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ASYMMETRICAL NONBRIDGEHEAD NITROGEN—XXVI†

SYNTHESIS, CONFIGURATIONAL STABILITY, AND RESOLUTION OF N,N-DIALKOXYAMINES INTO ANTIPODES

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Abstract—Alkoxyamines with tertiary N-alkyl substituents were chlorinated to N-chloro-N-alkoxyamines whose reaction with alcohols enabled synthesis of N,N-dialkoxyamines. The DNMR method was used to determine the barriers of inversion of these compounds. Alkaline hydrolysis (**13**) followed by subsequent reactions with *R*-(+)- and *S*-(−)-α-phenylethylamine yielded diastereomeric salts (+**29** and −**29**) whose crystallization and subsequent esterification resulted in optically active acyclic amines (−**13** and +**13**) with the asymmetric center only at the N atom in the open chain.

The possibility of existence of asymmetrical trivalent N was predicted by Hantzsch and Werner as far back as 1890.[2] However, all attempts to obtain optically active compounds with the center of asymmetry at the N atom were unsuccessful (e.g. Refs. [3, 4]). In 1924 Meisenheimer[5] concluded that it was impossible to resolve such amines because of rapid inversion of the N pyramid. In 1939–40 it was hoped that compounds with asymmetrical N in the 3-membered ring could be resolved,[6–9] but the expectations did not materialise,[6,8,10–12] and in 1958 Roberts[13] proved the impossibility of resolution of aziridines under normal conditions using the PMR method. In the following years, owing to elucidation of the factors controlling the stability of the N pyramid,[14–18] such heterocycles were obtained in an optically active form -N-chloroaziridines,[19–21] oxaziridines,[22–24] diaziridines,[25] and complete resolution of *N*-alkoxyaziridines,[26] diaziridines[27] and N-alkoxyisoxazolidines[28] into antipodes was achieved. However, the question as to the possibility of existence of acyclic amines in an optically active form remained unanswered. This paper is an attempt to solve the problem.

The data summarized in reviews[14–18] suggest that acyclic amines with two electronegative substituents on N, such as dihaloamines and dialkoxyamines, must exhibit high configurational stability. In the presence of one, even the most electronegative substituent, the configurational stability of N is not sufficient for the resolution, in case of Bz(t-Bu)NF $\Delta G^{\neq} = 15.2$ kcal/mole.[29] Dihaloamines are thermally and chemically unstable; therefore we selected dialkoxyamines as the subject of our investigation. There is only one communication[30] on the photochemical synthesis of $RN(OCF_3)_2$ dialkoxyamines, where R = CF_3, n-C_3F_7, i-C_3F_7, the yields not exceeding 5%.

It has therefore become necessary to develop a preparative method for the synthesis of functionally substituted dialkoxyamines suitable for the introduction of an auxiliary chiral substituent. The reaction between chloroamines and alcohols, yielding alkoxyamines[31–33] was used as the starting point. It was assumed that the use of N-chloro-N-alkoxyamines as the chloroamine component would enable the synthesis of dialkoxyamines. N-Chloro-N-alkoxyamines had not been described, but it was known that monochlorination of primary alkoxyamines yielded products of their rearrangement:

$$RONH_2 \xrightarrow{NaOHal} [RON(Hal)H \xrightarrow[-HHal]{} RO\ddot{N}:]$$

$$\rightarrow RON{=}NOR \quad R = t\text{-}Bu^{34},\ Et^{35}$$

$$\rightarrow (RN{=}O)_2 \quad R = t\text{-}Bu,\ EtCMe_2{}^{36}$$

That is why the scheme of rearrangement of the $PhCH_2ONH_2$ monochlorination product through the intermediate oxaziridine, proposed by Paquette,[37] seems to be erroneous. Just as in the previous case, the intermediate product of dissociation seems to be alkoxynitrene:

$$PhCH_2ONH_2 \xrightarrow{HOCl} [PhCH_2ON(Cl)H \xrightarrow[-HCl]{}$$

$$PhCH_2O\ddot{N}: \rightarrow PhCH_2N{=}O \rightarrow PhCH{=}NOH]$$

$$\downarrow$$

$$PhCONH_2$$

The N-chloro-N-alkoxy-N-alkylamines could not be obtained due to their easy dehydrochlorination:[38]

$$EtONHEt \xrightarrow{NaOCl} [EtON(Cl)Et] \xrightarrow[-HCl]{} EtON{=}CHMe$$

However, we succeeded in obtaining N-chloro-N-methoxyamine (**1**) which was thermally unstable and readily dehydrochlorinated, giving O-methylformaldoxime (identified by PMR):

$$MeONHMe \xrightarrow{NaOCl} MeON(Cl)Me \xrightarrow[-NaCl]{} MeON{=}CH_2$$

(**1**)

†See Ref. [1] for Part XXV.

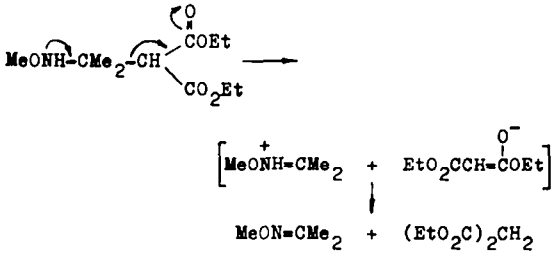
It was assumed that the introduction of a tertiary substituent on the N atom would exclude the possibility of dehydrochlorination, thus ensuring the stability of N-chloro-N-alkoxyamines. Accordingly, alkoxyamines (**2–4**) were obtained

$$MeONH_2 + Me_2C{=}CHCO_2Me \longrightarrow MeONHCMe_2CH_2CO_2Me \quad (\underline{2})$$

$$MeONH_2 + Me_2C{=}C(CO_2Et)_2 \longrightarrow MeONHCMe_2CH(CO_2Et)_2 \quad (\underline{3}) + (EtO_2C)_2CH_2$$

$$MeONH_2 + BrCMe_2CO_2Me \longrightarrow MeONHCMe_2CO_2Me \quad (\underline{4})$$

Owing to the low thermal stability of **3** it decomposes with breakage of the C–C bond into fragments when heated and exposed to bases:



Chlorination of alkoxyamines (**2–4**) under mild conditions in the presence of t-BuOCl yielded N-chloro-N-alkoxyamines (**5–7**):

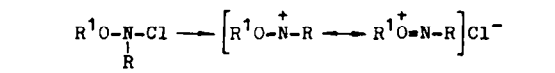
$$RNHOR^1 \xrightarrow{t\text{-}BuOCl} RN(Cl)OR^1$$

R=$MeO_2CCH_2CMe_2$, R^1=Me (**5**)
R=MeO_2CCMe_2, R^1=Me (**6**)
R=$(EtO_2C)_2CHCMe_2$, R^1=Me (**7**)

As expected, they are relatively stable under standard conditions: **5** is distilled in vacuum with heating up to 70° and does not change in CCl_4 within 1 month; **6** decomposes at 20° within 12 days as follows:

$$(\underline{6}) \xrightarrow{20^\circ} (MeO_2CCMe_2N{=}O)_2 \ (66.0\%) + MeO_2CCMe_2NHOMe\cdot HCl \ (21.8\%)$$

The thermal instability of N-chloro-N-alkoxyamines with a primary alkyl substituent at N, as well as their greater tendency to dehydrochlorination, as compared to N,N-dialkylchloroamines, seem to be due to the greater ionic mobility of Cl, promoted by the lone electron pair of oxygen:



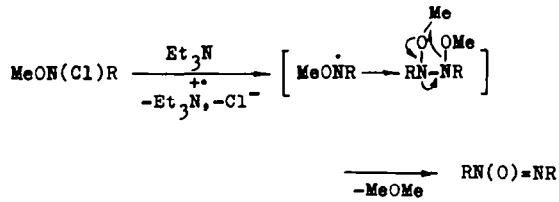
This scheme makes it clear why a nitroso compound is formed during the decomposition of **6**. Interestingly, when the alkoxyl substituent in N-chloro-N-alkoxyamines is replaced by an R_2N group exhibiting a strong +M-effect, that is, as we go from N-chloro-N-alkoxyamines to N-chlorohydrazines, the ionic nature of the N–Cl bond becomes more pronounced. While N-chloro-N-alkoxyamines are mobile distillable liquids, N-chlorohydrazines exist in the form of diazenium salts:[39]

$$R_2\overset{+}{N}{=}NRCl^-.$$

N-Chloro-N-alkoxyamines readily enter into nucleophilic substitution reactions. Thus, throught interaction of **5–7** with alcohols in the presence of a base, N,N′-dialkoxyamines (**8–25**) were synthesized (Tables 1 and 2):

$$R^1ON(Cl)R \xrightarrow[B]{R^2OH} R^1ON(OR^2)R + RN(O){=}NR \qquad B{=}Et_3N,\ R^2ONa$$

The reactions of **5** with t-BuOH and **6** with i-PrOH and t-BuOH in the presence of Et_3N also yield azoxy compounds, probably, in accordance with a radical mechanism involving electron transfer:



The radical nature of this reaction has been corroborated by the presence of a radical with parameters $a^N = 15.7$ and $a^H_{MeO} = 3.5$ G in the EPR spectrum of a freshly prepared solution of Et_3N and **6** in $CHCl_3$ at 20°. This radical is either an aminyl radical MeONR or a product of its oxidation MeON(Ȯ)R.

Thus, the interaction of N-chloro-N-alkoxyamines with alcohols seems to involve three competitive reactions: (1) nucleophilic substitution of $R^{II}O$ for Cl; (2) formation of a nitroso compound during the elimination of MeCl (indicated by the blue coloration during the reaction, typical of nitroso compounds); and (3) formation of an azoxy compound.

In most cases the interaction between N-chloro-N-alkoxyamines and alcohols yields only dialkoxyamines (Table 1). However, in the case of secondary and tertiary alcohols the rate of nucleophilic substitution decreases, and the competitive reactions become predominant. It should be noted that in the reactions **5** forms an azoxy compound only with t-BuOH, whereas **6** containing a larger N-alkyl substituent forms an azoxy compound which is the only product in the reaction with t-BuOH and in the reaction with i-PrOH. The above pattern prevails in reactions in an alcohol medium. When an inert solvent is used, the reaction of **6** with two equivalents of MeOH in Et_2O yields 25% of dialkoxyamine (**16**) and 75% of azoxy compound (**22**). This ratio of products depends on the degree of dilution of the reaction medium.

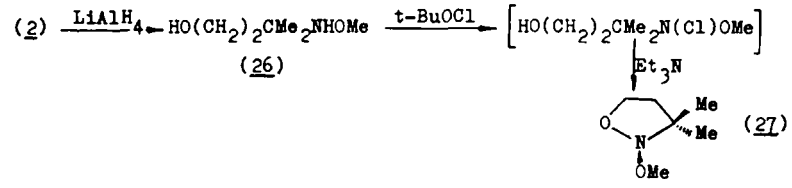
The proposed method for producing dialkoxyamines is applicable for synthesizing heterocyclic systems, such as

Table 1. N,N-Dialkoxyamines

Initial N-chloro-N-alkoxy-amines	Alcohol	Base	Reaction products (compound No.)	Yield, %	B.p., °C (mm Hg) m.p., °C
(5)	MeOH	MeONa	$MeO_2CCH_2CMe_2N(OMe)_2$ (8)	82.0	40 (1)
-,-	EtOH	EtONa	$EtO_2CCH_2CMe_2N(OMe)OEt$ (9)	83.0	53-56 (0.6)
-,-	EtOH	Et_3N	$MeO_2CCH_2CMe_2N(OMe)OEt$ (10)	78.0	56-58 (2)
-,-	i-PrOH	i-PrONa	$i\text{-}PrO_2CCH_2CMe_2N(OMe)OPr\text{-}i$ (11)	39.6	70-71 (1)
			$MeO_2CCH_2CMe_2N(OMe)OPr\text{-}i$ (12)[a]	45.7	67-71 (1)
-,-	$PhCH_2OH$	Et_3N	$MeO_2CCH_2CMe_2N(OMe)OCH_2Ph$ (13)	62.0	107-109 (1)
-,-	t-BuOH	-,-	$MeO_2CCH_2CMe_2N(OMe)OBu\text{-}t$ (14)	20.8	56-58 (1)
			$MeO_2CCH_2CMe_2N(O)=NCMe_2CH_2CO_2Me$ (15)	12.5	93-94 (1)
(6)	MeOH	-,-	$MeO_2CCMe_2N(OMe)_2$ (16)	72.0	42-43 (1)
-,-	EtOH	-,-	$MeO_2CCMe_2N(OMe)OEt$ (17)	75.1	41-42 (1)
-,-	CF_3CH_2OH	-,-	$MeO_2CCMe_2N(OMe)OCH_2CF_3$ (18)	58.9	65 (4)
-,-	$PhCH_2OH$	-,-	$MeO_2CCMe_2N(OMe)OCH_2Ph$ (19)	39.5	98-99 (1)
-,-	$HOCH_2CH_2OH$	-,-	$MeO_2CCMe_2N(OMe)OCH_2CH_2OH$ (20)	56.4	79-81 (1)
-,-	i-PrOH	-,-	$MeO_2CCMe_2N(OMe)OPr\text{-}i$ (21)	31.0	32-34 (1)
			$MeO_2CCMe_2N(O)=NCMe_2CO_2Me$ (22)	26.3	51-52
-,-	t-BuOH	-,-	(22)	70.2	-,-
(7)	MeOH	-,-	$(EtO_2C)_2CHCMe_2N(OMe)_2$ (23)	85.9	91-92 (1)
-,-	EtOH	-,-	$(EtO_2C)_2CHCMe_2N(OMe)OEt$ (24)	87.9	100 (1)
-,-	i-PrOH	-,-	$(EtO_2C)_2CHCMe_2N(OMe)OPr\text{-}i$ (25)	81.3	98 (1)

a) obtained by reesterification of (11)

N-alkoxyisoxazolidines:[40]



Scheme A.

This is the only way to obtain alkylated N-alkoxyisoxazolidines. The previously known method of synthesis by cycloaddition of nitron esters to olefines gives only N-alkoxyisoxazolidines with electronegative substituents in the cycle.[41]

Thus, one of the main tasks of this work has been accomplished—a synthesis of functionally substituted N,N-dialkoxyamines. To attain the principal objective, that is, to separate mirror isomers with an asymmetrical N atom in the open chain, a rational approach had to be taken to the selection of the subject of resolution. A prerequisite was the sufficiently high configurational stability of the selected compound ($\Delta G^{\neq} \geq 23$ kcal/mole). No data have been available on the configurational stability of acyclic amines with two electronegative substituents at *N*. Only an approximate value of $\Delta G^{\neq} > 16$ kcal/mole was mentioned for $CF_2ClN(Cl)F$ and $(CF_3)_2CFN(Cl)F$.[42] For most of the compounds synthesized we established the energy parameters of N inversion by the PMR method from the coalescence of signals belonging to the diastereotopic groups (Table 2) and plotted $\Delta G^{\neq}$ vs electronegativity of the substituent at N for $MeO_2CCH_2CMe_2N(OMe)X$ (Fig. 1). The derived relationship permits prediction of the inversion barriers for the compounds of this series. For example, at X = F an unprecedentedly high inversion barrier ($\Delta G^{\neq} \sim$ 27 kcal/mole) is expected.

The low configurational stability of N-chloro-N-alkoxyamines (5–7; Table 2) makes it impossible to obtain them in an optically active form under normal conditions. This, however, is possible in principle at temperatures below −30° for in the case of 5 $\tau_{1/2}$ = 13.1 hr at −30°. Therefore, we tried to optically activate N-chloro-N-methoxyamine (1) in accordance with the scheme of

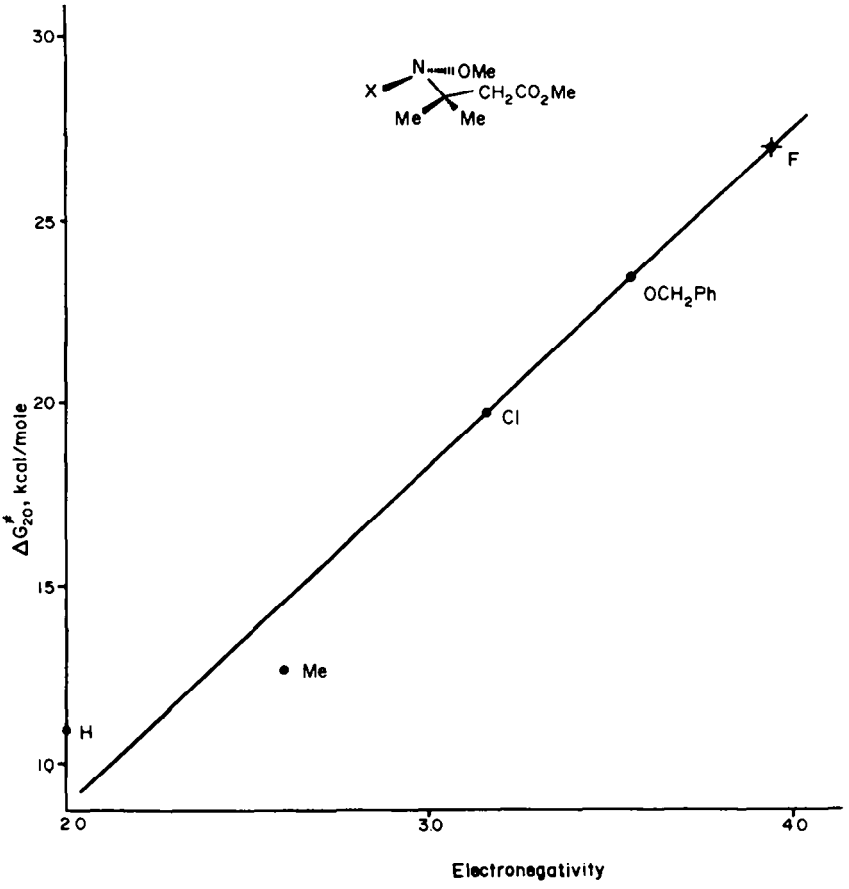
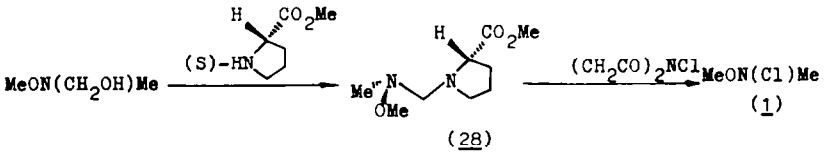


Fig. 1. Inversion barriers of N-derivatives of alkoxyamines vs electronegativity of group X (the electronegativity values of H 2.00, Me 2.60, Cl 3.15, MeO 3.55 and F 3.93 are taken from Ref. [45]). The point for the F was calculated from this plot.

asymmetric synthesis of 1-chloro-2,2-dimethylaziridine:[21] Thus, it took 90 yr for the prediction made by



Scheme B.

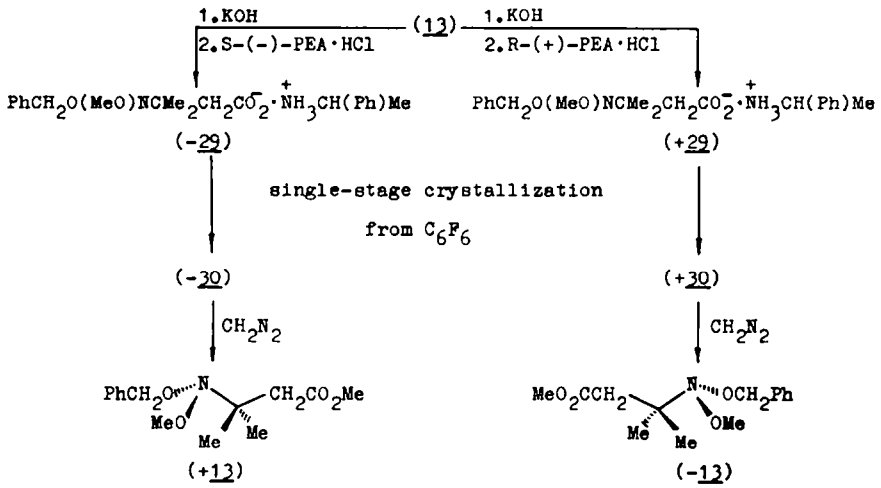
The PMR spectra of **28** at −80° in toluene-d_8 featured diastereomers (ratio 1:1, $MeN\Delta\nu = 11.2$, $MeO_2C\Delta\nu = 1.8$ Hz) which undergo rapid epimerization under normal conditions. Compound **28** was chlorinated at −30°, assuming various rates of the reactions between these diastereomers, but the resulting **1** did not exhibit any optical activity.

As expected,[43] the configurational stability of N,N-dialkoxyamines is sufficient for their existence in an optically active form under standard conditions (Table 2). This has been experimentally substantiated by partial resolution of **13** into antipodes via diastereomeric salts with *S*- and *R*-α-phenylethylamine (PEA; Table 3; preliminary communication[1]):

Hantzsch and Werner to be confirmed. Chances are that compounds of this type exist in Nature which for some purposes employs N chirality.

EXPERIMENTAL

PMR spectra were taken on "Tesla-BS-487 C" (80 MHz) and "JNM-C-60 HL" (60 MHz) spectrometers using HMDS as the internal standard; optical rotation was measured on "Polamat A" and "Perkin Elmer 141" polarimeters; circular dichroism spectra were taken on a "Jobin-Yvon-Dichrographe-III". Methoxyamine[46] (yield, 60%; b.p. 49–50°); N-methoxy-N-methylamine[47] (yield, 76%; b.p. 42°); β,β-dimethylacrylic acid methyl ester[48] (yield, 65%; b.p. 60° (50 mm), n_D^{20}, 1.4382); isopropylidene malonate[49] (yield, 22%; b.p. 140–141°; n_D^{17}, 1.4486); α-bromoisobutyric acid methyl ester[50] [yield, 84.2%; b.p. 53–55° (21 mm)];



Scheme C.

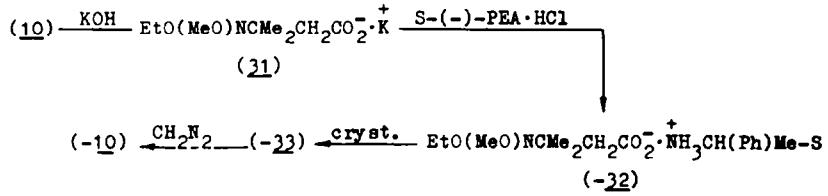
The absence of optically active impurities in +**13** and −**13** follows from their complete racemization at 20°. As found from the kinetics of −**13** racemization in MeOH at 20°, $K_{inv} = 1.85 \pm 0.12 \times 10^{-5} s^{-1}$, $\Delta G_{20}^{\neq} = 23.47 \pm 0.03$ kcal/mole and $\tau_{1/2} = 5.18$ hr. The optical purity of +**13** was determined by the PMR method, using a chiral shift-reagent, $Eu(tfc)_3$ (Fig. 2) and was found to approach 16%.

In a similar manner optically active −**10** was synthesized (Table 3; preliminary communication[44]):

and N-hydroxymethyl-N-methoxy-N-methylamine[51] (yield, 55%; b.p. 38° (8 mm); n_D^{20}, 1.4165) were prepared according to the literature methods.

α-Phenylethylamine was resolved,[52] and *S*-(−)-PEA of 97.4% optical purity, $[\alpha]_D$ − 39.3° pure liquid), and *R*-(+)-PEA of 95.5% optical purity, $[\alpha]_D$ + 38.5° (pure liquid) were used.

N-Chloro-N-methoxy-N-methylamine (**1**). To a soln of NaOCl prepared from 19.2 g (480 mmole) NaOH and 17.0 g (240 mmole) Cl_2 in 78 ml H_2O 12.3 g (200 mmole) N-methyl-N-methoxyamine were added dropwise at − 10°, and the mixture was kept at − 10°



Scheme D.

Table 2. PMR spectra and energy parameters of inversion of N synthesized compounds

Compound [a]	PMR spectrum (80 MHz, δ ppm, J Hz				Δν, Hz	T_c, °C	$\Delta G^{\neq}$ (20°)	$\tau_{1/2}$ (20°)
	Me_2C	CH_2	MeO_2C; MeO	Other groups				
(2)	0.92	2.25	3.21; 3.33	5.79 (NH)	7.0(Me_2C)	-60	11.0	$9.44 \cdot 10^{-6}$ s
(3)	1.21	-	3.30	0.85($\underline{Me}CH_2$, J=7.0) 3.82($\underline{CH_2}Me$), 3.90(CH)	6.0(Me_2C)	-62	10.9	$7.96\ 10^{-6}$ s
(34)[b]	1.00	2.30	3.22; 3.26	2.21 (MeN)	4.8(Me_2C)	-33	12.7	$1.75\ 10^{-4}$ s
(28)	-	-	3.65; 3.75	1.3-2.2(CH_2,m), 2.60(MeN) 2.7-4.3(CH_2N, CHN,m)	11.0 (MeN)	-57	11.0	$9.44\ 10^{-6}$ s
(5)	1.23; 1.26	2.49	3.22; 3.31	-	3.0(Me_2C)	82.5	19.7	29.5 s
(6)	1.33; 1.42	-	3.24; 3.30	-	7.1(Me_2C)	78.5	18.8	6.3 s
(7)	1.60; 1.63	-	3.33	0.80($\underline{Me}CH_2$, J=7.0) 3.78; 3.80($\underline{CH_2}Me$) 3.97(CH)	2.3(Me_2C)	55	18.6	4.4 s
(10)	1.17	2.50	3.27; 3.40	0.94($\underline{Me}CH_2$, J=7.0) 3.66; 3.75($\underline{CH_2}Me$, J_{AB}=2.3)	3.0($\underline{CH_2}Me$)	175	24.6	37.5 h
(13)	1.18	2.50	3.29; 3.41	4.74(CH_2O, J_{AB}=12.0)	2.5($\underline{CH_2}Ph$)	165	22.6	1.22 h
(12)	1.15	2.49	3.35; 3.48	1.03; 1.04 ($\underline{Me}_2CH$) 3.98(CH, J=6.9)	2.6($\underline{Me}_2CH$)	114	21.7	0.26 h
(17)	1.27	-	3.40; 3.48	0.95($\underline{Me}CH_2$, J=7.0) 3.79; 3.81($\underline{CH_2}Me$, J_{AB}=2.0)	2.0($\underline{CH_2}Me$)	143	23.6	6.8 h
(18)	1.24; 1.28	-	3.28; 3.34	3.99($\underline{CH_2}O$, $J_{CH_2CF_3}$=9.1)	3.5(Me_2C)	123	22.0	0.43 h
(20)	1.26; 1.33	-	3.38; 3.50	3.54; 3.81 (CH_2O)	3.3(Me_2C)	130	22.4	0.86 h
(21)	1.29; 1.33	-	3.38; 3.49	1.00; 1.03($\underline{Me}CH$, J=6.5) 4.03(CH)	2.7(Me_2C)	118	21.9	0.37 h
(25)	1.39; 1.43	-	3.46	0.91; 0.92($\underline{Me}CH_2$, J=7.0) 0.99; 1.02($\underline{Me}CH$, J=6.5) 3.89; 3.91($\underline{CH_2}Me$) 3.99(CH)	2.2(Me_2C)	121	22.2	0.61 h

[a] (7) in C_6H_6, (17), (12), (13), (20), (21), (25) in Ph_2O; the rest in toluene-d_8

[b] obtained by alkylation of (2) with MeI. see Experimental.

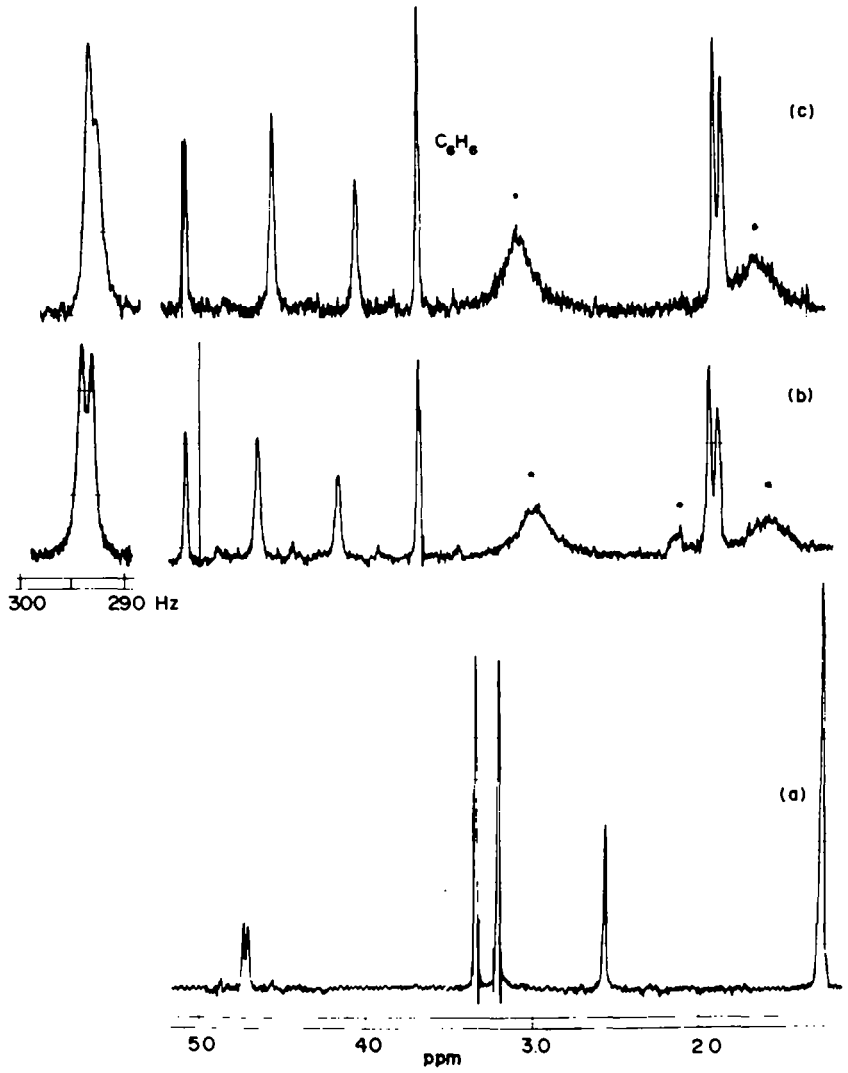


Fig. 2. PMR spectra (80 MHz, C_6H_6, δ of HMDS): (a) normal spectrum of racemate (13); (b) spectrum of racemate (13) in the presence of $Eu(tfc)_3$, $C_{p/s} = 0.87$; (c) spectrum of (+13) in the presence of $Eu(tfc)_3$, $C_{p/s} = 0.91$. In the case of (b) and (c) the asterisk indicates the shift-reagent signals; the signature of signals of MeO of enantiomer groups is on the left.

Table 3. Optically active N,N-dialkoxyamines

Compound	Yield, %	Melting point, °C	$[\alpha]_D^{20}$ (c MeOH)
(-29)	88.0 [a]	85–89	-2.84° (3.9)
(+29)	90.6 [a]	82–88	2.00° (5.5)
(-30)	28.0	99–102	-0.40° (5.2)
(+30)	40.0	98–102	0.36° (2.5)
(+13)	55.7	- [b]	3.48° (5.5) [c]
(-13)	64.3	- [b]	-3.21° (1.7)
(-32)	97.6	70–74	-6.13° (1.6)
(-33)	25.1	82–84	-4.50° (1.4)
(-10)	66.5	- [b]	-0.34° (5.8)

[a] as calculated for the reacted (13)

[b] separated chromatographically on silica gel

[c] $\Delta\varepsilon_{max}$ = -0.010 (266 nm), -0.014 (260 nm), -0.009 (254 nm) and > -0.041 (λ < 230 nm)

for 14 min. The upper layer of the product was separated, dried over $MgSO_4$, and distilled, yielding: 1.0 g (5.2%) of **1**, b.p. 34 to 34.5°C (200 mm), PMR spectrum ($CHCl_3$, δ ppm): 3.62 (MeO), 2.61 (MeN). (Found: C, 24.85; H, 6.30; N, 14.84. Calc. for C_2H_6ClNO: C, 25.14; H, 6.33; N, 14.66%).

β-Methoxyaminoisovaleric acid methyl ester (**2**). A mixture of 3.76 g (80 mmole) $MeONH_2$ and 4.30 g (38 mmole), β,β-dimethylacrylic acid methyl ester was heated in a sealed ampoule for 14 days at 60–80° yielding after distillation 1.8 g $MeONH_2$ and 3.97 g (63.3%) of **2**, b.p. 65° (10 mm), n_D^{18} 1.4250 (Table 2). (Found: C, 52.28; H, 9.31; N, 8.62. Calc. for $C_7H_5NO_3$: C, 52.16; H, 9.38; N, 8.69%).

β-Methoxyaminoisopropylmalonic acid diethyl ester (**3**). A soln of 18.46 g (92 mmole) isopropylidene malonate and 4.70 g (100 mmole) $MeONH_2$ in 30 ml abs C_6H_6 was kept at 20° for 16 days. The solvent was removed in vacuum, the residue was distilled, yielding 3.30 g (22.3%) malonic ester, b.p. 73° (6 mm), and 13.48 g (59%) of **3**, b.p. 76–77° (1 mm), n_D^{20} 1.4332 (Table 2). (Found: C, 53.41; H, 8.57: N, 5.60. Calc. for $C_{11}H_{21}NO_5$: C, 53.43; H, 8.56; N, 5.66%).

Thermal decomposition of **3**. 2.47 (10 mmole) of **3** were heated for 10 hr under reflux on a boiling water bath and then fractionated yielding 0.48 g (55.1%) *o*-methylacetoxime, b.p. 72° (lit. data: b.p. 70–73°,[53] also identified by the PMR spectrum), and 1.01 g (63%) malonic ester, b.p. 73° (6 mm).

α-Methoxyamino-isobutyric acid methyl ester (**4**). A mixture of 7.52 g (160 mmole) $MeONH_2$ and 14.4 g (79 mmole), α-bromo-isobutyric acid methyl ester was heated in a sealed ampoule for 75 hr at 60–70°. The mixture was diluted with 100 ml Et_2O, saturated with HCl, the ppt extracted with H_2O, the water extract washed with ether and neutralized with $NaHCO_3$aq. The product was extracted with ether, dried over $MgSO_4$, the ether was removed in vacuum, and the residue distilled yielding 4.13 g (35.3%) of **4**, b.p. 56° (13 mm), PMR spectrum (CCl_4, δ ppm): 3.60: 3.39 (MeO_2C, MeON), 1.16 (Me_2C). (Found: C, 48.67; H, 8.80; N, 9.72. Calc. for $C_6H_{13}NO_3$: C, 48.97; H, 8.90; N, 9.52%).

β - (N - Chloro - N - methoxyamino) - isovaleric acid methyl ester (**5**). To a soln of 0.81 g (5 mmole) of **2** in 10 ml abs Et_2O at −78° was added a soln of 0.76 g (7 mmole) t-BuOCl in 10 ml abs Et_2O, the mixture was kept at this temp for 1 hr, the solvent removed in vacuum, and the residue distilled yielding 0.62 g (64%) of **5**, b.p. 40–41° (0.7 mm) (Table 2). (Found: C, 43.31; H, 7.30; N, 7.11. Calc. for $C_7H_{14}NO_3Cl$: C, 42.97; H, 7.21; N, 7.16%).

α - (N - Chloro - N - methoxyamino) - isobutyric acid methyl ester (**6**). This was prepared under the same conditions as **5** from 1.03 g (7 mmole) of **4** and 1.16 g (11 mmole) t-BuOCl in 15 ml abs Et_2O. The product was not distilled; quantitative yield (Table 2).

β - (N - Chloro - N - methoxyamino) - isopropylmalonic acid dithyl ester (**7**). Prepared as for **6** from 1.24 g (5 mmole) of **3** and 0.76 g (7 mmole) t-BuOCl in 20 ml Et_2O; quantitative yield (Table 2).

Decomposition of **6**. 1.43 g (7.73 mmole) of **6** were kept in an open flask for 12 days, extracted with ether which was then removed in vacuum (70 mm) yielding 0.69 g (65%) of dimer of α-nitroso-isobutyric acid methyl ester, m.p. 111–113° from hexane (lit. data: m.p. 104–105° from MeOH[54]), PMR spectrum (CCl_4, δ ppm): 1.50 (Me_2C), 3.64 (MeO_2C). (Found: C, 46.25; H, 7.13; N, 10.67. Calc. for $C_{10}H_{18}N_2O_6$: C, 45.80; H, 6.92; N, 10, 68%). The residue undissolved in ether yielded 0.32 g (22%) hydrochloride of **4**, m.p. 105–109° (from $CHCl_3$–hexane, 1:1, PMR spectrum (CD_3OD, δ ppm): 1.53 (Me_2C); 3.79, 3.91 (MeO_2C, MeON).

β - (N,N - Dimethoxyamino) - isovaleric acid methyl ester (**8**). Compound **5** (obtained by the above procedure from 0.48 g (3 mmole) of **2** and 0.42 g (4 mmole) t-BuOCl) was treated at −78° with a soln of 4 mmole MeONa in 10 ml abs MeOH. The mixture was kept at this temp for 1 hr, then at 20° for another hour; the solvent was removed in vacuum, the residue was extracted with abs ether, the ether was removed in vacuum, and the residue was distilled yielding 0.47 g of **8**, n_D^{20} 1.4270 (Table 1), PMR spectrum (toluene − d_8, δ ppm): 1.1 (Me_2C), 2.39 (CH_2), 3.53 (MeO_2C), 3.62 (MeO). (Found: C, 50.10; H, 9.31: N, 7.52. Calc for $C_8H_{17}NO_4$: C, 50.25: H, 8.96; N, 7.32%).

β - (N - Methoxy - N - ethoxyamino) - isovaleric acid ethyl ester (**9**). To **5**, obtained from 3.22 g (20 mmole) of **2** and 3.15 g (30 mmole) t-BuOCl, a soln of 22 mmole EtONa in 20 ml abs EtOH was added at −78°. The mixture was kept for 1 hr at this temp, then for a day at 20°. The solvent was removed in vacuum, the residue was extracted with abs ether which was then removed in vacuum, and the residue was distilled yielding 3.65 g of **9** (Table 1), n_D^{20} 1.4270, PMR spectrum (C_6H_6, δ ppm, J Hz): 0.86, 3.70 (EtON, J = 7, J_{AB} = 2.3, $\Delta\nu_{AB}$ = 7.5), 0.89, 3.84 (EtO_2C, J = 7), 1.26 (Me_2C), 2.58 (CH_2), 3.39 (MeO). (Found: C, 54.51; H, 9.51; N, 6.41. Calc. for $C_{10}H_{21}NO_4$: C, 54.77; H, 9.65; N, 6.39%).

β - (N - Methoxy - N - isopropoxyamino) - isovaleric acid isopropyl ester (**11**). To a soln of 16 mmole i-PrONa in 100 ml abs i-PrOH, **5**, obtained from 2.42 g (15 mmole) of **2** and 2.11 g (20 mmole) t-BuOCl, was added dropwise at 20° under stirring. The mixture was allowed to stand for 2 days at 20°, the solvent was removed in vacuum, the residue was extracted with abs ether, the ether was removed in vacuum, and the residue was distilled yielding 1.47 g of **11** (Table 1), PMR spectrum (toluene-d_8, δ ppm, J Hz): 0.97, 1.01 and 3.93 (i-PrON, J = 6.5), 0.97 and 4.86 (i-PrO_2C, J = 6.5), 1.22 (Me_2C), 2.54 (CH_2), 3.42 (MeON).

β - (N - Methoxy - N - isopropoxyamino) - isovaleric acid methyl ester (**12**). Prepared by re-esterification of **11** by boiling for 20 hr in abs MeOH with a catalytic quantity of MeONa (Tables 1 and 2). (Found: C, 54.68, H, 9.59, N, 6.28. Calc. for $C_{10}H_{21}NO_4$: C, 54.77, H, 9.65, N, 6.39%).

General procedure of synthesis of N,N-*dialkoxyamines* (**10**, **13**, **16–20** *and* **23–25**). To **5**, **6** or **7** a soln of an equimolar amount of Et_3N in alcohol was added at −78°. The mixture was kept for 1 hr at this temp, cooling was discontinued, the temp was raised to 20° and maintained for 1 hr. The alcohol was removed in vacuum, the residue was extracted with ether which was removed in vacuum, and the residue was distilled. In the case of $PhCH_2OH$ the mixture was washed with H_2O, dried over $MgSO_4$, and distilled. In case of reaction with ethylene glycol, the residue after the removal of the ether was extracted with CCl_4, the CCl_4 was removed in vacuum and the residue was distilled. The yields and b.ps of the products are given in Table 1; the data of the PMR spectra for some of these products are given in Table 2. (Found for **10**: C, 52.33; H, 9.01; N, 7.10. Calc. for $C_9H_{19}NO_4$: C, 52.67; H, 9.33; N, 6.82%; Found for **13**: C, 63.04; H, 7.93; N, 5.31. Calc. for $C_{14}H_{21}NO_4$: C, 62.90; H. 7.92; N, 5.24%). For **16**, PMR spectrum (CCl_4, δ ppm): 1.21 (Me_2C), 3.59 (MeO_2C), 3.64 (MeO). (Found: C, 47.66; H, 8.64; N, 7.99. Calc. for $C_7H_{15}NO_4$: C, 47.45; H, 8.53; N, 7.90%: Found for **17**: C, 50.07; H, 8.87; N, 7.60. Calc. for $C_8H_{17}NO_4$: C, 50.25; H, 8.96; N, 7.32%; Found for **18**: C, 39.70; H, 6.15; N, 5.72. Calc. for $C_8H_{14}NO_4F_3$: C, 39.19; H, 5.76; N, 5.71%). For **19**, PMR spectrum (toluene-d_8, δ ppm): 1.34 (Me_2C), 3.27, 3.41 (MeON, MeO_2C), 4.8 (CH_2), 7.04 (Ph). (Found: C, 61.41; H, 7.47; N, 5.29. Calc. for $C_{13}H_{19}NO_4$: C, 61.64; H, 7.56; N, 5.53%; Found for **20**: C, 46.21; H, 8.25; N, 6.87. Calc. for $C_8H_{17}NO_5$: C, 46.37; H, 8.27; N, 6.76%). For **23**, PMR spectrum (60 MHz, CCl_4, δ ppm, J Hz): 1.26 (Me_2C), 1.26, 4.18 (Et, J = 7.5), 3.7 (MeO and CH). (Found: C, 51.46; H, 8.02; N, 5.03. Calc. for $C_{12}H_{23}NO_6$: C, 51.97; H, 8.35; N, 5.05%). For **24**, PMR spectrum (60 MHz, CCl_4, δ ppm): 1.09, 4.13 (EtON, J = 7), 1.25 (Me_2C), 1.25, 4.13 (EtO_2C, J = 7.5), 3.63 (MeON), 3.66 (CH). (Found: C, 53.37; H, 8.59; N, 4.60. Calc. for $C_{13}H_{25}NO_6$: C, 53.59; H, 8.64; N, 4.81%; Found for **25**: C, 55.57; H, 8.52; N, 4.73. Calc. for $C_{14}H_{27}NO_6$: C, 55.07; H, 8.91; N, 4.59%).

Reaction of **5** *with* t-BuOH. To a soln of 1.01 g (10 mmole) Et_3N in 10 ml t-BuOH, 1.56 g (8 mmole) of **5** was added dropwise at 20° under stiring; after 3 hr t-BuOH was removed in vacuum, the residue was extracted with ether, the ether was removed in vacuum, and the residue was distilled yielding 0.38 g of **14** (Table 1), PMR spectrum (CCl_4, δ ppm): 1.08 and 1.11 (Me_2C), 1.15 (Me_3CO), 2.48 (CH_2), 3.51 (MeON and MeO_2C). (Found: C, 56.64; H, 9.68; N, 6.36. Calc. for $C_{11}H_{23}NO_4$: C, 56.53; H, 9.94; N, 6.00%. In addition, 0.14 g of **15** (Table 1) were obtained, PMR spectrum (CCl_4, δ ppm): 1.28 and 1.50 (Me_2C), 2.68 and 2.73 (CH_2), 3.50 and 3.54 (MeO_2C). (Found: C, 52.55; H, 8.08; N, 10.37. Calc. for $C_{12}H_{22}N_2O_5$: C, 52.54; H, 8.08; N, 10.21%).

Reaction of **6** *with* i-PrOH. To 1.40 g (7.7 mmole) of **6**, a soln of 1.01 g (10 mmole) Et_3N in 15 ml abs i-PrOH was added at

−78°, the mixture was kept at this temp for 10 min, at −8° for 1.5 hr, and at 20° for 2 hr. The alcohol was removed in vacuum, the residue was extracted with ether which was then removed in vacuum, and the residue was distilled yielding 0.49 g of **21** (Tables 1 and 2). (Found: C, 52.51; H, 9.24; N, 6.88. Calc. for $C_9H_{19}NO_4$: C, 52.67; H, 9.33; N, 6.82%). Isolated from the bottoms by sublimination in vacuum (75–85° at 1 mm) were 0.25 g of **22** (Table 1), PMR spectrum (C_6H_6, δ ppm): 1.36 and 1.48 (Me_2C), 3.21 and 3.26 (MeO_2C). (Found: C, 49.37; H, 7.54; N, 11.00. Calc for $C_{10}H_{18}N_2O_5$: C, 48.77; H, 7.37; N, 11.36%).

Reaction of **6** *with* t-BuOH. To a soln of 1.01 g (10 mmole) Et_3N in 10 ml t-BuOH, 1.44 g (8 mmole) of **6** was added dropwise at 20° under stirring, the mixture was stirred for 3.5 hr, t-BuOH was removed in vacuum, the residue was extracted with ether, the ether was removed in vacuum, and 0.69 g of **22** (Table 1) was obtained from the residue by sublimation (80–100° at 1 mm).

3 - *Methoxyamino* - 3 - *methylbutanol* - 1 (**26**). To a suspension of 0.57 g (15 mmole) of LAH in 10 ml abs ether, 1.93 g (12 mmole) of **2** in 10 ml abs ether was added dropwise under stirring and simmering. The mixture was stirred for another hour and kept overnight. For decomposition of excess LAH, 0.5 ml H_2O, 0.5 ml 15% KOHaq, and 1.5 ml H_2O were added dropwise in succession, the residue was separated, the filtrate was evaporated in vacuum, and the residue was distilled yielding 0.92 g (57.5%) of **26**, b.p. 83° (11 mm), PMR spectrum (CCl_4, δ ppm, J Hz): 1.04 (Me_2C), 1.53 (CH_2), 3.22 (NH), 3.28 (OH), 3.43 (MeON), 3.58 (CH_2O, J = 6). (Found: C, 54.32; H, 11.21; N, 10.46. Calc. for $C_6H_{15}NO_2$: C, 54.11; H, 11.35; N, 10.52%).

2 - *Methoxy* - 3,3 - *dimethylisoxazolidine* (**27**). To a soln of 0.71 g (6.5 mmole) t-BuOCl in 3 ml abs ether, a soln of 0.85 g (6.3 mmole) of **26** in 5 ml abs ether was added dropwise at −78° under stirring; then, 5 min later, a soln of 0.66 g (6.5 mmole) Et_3N in 3 ml abs ether. The temp was raised to 20°, the residue was separated, the filtrate was washed with H_2O and dried over $MgSO_4$, the ether was removed in vacuum (70 mm), and the residue was distilled yielding 0.37 g (44.8%) of **27**, b.p. 66–67° (80 mm), PMR spectrum (C_6H_6, δ ppm): 0.88 and 1.14 (Me_2C), 1.24 to 2.18 and 3.55–4.02 (CH_2 and CH_2O), 3.43 (MeO). (Found: C, 54.91; H, 9.62; N, 10.72. Calc. for $C_6H_{13}NO_2$: C, 54.94; H, 9.99; N, 10.68%).

(S) - N - *Methoxy* - N - *methylaminomethylproline methyl ester* (**28**). A soln of 7.40 g (57 mmole), *l*-proline methyl ester in 10 ml C_6H_6 was added to a soln of 5.23 g (57 mmole) N - hydroxymethyl - N - methoxy - N - methylamine in 10 ml C_6H_6 at 20° under stirring. Two days later the separated H_2O was removed, the benzene soln was dried over $MgSO_4$, the benzene was removed in vacuum, and the residue was distilled yielding 5.31 g (45.7%) of **28**, b.p. 65° (1 mm), $[\alpha]_D^{20}$ −58.4° (*c* 1.49 MeOH) (Table 2). (Found: C, 53.30; H, 8.81; N, 13.87. Calc. for $C_9H_{18}N_2O_3$: C, 53.44; H, 8.97; N, 13.85%).

Reaction of **28** *with* N-*chlorosuccinimide.* A soln of 1.01 g (5 mmole) of **28** in 4 ml abs $CHCl_3$ was added during 15 min to a suspension of 1.51 g (8 mmole) N-chlorosuccinimide in 4 ml abs $CHCl_3$ at −60° under stirring. The mixture was stirred for 1 hr at −30° then in vacuum at the same temp (1 mm), the solvent and the product were recondensed into a trap cooled down to −78°. The product, namely N - chloro - N - methoxy - N - methylamine, was identified in soln by the PMR spectrum.

(S) - (−) - α - *Phenylethylammonium salt of* β - (N - *methoxy* - N - *benzyloxyamino*) - *isovaleric acid* (−**29**). A soln of 2.52 g (9.4 mmole) of **13** and 0.53 g (9.4 mmole) KOH in 10 ml abs MeOH was kept for 2 days at 20°, then boiled for 8 hr with a reflux condenser and, after cooling, treated with a soln of 1.48 g (9.4 mmole) (*S*) - (−) - α - phenylethylamine hydrochloride in 5 ml MeOH. After the removal of MeOH in vacuum the residue was extracted with abs ether, the ether was removed in vacuum, and the residue was extracted with pentane. The residue, insoluble in pentane, was dried in vacuum yielding 2.62 g of −**29** (Table 3), PMR spectrum ($CDCl_3$, δ ppm, J Hz): 1.08 (Me_2C), 1.46 (MeCH, J = 7), 2.28 (CH_2), 3.53 (MeON), 4.11 (CHMe), 4.71 and 4.89 (CH_2O, J_{AB} = 12), 7.21 (Ph). 0.39 g of unreacted **13** were isolated from the pentane extract.

(R) - (+) - α - *Phenylethylammonium salt of* β - (N - *methoxy* - N - *benzyloxyamino*) - *isovaleric acid* (+**29**). Under similar conditions, 1.64 g of +**29** (Table 3) (spectrally identical with −**29**) and 0.44 of unreacted **13** were obtained from 1.73 g (6.5 mmole) of **13**, 0.39 g (7 mmole) KOH, and 1.01 g (6.5 mmole) (*R*) - (+) - α - phenylethylamine hydrochloride.

Crystallization of diastereomeric salts (−**29** *and* +**29**). 2.53 g of −**29** were crystallyzed from 15 ml C_6F_6 yielding 0.71 g of −**30** (Table 3), the PMR spectrum is similar to that of −**29**. (Found: C, 67.21; H, 7.91; N, 7.59. Calc. for $C_{21}N_{30}N_2H_4$: C, 67.21; H, 8.07; N, 7.48%). 1.6 g of +**29** were crystallized from 8.5 ml C_6F_6 yielding 0.64 g of +30 (Table 3), the PMR spectrum is similar to that of +29. (Found: C, 67.31; H, 8.01; N, 7.32. Calc. for $C_{21}H_{30}N_2O_4$: C, 67.36; H, 8.07; N, 7.48%).

(+) - β - (N - *Methoxy* - N - *benzyloxyamino*) - *isovaleric acid methyl ester* (+**13**). An ether soln of CH_2N_2 was added to a soln of 0.63 g (1.7 mmole) of −**30** in 2 ml MeOH at 0° till a stable yellow color was achieved. The solvent was removed in vacuum, the residue was dissolved in 50 ml cold pentane and bubbled with CO_2 at 0°. The ppt was separated, the solvent was removed in vacuum, the residue was dissolved in 1 ml abs ether, and 0.1 g MeI was added to the resulting soln. The mixture was kept overnight at −4°, the solvent was removed in vacuum, the residue was chromatographed on a column (silica gel, ether–pentane, 1:1). 0.25 g of +**13** (Table 3) was obtained. Its PMR and mass spectra were identical to those of **13**.

(−) - β - (N - *Methoxy* - N - *benzyloxyamino*) - *isovaleric acid methyl ester* (−**13**). Under similar conditions, 0.28 g of −**13** (Table 3) was obtained from 0.61 g (1.6 mmole) of +**30** and an ether soln of CH_2N_2. Its pmr and mass spectra are similar to those of **13**.

β - (N - *Methoxy* - N - *ethoxyamino*) - *isovaleric acid potassium salt* (**31**). A soln of 2.03 g (9.3 mmole) of **10** and 0.56 g (10 mmole) KOH in 10 ml abs MeOH was kept overnight at 20°, then boiled for 1 hr with a reflux condenser. MeOH was removed in vacuum, the residue was washed with abs ether and dried in vacuum. 2.04 g (96.1%) of hygroscopic **31** was obtained, which was identified by the PMR spectra (CD_3OD, δ ppm, J Hz): 1.10 (MeCH$_2$), 1.16 (Me_2C), 2.34 (CH_2), 3.62 (MeON), 3.87 and 3.96 (CH$_2$Me, J_{AB} = 7.1).

(S) - (−) - α - *Phenylethylammonium salt of* β - (N - *methoxy* - N - *ethoxyamino*) - *isovaleric acid* (−**32**). To a soln of 2.64 g (11.5 mmole) of **31** in 5 ml abs MeOH, a soln of 1.81 g (11.5 mmole) (*S*) - (−) - α - phenylethylamine hydrochloride was added, the ppt was separated, MeOH was removed, the residue was extracted with abs ether, and the ether was removed in vacuum yielding 3.52 g of −**32** (Table 3), PMR spectrum ($CDCl_3$, δ ppm, J Hz): 1.03 (Me_2C), 1.09 (MeCH$_2$, J = 7), 1.46 (MeCH, J = 7), 2.14 (CH_2), 3.58 (MeON) 3.95 (CH$_2$Me, CH mult.), 7.25 (Ph).

Crystallization of diastereomeric salt (−**32**). 3.3 g of −**32** were crystallized from a mixture of 15 ml pentane and 8 ml CCl_4 yielding 0.83 g of −**33** (Table 3). Its PMR spectrum is similar to that of −**32**. (Found: C, 61.63; H, 8.96; N, 8.71. Calc. for $C_{16}H_{28}N_2O_4$: C, 61.51; H, 9.03; N, 8.97%).

(−) - β - (N - *Methoxy* - N - *ethoxyamino*) - *isovaleric acid methyl ester* (−**10**). To a soln of 0.78 g (2.5 mmole) of −**33** in 2 ml MeOH an ether soln of CH_2N_2 was added till a stable yellow color was obtained. The solvent was removed in vacuum, the residue was chromatographed on a column (silica gel, eluent—first ether, then $CHCl_3$). 0.34 g of −**10** (Table 3) were obtained. Its PMR and mass spectra are similar to those of **10**.

β - (N - *Methoxy* - N - *methylamino*) - *isovaleric acid methyl ester* (**34**). A mixture of 1.13 g (7 mmole) of **2**, 1.99 g (14 mmol) MeI, and 1.93 g (14 mmole) K_2CO_3 in 10 ml abs MeCN was boiled with a reflux condenser for 20.5 hr, the ppt was separated, MeCN was removed, and the residue was distilled yielding 0.48 g (39%) of **34**, b.p. 64–65° (7 mm) (Table 2). (Found: C, 55.20; H, 9.64; N, 8.29. Calc. for $C_8H_{17}NO_3$: C, 54.81; H, 9,78; N, 8.00%).

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