Intramolecular Cyclization of 1,2-Bis(*N*-alkoxy-*N*-nitrosoamino)alkanes: A Unique Route to 4,5-Dihydro-1,2,3-triazole 2-Oxides

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Dedicated to Prof. Leonid B. Volodarsky, founder of the Laboratory of nitrogenous compounds

Abstract: 1,2-Bis(*N*-alkoxy-*N*-nitroso)amines **7** obtained by nitrosation of the corresponding 1,2-bisalkoxyamines **4** were smoothly converted into 1-alkoxy-4,5-dihydro-1,2,3-triazole 2-oxides **8** under reflux in methanol in high yields. 4*H*-1,2,3-Triazole 2-oxides **9,** a novel type of triazole oxides, and 2-hydroxy-2*H*-1,2,3-triazoles **10** were obtained by the reaction of 1-alkoxy-4,5-dihydro-1,2,3-triazole 2-oxides **8** with sodium methoxide.

Key words: 1,2-bisalkoxyamines, 1,2-bis(*N*-alkoxy-*N*-nitroso)amines, 1,2-bis(nitrosohydroxylamines), 1,2,3-triazole 2-oxides, intramolecular cyclization, nitrogen, nitrosation, heterocycles

Introduction

N-Nitroso derivatives of *N,O*-disubstituted hydroxylamines still remain an insufficiently known class of organic compounds. Despite the fact that they were first synthesized in the last century,[1] their study was limited to the examination of spectroscopy data[2] and *E,Z*-isomerism of *N*-nitroso group.[3] Their reduction leads to corresponding alkoxyamines[4] whereas reaction with organolithium compounds and Grignard reagents is known to form azoxyalkanes.[5] In the last decade *N*-nitroso derivatives of *N,O*-disubstituted hydroxylamines have been drawing attention as isosteric biomimetics of unstable carcinogenic α-hydroxynitrosoamines generated from nitrosoamines in vivo. In this connection their thermolysis and hydrolysis have been investigated by Kano and Anselme.[6] In addition, a new deamination of *N,O*-disubstituted hydroxylamine *N*-nitroso derivatives, resulting in ethers has been reported recently.[7] There are no examples of the involvement of *N*-nitrosoalkoxyamines into heterocyclic ring construction in contrast to the parent *N*-nitrosohydroxylamines.[8]

Furthermore *N*-nitroso derivatives of *N,O*-disubstituted hydroxylamine might appear to resemble *N*-nitrosohydroxylamines as donors of nitric oxide (NO), a well-known multifunctional cell mediator.[9] Finally NO liberation has been shown to cause specific DNA cleavage under thermal or photoinduced conditions.[8]

Two basic approaches to the *N*-nitrosoalkoxyamines are known. The first is alkylation of *N*-nitrosohydroxylamines. However, this reaction gives alkoxydiazene oxides as major products while the unstable *N*-nitrosohydroxylamines could not be isolated in satisfactory yields.[2,10] More conveniently *N,O*-disubstituted hydroxylamine *N*-nitroso derivatives can be prepared by nitrosation of the corresponding *N,O*-dialkylhydroxylamines.[1,2,4,6a]

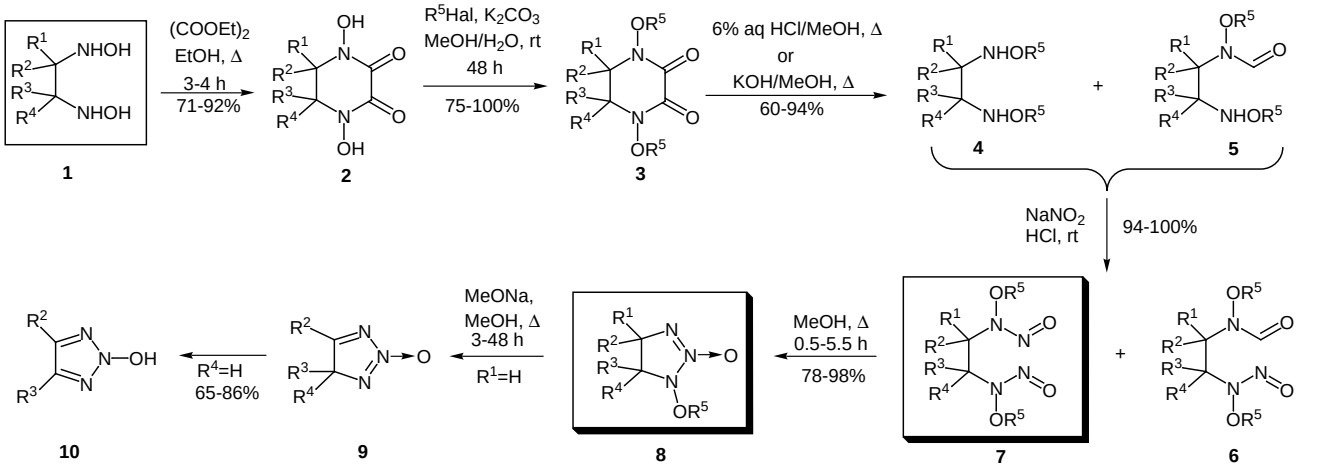
In a preliminary communication we reported a synthesis of *cis*-1,2-bis(*N*-methoxy-*N*-nitrosoamino)cycloalkanes, compounds bearing two *N*-nitroso-*N*-alkoxyamine groups, and their thermal transformation into 4,5-dihydro-1,2,3-triazole 2-oxides, a novel class of triazole *N*-oxides.[11] Previously known 1,2,3-triazole 2-oxides represented condensed 1,2,3-triazoles prepared photochemically[12] or via oxidative cyclization of aromatic nitro- or nitrosoamines.[13–15] In contrast, there are no data on uncondensed 1,2,3-triazole 2-oxides in the literature.

The present study was conducted to establish an influence of substrate structure features on the discovered cyclization of 1,2-bis(alkoxynitrosoamines) as well as to ascertain a scope of this reaction.

Preparation of 1,2-Bisalkoxyamines

A series of new 1,2-bisalkoxyamines **4** both with an acyclic or alicyclic backbone was synthesized via acyl protection of hydroxylamino groups of the appropriate 1,2-bishydroxylamines **1**,[16,17] and alkylation followed by hydrolysis of the resulting cyclic diesters **3**. Thus, reflux of 1,2-bishydroxylamines **1** with diethyl oxalate in ethanol gave the corresponding cyclic bishydroxamic acids **2** in a 80–90% yield. Subsequent alkylation of **2** with methyl iodide in the presence of K_2CO_3 in aqueous methanol led to the diesters **3a–e**. Reaction of compound **2a** with allyl bromide and benzyl chloride, and compound **2d** with allyl bromide led to the corresponding diesters of bishydroxamic acids **3f**, **3g** and **3j** under the same conditions. Diester **3h** was obtained by alkylation of bishydroxamic acid **2a** with ethyl chloroacetate in DMF in the presence of triethylamine (Scheme 1).

It was found that the reaction rate and products of the pyrazine ring opening of diesters **3** depend on the number of alkyl substituents at C-5 and C-6 of the heterocycle. Thus, reflux of diesters **3a,b** (C-5 and C-6, secondary carbon atoms) in 6% HCl (water/methanol, 1:5) for 16 hours or in 10% KOH in methanol for 10–14 hours afforded the corresponding 1,2-bisalkoxyamines hydrochlorides or the

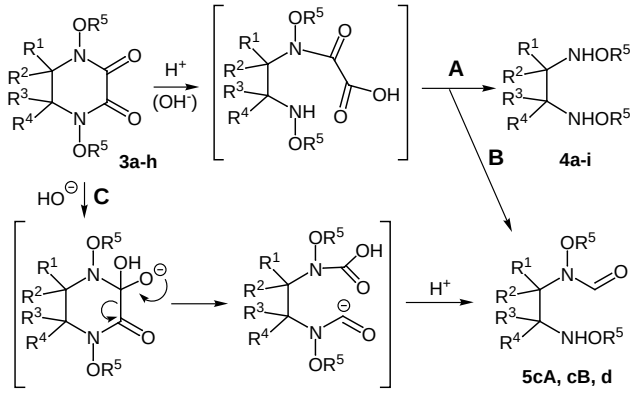


Compound	R^1	R^2	R^3	R^4	R^5
1-4a, 7a, 8a, 10a	H	$(CH_2)_4$		H	Me
1-4b, 7b, 8b, 10b	H	$(CH_2)_5$		H	Me
1-4c, 5cA	H	$(CH_2)_4$		Me	Me
5cB	Me	$(CH_2)_4$		H	Me
1-8d	Me	Me	Me	Me	Me
1-4e, 7e, 8eA	H	Me	Me	Me	Me
8eB	Me	Me	H	Me	Me
9e		Me	Me	Me	
3f, 4f, 7f, 8f	H	$(CH_2)_4$		H	Allyl
3g, 4g, 7g, 8g	H	$(CH_2)_4$		H	CH_2Ph
3h, 4h, 7h, 8h	H	$(CH_2)_4$		H	CH_2COOEt
4i	H	$(CH_2)_4$		H	CH_2COOH
3j	Me	Me	Me	Me	Allyl

Scheme 1

free bases **4a,b** in excellent yields. It took 5−24 hours to hydrolyze diesters **3e−h** by refluxing in 6% aqueous HCl. Hydrolysis of hydroxamic ester **3h** was accompanied by hydrolysis of side chain ester groups and resulted in 1,2-bisalkoxyamines **4h** in 26% yield and **4i** in 37% yield.

Acid hydrolysis of compound **3c** (C-5, tertiary; C-6, secondary carbon atoms) also gave 1,2-bisalkoxyamine **4c**. However, prolonged reflux of diester **3c** with alkali led exclusively to the mixture of *N*-formyl derivatives **5cA, 5cB**. Acid hydrolysis of compound **3d** with tertiary C-5 and C-6 carbon atoms led to a mixture of the desired 1,2-bismethoxyamine **4d** and its *N*-formyl derivative **5d**. Obviously, consecutive cleavage of the two C−N bonds in diesters **3a−h** results in bisalkoxyamines **4a−i** (Scheme 2, route **A**) whereas cleavage of one C−N bond and subsequent decarboxylation affords the *N*-formyl derivatives **5cA, cB, d** (Scheme 2, route **B**). However, formation of the formyl derivatives **5cA, cB, d** via cleavage of C-2 - C-3 bond can not be excluded (Scheme 2, route **C**).



Scheme 2

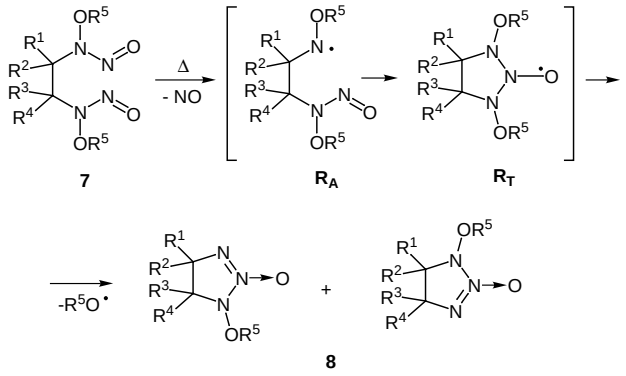
Synthesis and Intramolecular Cyclization of 1,2-Bis(*N*-alkoxy-N-nitrosoamino)alkanes

1,2-Bisalkoxyamines **4** are stable colorless oils which can be converted into crystalline salts when reacted with acids. In contrast to *N,N'*-disubstituted 1,2-diamines, 1,2-bisalkoxyamines **4** can be easily nitrosated by $NaNO_2$ in 6% aqueous HCl to give 1,2-bis(*N*-alkoxy-*N*-nitrosoamines) **7** in quantitative yields. Bisnitroso derivatives **7a, b, e, f, h** represent relatively stable yellow oils with a specific smell, while compounds **7d** and **7g** are crystalline. Compound **7d** was produced by nitrosation of a mixture of 1,2-bismethoxyamine **4d** and *N*-formyl derivative **5d** and separated from *N*-formyl-*N'*-nitroso derivative **6d** during workup. X-ray structures have been obtained for **6d** and **7d**.[18]

Thermolysis of *N,O*-disubstituted hydroxylamines *N*-nitroso derivatives results in a complex mixture of prod-

ucts.[6b] We found that reflux of 1,2-bis(*N*-alkoxy-*N*-nitrosoamines) **7** both in polar or non-polar solvents led to 4,5-dihydro-1,2,3-triazole 2-oxide derivatives **8** - a novel type of heterocyclic *N*-oxide - as a result of an intramolecular cyclization. Maximum yields (76−92%) were obtained by use of methanol as a solvent. A mixture of isomeric 4,5-dihydro-1,2,3-triazoles **8eA** and **8eB** (ratio 5:7) was obtained under the thermolysis of unsymmetrical *N,N'*-bisnitroso derivative **7e**.

According to literature data, homolytic cleavage of N−N bond with liberation of nitric oxide (NO) takes place as the first step of *N*-nitrosoalkoxyamines thermolysis.[6b] The same process is supposed to occur as the first stage of the intramolecular cyclization of *N,N'*-bisnitroso derivatives **7**. Next, the intermediate alkoxyaminyl radical $\mathbf{R_A}$ is trapped by the nitroso group. Subsequent elimination of alkoxyl radical from the triazinyloxyl radical $\mathbf{R_T}$ gives 4,5-dihydro-1,2,3-triazole 2-oxides **8** (Scheme 3).



Scheme 3

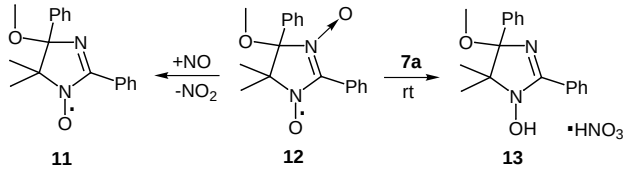
Cyclization rates for acyclic bisnitroso compounds are significantly higher than those for alicyclic ones. This fact may be explained by higher conformational flexibility of acyclic bisnitroso derivatives. Time for complete conversion decreases in the series R^5O = MeO > CH_2=$CHCH_2O$ ≅ $PhCH_2O$ > EtO_2CCH_2O (see Table 3). Thermolysis of compound **7g** produced 4,5-dihydrotriazole 2-oxide **8g** (81% yield) as well as benzhydroxamic acid (60% yield). The latter is supposed to be formed via reaction of the NO• with benzyloxyl radical ($PhCH_2O$•) and products of its transformation.

It should be noted that crystalline bisnitroso derivative **7g** completely decomposes at room temperature in a few weeks while **7a, b, d, e, f** are stable for months. No 4,5-dihydrotriazole **8g** was observed in the decomposition products of **7g**.

4,5-Dihydro-1,2,3-triazole 2-oxides **8** are colorless low-melting and volatile crystals (**8a, b, d, g**) or oils (**8eA, eB, f, h**). The observed broadening of the C-5 methyl group signals in the ^{1}H NMR spectra and the absence of C-5 signal in ^{13}C NMR spectra of compounds **8eA** and **8d** indicate a high inversion barrier of the tetrahedral N-1 possessing electron withdrawing groups.[19] At 60°C no signal broadening was observed.

The Trapping

To confirm NO-liberation the reaction was carried out in the presence of 4-methoxy-5,5-dimethyl-2,4-diphenyl-4,5-dihydroimidazol-1-yl 3-oxide (**12**) known as a specific NO-trap[20a] that is able to react with NO in situ with change of ESR spectrum due to the radical **11** formation.[20]



Scheme 4

However, more than two equivalents of nitronylnitroxide **12** were found to react with the bisnitroso derivative **7a**. A preparative experiment showed 1,2-bis(methoxynitrosoamine) **7a** to react with nitronylnitroxide **12** even at room temperature to give only trace amounts of 4,5-dihydro-1,2,3-triazole **8a**, whereas nitronylnitroxide **12** was transformed into 1-hydroxy-2-imidazoline nitrate **13** in a 29% yield (Scheme 4).

Since compound **12** did not work as a passive NO-trap, the reaction was carried out under continuous bubbling of argon through the boiling acetonitrile solution of **7a**. The stream of argon containing the NO formed was introduced into a separate acetonitrile solution of nitronylnitroxide **12**. ESR spectra recorded at intervals showed a progressive transformation of nitronylnitroxide **12** ($a_{N1} = a_{N3} = 7.1$ G) into iminonitroxide **11** ($a_{N1} = 7.5$ G, $a_{N3} = 4.0$ G) confirming NO formation during the cyclization reaction.

We failed to detect an intermediate radical $\mathbf{R_T}$ (Scheme 3) when carrying out the reaction in an ESR spectrometer vial. Data on the NO• and H_3CO• radical fixation have been given previously.[11]

Synthesis and Structures of 2*H*- and 4*H*-1,2,3-Triazoles

Treatment of 4,5-dihydro-1,2,3-triazole 2-oxides **8a,b** with sodium methoxide in methanol solution afforded aromatic 2-hydroxy-2*H*-1,2,3-triazoles **10a,b** in high yields. Under the same conditions the mixture of 2-oxides **8eA** and **8eB** gave 4*H*-1,2,3-triazole 2-oxide **9e** by elimination of methanol from **8eA**. In contrast **8eB** remained unchanged (Scheme 1).

The X-ray structures of 4*H*-1,2,3-triazole 2-oxide **9e** and 2-hydroxy-2*H*-1,2,3-triazole **10a** are illustrated in Figures 1 and 2. Selected bond lengths and other crystallographic data are presented in Tables 1 and 2. Compound **9e** features a marked lengthening of N1−N2 bond [1.458(3) Å] as compared to the N1−N2 bond of 5-amino- and 5-dimethylamino-4,4-diphenyl-4*H*-1,2,3-triazole[21] [1.423(3) and 1.401(4) Å] and calculated N(sp^2)−N(sp^2) bond length [1.401(8) Å].[22] Such N−N bond lengthening has been reported earlier for 4,5-dihydrotriazole 2-oxide derivatives.[11] The 4*H*-triazole ring of is planar within 0.011 Å. In compound **10a** normal triazole ring bond lengths[23] were found and the 2*H*-triazole ring is planar within ±0.003 Å. The cyclohexane ring adopts half chair form.

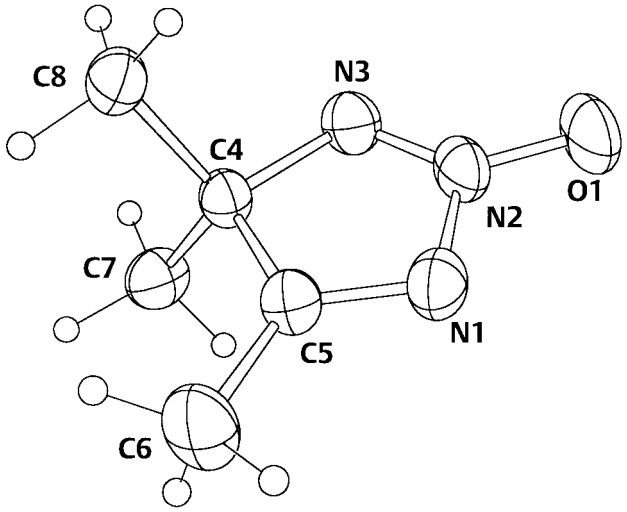


Figure 1 ORTEP presentation of 4*H*-1,2,3-triazole 2-oxide **9e**.

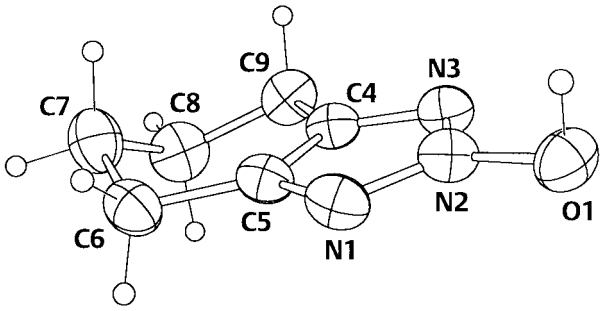


Figure 2 ORTEP presentation of 2-hydroxy-2*H*-1,2,3-triazole **10a**.

Synthesis and Thermolysis of 1,2-Bisnitrosohydroxylamines

To establish an influence of substrate features on intramolecular cyclization reaction, it seemed to be of interest to synthesize *O*-unsubstituted derivatives, 1,2-bisnitrosohydroxylamines and to study their behaviour under the thermal cyclization conditions. *N*-Nitrosohydroxylamines have been shown to exist predominantly as a tautomeric

Table 1 Selected Bond Lengths [Å] of Compounds **9e** and **10a**

Atoms	**9e**	**10a**
N1−N2	1.458(3)	1.317(3)
N2−N3	1.264(3)	1.319(3)
N3−C4	1.463(3)	1.344(3)
C4−C5	1.488(4)	1.380(3)
C5−N1	1.278(3)	1.343(3)
N2−O1	1.241(3)	1.356(2)

Table 2 Crystallographic Data and Summary of Data Collection and Refinement

Data	**9e**	**10a**
empirical formula	$C_5H_9N_3O$	$C_6H_9N_3O$
formula weight	127.15	139.16
color	colorless	colorless
crystal size, mm	0.45 × 0.38 × 0.20[a]	0.80 × 0.16 × 0.10
crystal system	orthorhombic	orthorhombic
space group	$P2_12_12_1$	Pbca
a, Å	6.0490(8)	6.800(1)
b, Å	7.7203(9)	11.332(2)
c, Å	14.687(2)	18.257(4)
V, $Å^3$	685.9(2)	1406.8(4)
Z	4	8
ρ_{calc}, g cm^{-3}	1.231	1.314
μ (CuKα), mm^{-1}	0.746	0.778
F(000)	272	592
difractometer	Syntex $P2_1$	Syntex $P2_1$
radiation	CuKα	CuKα
λ, Å	1.54178	1.54178
T, K	296	298
monochromator	graphite	graphite
$2\Theta_{max}$	158	120
reflections collected	932	1046
independent reflections	853	1046
wR2	0.1080	0.1353
R [for I>2σ (I)]	0.0393	0.0454
goodness-of-fit on F^2	1.048	1.008

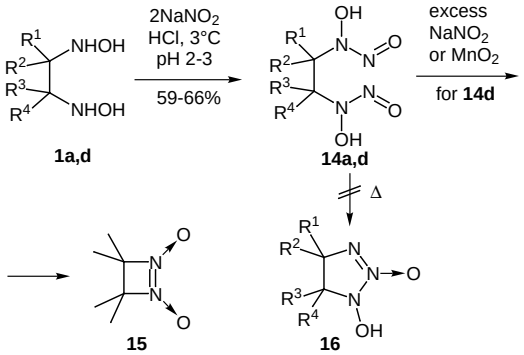
[a] Volatile crystal was placed into polyethylene capillary to prevent sublimation.

N-oxide form both in crystal or in solution[2a] (Scheme 5). Nevertheless in some cases transformations of this compounds propose to proceed via the less stable tautomer.[7]

Scheme 5

Nitrosation of 1,2-bishydroxylamines **1a,d** by $NaNO_2$ at pH 2−3 led to 1,2-bis(nitrosohydroxylamines) **14a,d** in a high yield. Temperature, quantity of $NaNO_2$ and pH value should be strictly controlled to avoid side reactions. *N*-Nitrosohydroxylamines have been previously shown to be quite capable of deamination reaction.[7] Furthermore, an

oxidation process known for *N*-nitrosohydroxylamines[9] may take place under an excess of HNO_2. In fact, reaction of 1,2-bishydroxylamine **1d** with an excess of $NaNO_2$ in acid media resulted in stable 3,3,4,4-tetramethyl-3,4-dihydro-1,2-diazete 1,2-dioxide **(15)**.[24] The same compound was obtained by oxidation of 1,2-bis(nitrosohydroxylamine) **14d** by MnO_2 (Scheme 6). 1,2-Bis(nitrosohydroxylamines) **14a,d** are stable crystalline solids that could be stored at least for several months at room temperature in contrast to mononitrosohydroxylamines usually stabilized as salts.



Scheme 6

Thermolysis of 1,2-bis(nitrosohydroxylamines) **14a,d** under the intramolecular cyclization reaction conditions failed to give corresponding 1-hydroxy-4,5-dihydrotriazoles **16** and led to a complex mixture of products. For instance, 1,2-cyclohexanedione dioxime was isolated in the case of **14a** thermolysis.

In conclusion, we have demonstrated that 1,2-bis-alkoxyamines **4** of any structure both with alicyclic fragments or opened chain compounds efficiently give corresponding *N,N'*-bisnitroso derivatives **7** which undergo an intramolecular cyclization under the mild thermolytical conditions to form 4,5-dihydro-1,2,3-triazole 2-oxide derivatives **8**. The aforementioned reaction of intramolecular cyclization is considered to be a general method for preparation of this type of heterocyclic *N*-oxides.

IR spectra were recorded on UR-20 and Specord M-80. UV spectra were recorded on a Specord UV/vis spectrometer. ^{1}H NMR spectra: Bruker AM-400 (400.13 MHz), Bruker WP-200SY (200.2 MHz) and Bruker AC-200 (200.2 MHz). ^{13}C NMR spectra: Bruker AM-400 (100.2 MHz), Bruker AC-200 (50.3 MHz). Mp's were measured on Kofler plate (uncorrected). Analytical and preparative TLC was performed on Silufol UV_{254} plates (Cavalier, CSFR) and silica gel (Lachema, CSFR), respectively. 1,2-Bishydroxylamines **1a-e** were prepared according to literature procedures.[16,17] All spectral and physical data of the synthesized compounds are presented in the Table 3. For the spectral data of compounds **2a-c, 3a-c, 4a–c**, see: Ref. 25; for **7a,b, 8a,b, 10a,b**, see: Ref. 11.

The X-ray structures was solved using direct methods (SHELXS-86).[26] The non-hydrogen atoms were refined anisotropically on F^2 with full matrix least squares procedure (SHELXL-93);[27] H-atoms positions were found from D-synthesis and refined isotropically.[28]

Bishydroxamic Acids 2a–e; General Procedure

A solution of **1a–e** (0.15 mol) and diethyl oxalate (24.4 mL, 0.18 mol) in EtOH (200 mL) was refluxed for 2–4 h. The mixture was concentrated in vacuo, the residue was treated with acetone. The precipitate was filtered and washed with Me_2CO (20 mL) to give **2a–c,e**. Compound **2d**[29] failed to solidify and was used in the further reaction without purification.

***cis*-1,4-Dimethoxydecahydro-2,3-quinoxalinedione (3a); Typical Procedure**

Solid K_2CO_3 (32.29 g, 0.23 mol) and bishydroxamic acid **2a** (26 g, 0.13 mol) were successively dissolved in H_2O (110 mL) and the solution was diluted with MeOH (250 mL). After addition of MeI (48.6 mL, 0.78 mol), the mixture was allowed to stand for 1–3 d with occasional shaking. MeOH was evaporated, the aqueous solution was extracted with $CHCl_3$ (4 × 50 mL) and organic layer was dried ($MgSO_4$) and concentrated in vacuo. The white solid residue was treated with hexane (50 mL) and filtered to give 99% of **3a**.

Compounds 3 b–e, f, g, j

Ethers **3b–e, f, g, j** were synthesized according to the typical procedure described above (with allyl bromide instead of MeI for **3f, j** and with benzyl chloride for **3g**). In the case of diether **3d** the residue obtained after evaporation of $CHCl_3$ was subjected to chromatography (silica gel, $CHCl_3$/MeOH, 30:1) to provide **3d**. In the case of diether **3g** the precipitate formed in the reaction mixture was filtered, triturated with H_2O, washed with cold aq 50% EtOH and dried to give **3g**.

***cis*-1,4-Bis(ethoxycarbonylmethoxy)decahydro-2,3-quinoxalinedione (3h)**

A solution of **2a** (0.45 g, 2.25 mmol), Et_3N (1.25 mL, 9 mmol) and $ClCH_2CO_2Et$ (0.96 mL, 9 mmol) in anhyd DMF (12 mL) was allowed to stand for 24 h. The solvent was removed in a current of air stream and H_2O (10 mL) was added. White precipitate was filtered, washed with H_2O (5 mL) and dried in the air; yield: 0.77 g (92%).

***cis*-*N,N'*-Dimethoxy-1,2-cyclohexanediamine (4a); Typical Procedure**

A solution of **3a** (22.38g, 98.2 mmol) in a solution of 6% HCl in MeOH (250 mL) was refluxed for 11 h, then cooled and concentrated in vacuo. The residue was dissolved in H_2O (100 mL) and pH was adjusted to 8 with aq 30% NaOH. The solution was extracted with $CHCl_3$ (4 × 50 mL) and the organic layer was dried ($MgSO_4$) and evaporated to give **4a** (colorless oil) in 85% yield. Compounds **4b,c,e,f** were synthesized by the similar method (for the refluxing time see Table 3).

***cis*-*N,N'*-Bis(benzyloxy)-1,2-cyclohexanediamine Dihydrochloride (4g•2HCl)**

A suspension of **3g** (3.29 g, 8.66 mmol) in solution of concd HCl (6.5 mL) in MeOH (33 mL) was refluxed for 24 h. The precipitate was filtered, washed with EtOH (2 × 10 mL) and dried to give 2.92 g of the salt **4g**•2HCl. The filtrate was concentrated and residue was treated with $CHCl_3$ (10 mL) to provide additionally 0.22 g of **4g**•2HCl; total yield: 3.14 g (91%).

Free Base 4g

Free base of **4g** was prepared by stirring of **4g**•2HCl in aq 50% MeOH followed by slow addition of aq 20% NaOH solution (up to pH 8). Evaporation and extraction of residue with $CHCl_3$, drying ($MgSO_4$) and removing of the solvent gave **4g** as colorless oil.

Table 3 Physical Data, Conditions for Reactions and Yields of the New Compounds Prepared

Product	Time, Temp.	Yield (%)	mp (°C)[a]	IR ν (cm^{-1})	UV, λ_{max} (log ε)[b]	^{1}H NMR, δ, *J* (Hz)	^{13}C NMR,[c] δ
2e	4 h, 78 °C	80 78	179–183	1690[d]	231 (3.90)	1.22 (d, 3 H, *J* = 7, 6-CH_3), 1.24 (s, 3 H, 5-CH_3), 1.34 (s, 3 H, 5-CH_3), 3.74 (q, 1 H, *J* = 7, CH), 10.14 (br s, 1 H, OH)[e]	13.32 (+, CH_3), 21.25 (+, CH_3), 24.15 (+, CH_3), 60.86 [–, *C*$(CH_3)_2$], 62.84 (+, CH), 153.39 (–, CO), 154.28 (–, CO)[e]
3d	2 d, 20 °C		123–125	2820, 1700, 1680[d]	232 (3.87)	1.33 (s, 12 H, CH_3), 3.77 (s, 6 H, OCH_3)[e]	19.96 (+, CH_3), 63.12 (+, OCH_3), 66.14 [–, *C*$(CH_3)_2$], 154.46 (–, CO)[e]
3e	2 d, 20 °C	90	63	2822, 1696[d]	228 (4.00)	1.35 (d, 3 H, *J* = 6.5, CH_3), 1.37 (s, 3 H, CH_3), 1.45 (s, 3 H, CH_3), 3.66 (q, 1H, *J* = 6.5, CH), 3.80 (s, 3 H, OCH_3), 3.83 (s, 3 H, OCH_3)[f]	–
3f	2 d, 20 °C	85	59–60	1690, 1700[d]	230 (3.97)	0.24–0.72, 0.72–2.1 [2 m, 8 H, $(CH_2)_4$], 3.89 (m, 2 H, CH), 4.49 (dt, 4 H, *J* = 6.5, 1.2, OCH_2), 5.27 (ddd, 2 H, *J* = 10, 0.7, 0.7, CH_a=C*H*$_b$H$_c$), 5.32 (dd, 2 H, *J* = 17.5, 1.5, CH_a=CH_b*H*$_c$), 5.95 (ddt, *J* = 17.5, 10, 6.5, 2 H C*H*$_a$=CH_bH$_c$)[f]	21.50 (–, CH_2), 26.49 (–, CH_2), 57.54 (+, CH), 75.8 (–, OCH_2), 121.01 (–, CH_2, allyl), 131.4 (+, CH, allyl), 155.54 (–, CO)[f]
3g	3 d, 20 °C	100	158–159	1715[d]	233 sh (3.75)	1.25–1.60, 1.65–1.95 [2 m, 8 H, $(CH_2)_4$], 4.05–4.15 (m, 2 H, CH), 4.98, 5.01 (AB-system, 4 H, *J* = 10, OCH_2), 7.3–7.6 (m, 10 H, C_6H_5)[e]	21.13 (–, CH_2), 25.95 (–, CH_2), 56.15 (+, CH), 75.68 (–, OCH_2), 128.33 (+, Ph, C_o), 128.64 (+, Ph, C_p), 129.23 (+, Ph, C_m), 134.73 (–, Ph, C_i), 154.72 (–, C=O)[e]
3h	1 d, 20 °C	92	84–86	1756, 1731, 1700[d]	228 (3.90)	1.20 (t, 6 H, *J* = 7, CH_3), 1.3–1.6, 1.7–2.1 [2 m, 8 H, $(CH_2)_4$], 4.13 (q, 4 H, *J* = 7, CH_2), 4.26 (m, 2 H, CH), 4.47 (d, 2 H, *J* = 16.5, OC*H*$_a$H$_x$), 4.75 (d, 2 H, *J* = 16.5, 2OCH_a*H*$_x$)[f]	13.83 (+, CH_3), 21.52 (–, CH_2, ring), 26.38 (–, CH_2, ring), 58.54 (+, CH), 61.13 (–, OCH_2), 71.33 (–, OCH_2), 155.46 (–, CO), 168.21 (–, CO_2)[f]
3j	2 d, 20 °C	43	80–82	1685[d]	234 (3.66)	1.37 (s, 12 H, CH_3), 4.48 (d, 4 H, *J* = 6.5, CH_2), 5.26 (d, 2 H, *J* = 10, CH_a=C*H*$_b$H$_c$), 5.33 (d, 2 H, *J* = 15, CH_a=CH_b*H*$_c$), 5.97 (ddt, 2 H, *J* = 15, 10, 6.5, C*H*$_a$=CH_bH$_c$)[f]	–
4d[g]	21 h, 65 °C	–	oil	3275, 2810[h]	–	1.08 (s, 12 H, CH_3), 3.48 (s, 6 H, OCH_3), 5.84 (br s, NH)[f]	–
4e	12 h, 65 °C	94	oil	3260, 2810[h]	–	0.87 (s, 3 H, CH_3), 1.02 (s, 3 H, CH_3), 1.03 (d, 3H, *J* = 6.5, CH_3), 3.02 (q, 1 H, *J* = 6.5, CH), 3.44 (s, 3 H, OCH_3), 3.45 (s, 3 H, OCH_3), 5.66 (br, NH)[f]	13.73 (q, CH_3), 19.29 (q, CH_3), 23.20 (q, CH_3), 58.39 (d, CH), 59.47 (s, C), 61.76 (q, OCH_3), 62.68 (q, OCH_3)[f]
4f	10 h, 65 °C	79	oil	2860, 1645[i]	–	1.2–1.5, 1.5–1.8 [2 m, 8 H, $(CH_2)_4$], 3.18 (m, 2 H, CH), 4.17 (ddd, 4 H, *J* = 6, 3.5, 1.8, 2 CH_2), 5.16 (dm, 2 H, *J* = 14, CH_a=C*H*$_b$H$_c$), 5.23 (ddd, 2 H, *J* = 17.5, 3.5, 1.8, CH_a=CH-$_b$*H*$_c$), 5.71 (s, 2 H, 2 NH), 5.92 (ddt, *J* = 17.5, 14, 6, 2 H, C*H*$_a$=CH_bH$_c$)[f]	22.22 (–, CH_2), 25.96 (–, CH_2), 58.36 (+, CH), 75.44 (–, OCH_2), 117.29 (–, CH_2, allyl), 134.57 (+, CH, allyl)[f]
4g•2HCl	24 h, 65 °C	91	145–150	–	–	1.40–2.05 [m, 8 H, $(CH_2)_4$], 3.75–3.85 (m, 2 H, CH), 4.97 (s, 4 H, OCH_2), 7.41 (s, 10 H, C_6H_5)[j]	–
4g		90	oil	3259, 2857[h]	–	1.27–1.50, 1.62–1.83 [2 m, 8 H, $(CH_2)_4$], 3.25–3.35 (m, 2 H, CH), 4.73 (s, 4 H, OCH_2), 5.55–5.85 (br s, 2 H, NH), 7.36 (s, 10 H, C_6H_5)[f]	22.20 (–, CH_2), 25.98 (–, CH_2), 58.36 (+, CH), 76.55 (–, OCH_2), 127.54 (+, Ph, C_p), 128.15 (+, Ph, $C_{m(o)}$), 128.27 (+, Ph, $C_{o(m)}$), 137.95 (–, Ph, C_i)[f]

Table 3 (continued)

Product	Time, Temp.	Yield (%)	mp (°C)[a]	IR ν (cm^{-1})	UV, λ_{max} (log ε)[b]	^{1}H NMR, δ, *J* (Hz)	^{13}C NMR,[c] δ
4h	5h, 85 °C	27	oil	–	–	1.25 (t, 6 H, *J* = 7, CH_3), 1.2−1.5, 1.5−1.75 [2 m, 8 H, $(CH_2)_4$], 3.23 (m, 2 H, CH), 4.18 (q, 4 H, *J* = 7, OCH_2CH_3), 4.24, 4.25 (AB-system, 2 H, *J* = 16, $OCH_aH_bCO_2Et$), 6.32 (s, 2 H, NH)[f]	14.04 (+, CH_3), 22.14 (−, CH_2), 25.85 (−, CH_2), 58.22 (+, CH), 60.53 (−, OCH_2), 71.66 (−, OCH_2), 170.75 (−, CO)[f]
4i	5 h 85 °C	37	158 −162	1722, 1646[d]	–	1.35−1.48, 1.53−1.77, 1.78−1.90 [3 m, 8 H, $(CH_2)_4$], 3.39 (m, 2 H, 2 CH), 4.31, 4.39 (AB-system, 4 H, *J* = 16.5, OCH_2)[j]	23.32 (−, CH_2), 26.46 (−, CH_2), 59.46 (+, CH), 71.79 (−, OCH_2), 175.27 (−, CO_2H)[j]
5cA, 5cB	50 h, 65 °C	25	oil	2939, 2860, 1687[i]	–	0.75−2.30 [m, 8 H, $(CH_2)_4$], 1.06 (s, 3 H, CH_3), 1.10 (s, 3 H, CH_3), 3.28−3.35 (m, 1 H, CH), 3.51 (s, 6 H, OCH_3), 3.85 (s, 3 H, OCH_3), 4.12−4.23 (m, 1 H, CH), 5.80−5.90 (br s, 1 H, NH), 5.90−6.00 (br s, 1 H, NH), 7.94 (s, 1 H, CHO), 8.47 (s, 1 H, CHO)[f]	20.40 (−, CH_2), 20.83 (−, CH_2), 21.37 (+, CH_3), 23.54 (+, CH_3), 25.44 (−, CH_2), 25.94 (−, CH_2), 26.43 (−, CH_2), 29.54 (−, CH_2), 30.15 (−, CH_2), 33.55 (−, CH_2), 60.32 (−, C), 60.57 (−, C), 61.89, 62.59, 63.47, 64.89, 65.53, 66.67 (6 s, +, OCH_3 and CH), 154.19 (+, CHO), 158.37 (+, CHO)[f]
5d[k]	21h, 65 °C	–	–	–	–	–	–
6d	–	34[l]	92−95	1670, 1400[d]	241 (3.86)	1.44 (s, 6 H, CH_3), 1.67 (s, 6 H, CH_3), 3.80 (s, 3 H, OCH_3), 3.81 (s, 3 H, OCH_3), 8.15 (s, 1 H, CHO)[f]	23.49 (+, CH_3), 23.80 (+, CH_3), 64.22, 64.55 (+, OCH_3), 67.90 (−, C), 73.80 (−, C), 148.33 (+, CO)[f]
7d	–	30[l]	97−100	1405[d]	240 (3.99)	1.62 (s, 12 H, CH_3), 3.80 (s, 6 H, OCH_3)[f]	23.49 (+, CH_3), 64.47 (+, OCH_3), 73.22 (−, C)[f]
7e	–	97	oil	1463, 1410[i]	240 (3.93) 365 (2.20)	1.44 (d, 3 H, *J* = 17, CH_3), 1.59 (s, 3 H, CH_3), 1.69 (s, 3 H, CH_3), 3.85 (s, 3 H, OCH_3), 3.87 (s, 3 H, OCH_3), 5.20 (q, 1 H, *J* = 17, CH)[f]	–
7f	–	100	oil	1640, 1450, 1410[h]	240 (4.09) 363 (2.42)	–	–
7g	30 min, 20 °C	81	71−72.5	1450, 1430[d]	238 (3.95)	1.38−1.52, 1.77−1.96, 2.21−2.35 [3 m, 8 H, $(CH_2)_4$], 4.43−4.58 (br s, 2 H, CH), 4.91, 4.97 (AB-system, 4 H, *J* = 10.4, OCH_2), 7.27−7.44 (m, 10 H, C_6H_5)[f]	22.22 (−, CH_2), 26.82 (−, CH_2), 64.09 (+, CH), 77.10 (−, OCH_2), 128.45 (+, Ph, C_o), 129.01 (+, Ph, C_p), 129.29 (+, Ph, C_m), 133.93 (−, Ph, C_i)[f]
7h	–	90	oil	1750,1440, 1210[h]	234 (3.77)	–	–
8d	50 min, 65 °C	92	38	2810, 1560[d]	219 (4.36)	1.10 (br s, 6 H, CH_3), 1.22 (s, 6 H, CH_3), 3.90 (s, 3 H, OCH_3)[f]	17.27 (+, br, CH_3), 21.02 (+, CH_3), 64.88 (+, OCH_3), 67.65 (−, C), 69.43 (−, C)[f]
8eA	135 min, 65 °C	98	oil	–	–	1.00 (br s, 3 H, CH_3), 1.25 (d, 3 H, *J* = 6.9, CH_3), 1.29 (s, 3 H, CH_3), 3.75 (q, 1 H, *J* = 6.9, CH), 3.95 (s, 3 H, OCH_3)[f]	11.91 (+, CH_3), 13.99 (+, CH_3), 21.09 (+, CH_3), 64.52 (+, CH), 64.95 (+, OCH_3), 68.01 (−, C)[e,m]
8eB	135 min, 65 °C		oil	2810, 1570[h]	218 (3.82)	1.20 (s, 3 H, CH_3), 1.27 (d, 3 H, *J* = 7, CH_3), 1.32 (s, 3 H, CH_3), 3.16 (q, 1 H, *J* = 7, CH), 3.98 (s, 3 H, OCH_3)[f]	10.85 (q, CH_3), 19.58 (q, CH_3), 25.32 (q, CH_3), 64.81 (q, OCH_3), 65.84 (s, C), 67.98 (d, CH)[f]
8f	90 min, 65 °C	78	oil	1575[i]	219 (4.00)	0.9−2.3 [m, 8 H, $(CH_2)_4$], 3.5 (br, 1 H, CH), 3.94 (m, 1 H, CH), 4.63 (m, 2 H, OCH_2), 5.23 (dm, 1 H, *J* = 10.5, CH_a=C$H_b$$H_c$), 5.29 (ddd, 1 H, *J* = 17.5, 3, 1.5, CH_a=$CH_b$$H_c$), 5.93 (ddt, 1 H, *J* = 17.5, 10.5, 6.5, CH_a=$CH_b$$H_c$)[f]	20.00 (−, CH_2), 21.92 (−, CH_2), 23.50 (−, br, CH_2), 28.69 (−, CH_2), 60.28 (+, CH), 62.27 (+, CH), 77.50 (−, OCH_2), 119.57 (−, CH_2allyl), 132.39 (+, CHallyl)[f]

Table 3 (continued)

Product	Time, Temp.	Yield (%)	mp (°C)[a]	IR ν (cm^{-1})	UV, λ_{max} (log ε)[b]	^{1}H NMR, δ, *J* (Hz)	^{13}C NMR,[c] δ
8g	100 min, 65 °C	81	92–94	1565[d]	210 (4.20)	0.8–2.2 [m, 8 H, $(CH_2)_4$], 3.3–3.6 (br s, 1 H, CH), 3.8–4.0 (m, 1 H, CH), 5.13, 5.23 (AB-system, 4 H, *J* = 11, OCH_2), 7.3–7.5 (m, 10 H, C_6H_5)[f]	19.69 (–, CH_2), 21.95 (–, CH_2), 23.53 (–, br, CH_2), 26.77 (–, CH_2), 60.44 (+, CH), 62.27 (+, CH), 78.65 (–, OCH_2), 128.26 (+, Ph, C_o), 128.45 (+, Ph, C_p), 129.44 (+, Ph, C_m), 135.79 (–, Ph, C_i)[f]
8h	30 min 65 °C	78	oil	1750, 1563[h]	217 (4.29)	0.9–2.7 [m, 8 H, $(CH_2)_4$], 1.27 (t, 3 H, *J* = 7.5, CH_3), 3.4–3.6 (br s, 1 H, CH), 3.95–4.05 (m, 1 H, CH),), 4.20 (q, 2 H, *J* = 7.5, CH_2), 4.73, 4.97 (AB-system, 2 H, *J* = 18, $NOCH_2$)[j]	–
9e	2 d, 20 °C	13	78–81	1630, 1545[d]	243 (3.60)	1.47 (s, 6 H, 2 CH_3), 2.31 (s, 3 H, CH_3)[f]	10.35 (+, CH_3), 21.40 (+, CH_3), 81.43 (–, C), 189.56 (–, C)[f]
13[n]	–	29	116–119	1610, 1380, 1290[d]	–	0.73 (s, 3 H, CH_3), 1.50 (s, 3 H, CH_3), 3.46 (s, 3 H, OCH_3), 7.26–7.60 (m, 8 H, C_6H_5), 8.03 (d, *J* = 7.5, 2 H, C_6H_5), 11.04 (s, 1 H, OH)[f]	–
14a	1 h, 3 °C	66	78–81	1448, 1430[d]	232 (4.10)	1.46 (m, 2 H, CH_2), 1.6–2.1 [m, 4 H, $(CH_2)_2$], 2.10–2.40 (m, 2 H, CH_2), 4.82 (m, 2 H, 2CH), 12.8 (br, 2 H, OH)[e]	21.41 (–, CH_2), 26.12 (–, CH_2), 68.73 (+, CH)[e]
14d	1 h, 3 °C	59	125–128	1465, 1245, 1125, 1063[d]	232 (4.01)	1.56 (s, 12 H, CH_3)[e]	22.29 (+, CH_3), 78.12 (–, C)[e]

[a] Analytical samples were purified by recrystallization: **3g, 8g**, from EtOH; **7g**, from Et_2O; **4g**·2HCl, from MeOH; **6d, 7d, 9e, 3h**, from hexane/EtOAc; **8d**, from pentane. Free base of **4g** was purified by sublimation at 160 °C/3 Torr. Satisfactory microanalyses obtained: C ±0.5; H ±0.2; N ±0.3.
[b] In EtOH (10^{-4} mol/L).
[c] ^{13}C NMR spectra (except for **4e** and **8eB**) were performed in *J*-modulation mode.
[d] As KBr pellet (0.25%).
[e] In DMSO-d_6, standard: DMSO.
[f] In $CDCl_3$, standard: $CHCl_3$.
[g] Analyzed as **4d**·HCl.
[h] Film.
[i] In CCl_4 (3%).
[j] In CD_3OD, standard: CH_3OH.
[k] Isolated as a mixture with **4d**.
[l] Prepared from a mixture of **4d** and **5d**.
[m] Spectrum was recorded at 60 °C.
[n] Analyzed as **13**·HNO_3.

***N,N'*-Dimethoxy-2,3-dimethylbutane-2,3-diamine (4d) and *N*-Formyl-*N'*-methoxy-2,3-dimethylbutane-2,3-diamine (5d)**

A solution of **3d** (3.5 g, 15.3 mmol) in a 12% solution of HCl in MeOH (70 mL) was refluxed for 21 h, then cooled and concentrated in vacuo. The aqueous residue was brought to pH 8 with aq 30% NaOH and solution was extracted with $CHCl_3$ (3 × 30 mL). Combined organic extracts were dried ($MgSO_4$) and concentrated in vacuo to give a mixture of **4d** and **5d** as colorless oil (2.77g).

***cis*-*N,N'*-Bis(ethoxycarbonylmethoxy)-1,2-cyclohexanediamine (4h) and *cis*-*N,N'*-Bis(carboxymethyloxy)-1,2-cyclohexanediamine (4i)**

A solution of **3h** (2 g, 5.38 mmol) in a solution of concd HCl (4 mL) in EtOH (20 mL) was refluxed for 5 h, then cooled and concentrated in vacuo. The residue was dissolved in H_2O (10 mL) and the pH was adjusted to 9 with aq 30% NaOH solution. The mixture was extracted with Et_2O (3 × 10 mL) and the combined organic extracts were dried ($MgSO_4$) and evaporated in vacuo to give **4h** in 27% yield. Analytical sample was purified by column chromatography (silica gel, Et_2O/hexane, 1:4).

Aqueous solution was concentrated in vacuo, the residue was treated with EtOH (5 mL) and the precipitate was filtered off. Filtrate was evaporated up to 1/5 of its initial volume and EtOAc (4 mL) was added to give the precipitate of **4i** (0.76 g, 37%).

***N*-Methoxy-*N*-(2-methoxyamino-2-methylcyclohexyl)formamide (5cA) and *N*-Methoxy-*N*-(2-methoxyamino-1-methylcyclohexyl)formamide (5cB)**

A solution of KOH (0.30 g, 5.36 mmol) in MeOH (5 mL) was added to a solution of **3c** (0.22 g, 0.92 mmol) MeOH (5 mL) and the mixture was refluxed for 50 h. The solution was brought to pH 9 with aq 6% HCl and MeOH was evaporated in vacuo. Residue was

mixed with H_2O (5 mL) and extracted with $CHCl_3$ (2 × 5 mL). The organic extract was dried ($MgSO_4$) and concentrated to give colorless oil which was purified by column chromatography (silica gel, hexane/Et_2O, 2:1) to yield 0.05 g (25%) of the mixture **5cA** and **5cB** in ~1:1 ratio.

Nitrosation of 1,2-Bis(alkoxyamines) 4a, b, e-h; General Procedure

A solution of $NaNO_2$ (0.27 g, 4.05 mmol) in H_2O (1 mL) was added dropwise to a stirred mixture of solution of **4a** (2 mmol) in 6% HCl (5 mL) and Et_2O (5 mL). After additional 10−30 min of stirring, the yellow organic layer was separated, and the aqueous layer was extracted with Et_2O. The combined organic extracts were dried ($MgSO_4$) and concentrated in vacuo to give **7a** in quantitative yield.

7b, e−h

Compounds **7b, e−h** were synthesized similarly.

***N*-Formyl-*N,N'*-dimethoxy-2,3-dimethyl-*N'*-nitrosobutane-2,3-diamine (6d) and 2,3-Bis(*N*-methoxy-*N*-nitroso)dimethylbutane-2,3-diamine (7d)**

A solution of $NaNO_2$ (0.8 g, 11.7 mmol) in H_2O (10 mL) was added dropwise to a stirred solution of mixture of **4d** and **5d** (1 g) in 6% HCl (10 mL). After additional 10 min of stirring, the precipitate was filtered and washed with H_2O (5 mL) to furnish 0.42 g (30%) of **6d**. The aqueous solution was extracted with $CHCl_3$ (2 × 20 mL), the combined organic extracts were dried ($MgSO_4$) and concentrated in vacuo. Treatment of the residue with Et_2O/pentane (5 mL, 1:1) gave **7d** in 34% yield.

4,5-Dihydro-1,2,3-triazole 2-Oxides (8); General Procedure

A solution of **7** (6 mmol) in MeOH (60−70 mL) was refluxed for 0.5−5.5 h (for the time of thermolysis, see Table 3), cooled to r.t. and concentrated in vacuo. The resulted oil was purified by column chromatography (silica gel, Et_2O/hexane, 1:3 and $CHCl_3$ as eluent in the case of **8g**) to give 2-oxides **8** in 76−92% yield (**8eA, eB** as the mixture of isomers; **8a, b, d, g**: colorless crystals; **8eA, eB, f, h**: colorless oils). Isomers **8eA, eB** were separated by TLC (silica gel, Et_2O/pentane 1:40). In the case of thermolysis of **7g** benzhydroxamic acid as byproduct was isolated by means of TLC chromatography (silica gel, $CHCl_3$/MeOH, 20:1) with ca 60% yield and was identified by comparison of its IR spectrum (Sadtler).

1-Hydroxy-4-methoxy-5,5-dimethyl-2,4-diphenyl-4,5-dihydroimidazole Nitrate (13)

Compound **12** (0.54 g, 1.72 mmol) was added to a solution of **7a** (0.2 g, 0.86 mmol) in Et_2O (3 mL). After 30 min precipitate was filtered and washed with Et_2O (3 mL) to give 0.18 g (29%) of **13**.

4,4,5-Trimethyl-4*H*-1,2,3-triazole 2-Oxide (9e)

Solution of 4 N MeONa in MeOH (2 mL) was added to a solution of a mixture of **8eA, eB** (0.4 g, 2.5 mmol) in MeOH (2 mL). After 48 h, the mixture was concentrated in vacuo and H_2O (5 mL) was added to the residue. The mixture was extracted with CH_2Cl_2 (3 × 5 mL), the combined organic extracts were dried ($MgSO_4$) and evaporated. The column chromatography of the residue (silica gel, $CHCl_3$/MeOH, 60:3) gave **8eB** (0.14 g, 35%) and **9e** (0.04 g, 13%).

2-Hydroxy-4,5,6,7-tetrahydro-2*H*-benzotriazole (10a); Typical Procedure

A solution of **8a** (0.54 g, 3.18 mmol) in 4 N MeONa in MeOH (25 mL) was stirred for 3 h, concd HCl was added until the solution had pH 4−5. The NaCl formed was filtered, the solvent MeOH was evaporated in vacuo and H_2O (10 mL) was added to the residue. The resulting precipitate was filtered to give **10a** (0.3 g). The filtrate was extracted with CH_2Cl_2 (3 × 10 mL) and the combined organic layers were dried ($MgSO_4$) and concentrated in vacuo. The residue was filtered to give an additional amount of **10a** (0.08 g); total yield: 86%.

10b

Compound **10b** was synthesized in a similar manner in a 65% yield.

Nitrosation of 1,2-Bishydroxylamines 1a, d; General Procedure

A solution of **1d** (9 mmol) in aq HCl (10 mmol) (pH 2−3), was cooled to 0°C and an aqueous solution of $NaNO_2$ (1.24 g, 18 mmol) was added dropwise with stirring for 40 min (temperature should not exceed 3°C, pH should not exceed 4). Then the mixture was allowed to stir for an additional 20 min. The precipitate was filtered, washed with ice-cold H_2O (5 mL) and dried in the air to yield 1.08 g (95%) of **14d**. Substance **14a** was synthesized in a similar manner.

Oxidation of 2,3-Bis(*N*-hydroxy-*N*-nitroso)-2,3-dimethylbutanediamine (14d) with MnO_2

A suspension of **14d** (0.25 g, 1.23 mmol) and MnO_2 (0.42 g, 4.9 mmol) in MeOH (10 mL) was stirred for 2 h, filtered and concentrated in vacuo. The residue was treated with Et_2O (4 mL) and kept for 48 h at 0°C. The precipitate was filtered to give 0.14 g (78%) of 3,4-dihydro-3,3,4,4-tetramethyl-1,2-diazete 1,2-dioxide (**15**).

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