxyamine (VId) was obtained analogously (see Table 2).

Reaction of (VIa) with MeCOCl. A solution of 1.39 g (10.36 mmoles) of (VIa) and 0.9 g (11.4 mmoles) of MeCOCl in 20 ml of absolute ether was kept for 1 day at 0°, and the precipitate was removed. There was obtained 0.64 g (50%) of N,N-dimethylacetamide hydrochloride, mp 112-113° (from C_6H_6), which was identified by comparison of PMR spectrum and mp with an authentic sample. The solvent was removed from the filtrate in vacuum, and the residue was distilled to yield 0.31 g (34.3%) of N,N-dimethylacetamide, bp 70° (30 mm), which was identified by comparison of PMR spectrum and bp with an authentic sample.

N,N-Dimethoxyaminomethyltrimethylammonium Iodide (VIIa). A solution of 0.1 g (0.74 mmole) of (VIa) and 0.11 g (0.74 mmole) of MeI in 6 ml of absolute ether was kept at 20° for 4 days. The precipitate was separated and crystallized from MeCN–Et_2O mixture to give 0.15 g of (VIIa) (see Table 2).

N-Methoxy-N-benzyloxyaminomethyltrimethylammonium iodide (VIId) was obtained analogously (see Table 2).

N-Aziridinomethyltrimethylammonium Iodide (IXa). A solution of 1.52 g (15.2 mmoles) of N-dimethylaminomethylaziridine (VIIIa) [16, 18] and 2.5 g (17.7 mmoles) of MeI in 20 ml of absolute ether was kept at 20° for 1 day; the precipitate was removed to give 2.93 g (79.6%)

of (IXa), mp 178°. PMR spectrum (60 MHz, $CDCl_3$); 1.95 (ring CH_2), 3.39 (Me_3N), 4.20 (NCH_2N). Found, %: C 29.40; H 6.09; N 11.19. $C_6H_{15}N_2I$. Calculated, %: C 29.76; H 6.25; N 11.57.

N-2,2-Diemthylaziridinomethyltrimethylammonium Iodide (IXb). This was obtained analogously to (IXa) from 0.68 g (5.3 mmoles) of N-dimethylaminomethyl-2,2-dimethylaziridine (VIIIb) [16, 18] and 0.87 g (6.2 mmoles) of MeI. There was obtained 0.92 g (64.3%) of hygroscopic crystals of (IXb). PMR spectrum (60 MHz, $CDCl_3$): 1.16, 1.32 (Me_2C), 1.92, 1.97 (ring CH_2), 3.34 (Me_2N), 4.24 and 4.42 (NCH_2N, J_{AB} = 11). Found, %: C 35.43; H 6.73; N 10.29. $C_8H_{19}N_2I$. Calculated, %: C 35.57; H 7.09; N 10.37.

CONCLUSIONS

1. Alkaline hydrolysis of N,N-dialkoxy-N',N'-dimethylureas gives NH-dialkoxyamines.

2. N-Hydroxymethyl- and N-aminomethyl-N,N,-dialkoxyamines have been synthesized and their reactions with nucleophiles and electrophiles have been studied.

3. The configurational stability of the N atom in NH-dialkoxyamines and their derivatives has been determined by NMR.

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