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SYNTHESIS OF PRECURSORS OF HETEROCYCLIC *cis*-β-AMINO ALCOHOLS BY INTRAMOLECULAR AMIDOALKYLATION OF 4-HYDROXYOXAZOLIDIN-2-ONES*

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The reaction of intramolecular amidoalkylation of 4-hydroxyoxazolidin-2-ones leads to formation of novel and rare heterocyclic systems: substituted 1,5,6,10b-tetrahydro[1,3]oxazolo[4,3-a]isoquinolin-3-ones, 3a,4,5,10b-tetrahydro[1,3]dioxolo[4',5':6,7]naphtho[1,2-d][1,3]oxazol-2(1H)-ones, and 5,6,10,10a-tetrahydro-1H-di[1,3]oxazolo[3,4-d:4,3-g][1,4]-diazepine-3,8-diones. Mild reaction conditions and the simplicity of isolation of the compounds formed make it possible to obtain the indicated heterocycles in high yields.

Keywords: *cis*-β-amino alcohols, 4-hydroxyazolidin-2-ones, di[1,3]oxazolo[3,4-*d*:4,3-*g*]diazepine-3,8-diones, [1,3]dioxolo[4',5':6,7]naphtho[1,2-*d*][1,3]oxazol-2(1H)-ones, [1,3]oxazolo[4,3-*a*]isoquinolin-3-ones, calycotomine, intramolecular amidoalkylation.

We earlier studied in details the reaction of dioxolanones **1** with amines, leading to oxazolidinones **2** [1]. Under intramolecular amidoalkylation conditions, such oxazolidinones are sources of acyliminium ions which can react with various π- and *n*-nucleophiles. If a π-electron donor functional group is present in the chain of one of the oxazolidinone substituents, then the acyliminium ion reacts with it. In particular, it has been shown that the presence of a 4-methyl-3-pentenyl residue in the position 5 of the oxazolidinone ring makes it possible to obtain derivatives of 1-oxa-3-azapentalen-2-one, which can be considered as precursors of cyclopentane *cis*-β-amino alcohols [2].

An activated benzene ring also can act as such a π-electron donor substituent. To study the behavior of the activated benzene ring under intramolecular amidoalkylation conditions, we synthesized the starting oxazolidinones **2a-d** from dioxolanones **1a-d** and 2-(3,4-dimethoxyphenyl)ethylamine (homoveratrylamine).

In the ^{1}H NMR spectra of oxazolidinones **2a-d** (Table 1), we see characteristic signals from the hydroxyl and methyl groups in the 4 position; for the benzene ring, there are three proton signals. In the IR spectrum (Table 2), we detect vibrations of the C=O and OH groups; in the mass spectrum (Table 2), there is a signal for the molecular ion peak.

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* Dedicated to the memory of A. N. Kost in celebration of the 85th anniversary of his birth.

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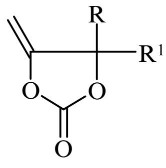
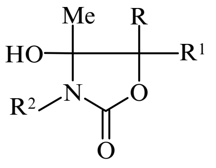
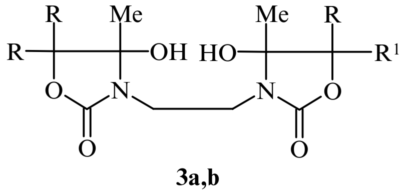


1a–e



2a–e

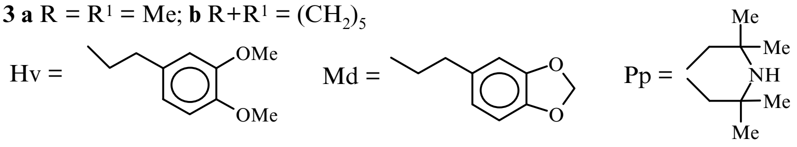


3a,b

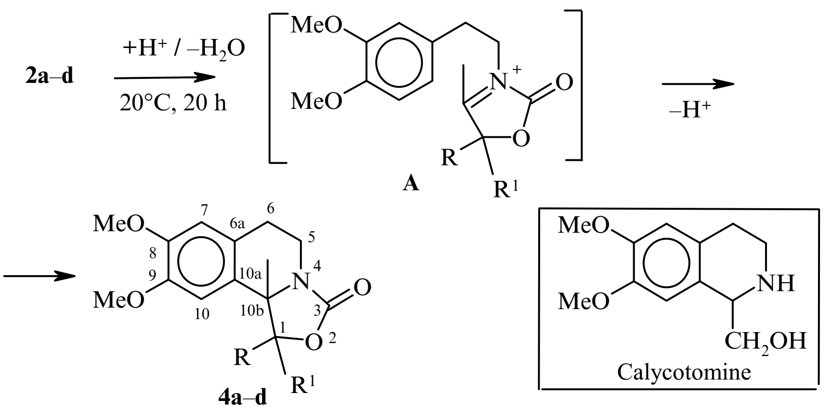
1 a R = R^1 = Me; **b** R = Me, R^1 = Et; **c** R+R^1 = $(CH_2)_5$; **d** R+R^1 = Pp;
e R = Me, R^1 = Md

2 a R = R^1 = Me, R^2 = Hv; **b** R = Me, R^1 = Et, R^2 = Hv;
c R+R^1 = $(CH_2)_5$, R^2 = Hv; **d** R = R^1 = Pp, R^2 = Hv, **e** R = R^2 = Me, R^1 = Md

3 a R = R^1 = Me; **b** R+R^1 = $(CH_2)_5$



From oxazolidinones **2a-d**, we obtained derivatives of the alkaloid calycotomine.



4 a R = R^1 = Me; **b** R = Me, R^1 = Et; **c** R+R^1 = $(CH_2)_5$; **d** R + R^1 = Pp

We used standard conditions described in [3]. In the opinion of the authors of that review, HCOOH is simultaneously the best acid agent and solvent. In our experiments, the results of cyclization were identical in HCOOH and CF_3COOH: tetrahydroisoquinolines **4a-d** were formed in high yields. The starting oxazolidinones **2a-d** were reacted without preliminary purification; they may contain the dehydration product (the corresponding 4-methyleneoxazolidin-2-one) as an impurity. But just as for oxazolidinone **2**, in acid medium it is converted to the same acyliminium species **A** through which the amidoalkylation process also occurs. In the ^1H NMR spectra of tetrahydroisoquinolines **4**, we see two singlets from the aromatic protons in the 7 and 10 positions (6.45-6.63 ppm) with intensities ^1H (sometimes, just one singlet with intensity 2H), which indicates the site of attack by the acyliminium ion on the benzene ring. Furthermore, we see signals from the methyl group at the 10b position (1.49-1.53 ppm, 3H), the protons on the CH_2CH_2 moiety of the piperidine ring (2.6-4.13 ppm, three or four series of multiplets with total intensity 4H), the OMe group on the benzene ring (3.82-3.84 ppm, one singlet (6H) or two singlets (3H each)). There is an absorption band for the C=O group in the IR spectra. In the mass spectra of tetrahydroisoquinolines **4**, there is a signal for the molecular ion.

According to our preliminary investigations, base hydrolysis of tetrahydroisoquinoline **4a** leads to formation of the corresponding trimethyl-substituted calycotomine; future publications will focus on the hydrolysis results.

In [4], the tetrahydroisoquinoline **E** is described, which is related to our tetrahydroisoquinoline **4a** but has an *n*-butyl group in the 10b position rather than a methyl group. It was synthesized in HCOOH from the corresponding oxazolidinone **C**. The starting oxazolidinone **C** was prepared from oxazolidin-2,4-dione **B** by reaction with butyllithium; in this case, the reaction was complicated by formation of the by-product **D**.

TABLE 1. ^{1}H NMR Spectra of Synthesized Compounds

Compound	Solvent	δ, ppm, *J*, Hz
1e	$CDCl_3$	[1.17 (6H, s), 1.38 (6H, s)] (7,7,9,9-Me), [1.42 (2H, d, *J* = 14.7), 2.01 (2H, d, *J* = 14.7)] (6,6,10,10-H), [4.26 (1H, d, *J* = 3.5), 4.80 (1H, d, *J* = 3.5)] (4-CH_2), 7.39 (1H, s, NH)
1d	$CDCl_3$	1.63 (3H, s, 4-Me), [1.89-2.05 (1H, m), 2.07-2.24 (1H, m)] (4-$ArCH_2\underline{CH_2}$), 2.51-2.76 (2H, m, 4-$Ar\underline{CH_2}CH_2$), [4.34 (1H, d, *J* = 3.3), 4.88 (1H, d, *J* = 3.3)] (5-CH_2), 5.92 (2H, s, OCH_2O), [6.61 (1H, d, *J* = 8.2), 6.74 (1H, d, *J* = 8.2)] (Ar 4',5'-H), 6.65 (1H, s, Ar 7'-H)
2a	DMSO-d$_6$	[1.12 (3H, s), 1.18 (3H, s), 1.29 (3H, s)] (1,1,4a-Me), 2.69 (2H, t, 3-$Ar\underline{CH_2}CH_2$), 3.12-3.39 (2H, m, 3-$ArCH_2\underline{CH_2}$), [3.67 (3H, s), 3.70 (3H, s)] (3-Ar 3',4'-OMe), 5.81 (1H, s, 4-OH), 6.68-6.86 (3H, m, 3-Ar 2',5',6'-H)
3a	DMSO-d$_6$	[1.23 (3H, s), 1.24 (3H, s), 1.29 (3H, s), 1.30 (3H, s), 1.34 (3H, s), 1.39 (3H, s)] (4,4',5,5,5',5'-Me), 3.17–3.39 (4H, m, 3,3'-CH_2CH_2), [5.95 (1H, s), 5.99 (1H, s)] (4,4'-OH)
3b	DMSO-d$_6$	[1.13-1.80 (18H, m), 1.90–2.10 (2H, m)] (two chains $(CH_2)_5$), [1.34 (3H, s), 1.35 (3H, s)] (4,4'-Me), [5.75 (1H, s), 5.78 (1H, s)] 4,4'-OH)
4a	$CDCl_3$	[0.98 (3H, s), 1.68 (3H, s)] (1,1-Me), 1.53 (3H, s, 10*b*-Me), {[2.65-2.75 (m), 2.85–3.05 (m) (3H)], [4.03-4.13 (1H, m)]} (5,5,6,6-H), [3.84 (3H, s), 3.86 (3H, s)] (8,9-OMe), 6.49, 6.62 (2H, 2s, 7,10-H)
4b	$CDCl_3$	0.80-0.91 (3H, m, 1-$CH_2\underline{CH_3}$), [0.89-1.08 (m), 1.62–1.83 (m), 1.25-1.43 (m), 2.21–2.35 (m)] (2H, 1-$\underline{CH_2}CH_3$), 0.89, 1.50, 1.52, 1.59 (6H, 4c, 1,10*b*-Me), [2.63–2.75 (1H, m), 2.85–3.01 (1H, m), 3.00-3.17 (1H, m), 4.01-4.13 (1H, m)] (5,5,6,6-H), [3.82 (3H, s), 3.86 (3H,s)] (8,9-OMe), [6.45, 6.48 (1H, 2s), 6.61 (1H, s)] (7,10-H)
4c	$CDCl_3$	0.90-1.82 (10H, m, 1,1-$(CH_2)_5$, 1.49 (3H, s, 10*b*-Me), [2.60-2.70 (1H, m), 2.80-3.15 (2H, m), 4.02-4.12 (1H, m)] (5,5,6,6-H), 3.86 (6H, s, 8,9-OMe), [6.50 (1H, s), 6.61 (1H, s)] (7,10-H)
4d	$CDCl_3$	[0.55-0.60 (1H, m), 1.30-1.40 (1H, m) 1.51-1.61 (1H, m), 2.20-2.30 (1H, m)] ($\underline{CH_2}$–C(Me)$_2$–NH–C(Me)$_2\underline{CH_2}$), [0.95 (3H, s), 1.25 (3H, s), 1.36 (3H, s), 1.44 (3H, s), 1.47 (3H, s)] (CH_2–C($\underline{Me}$)$_2$–NH–C($\underline{Me}$)$_2$–CH_2), [2.63-2.73 (1H, m), 2.86-3.00 (1H, m), 3.02–3.15 (1H, m), 4.05-4.15 (1H, m)] ($ArCH_2CH_2N$), [3.84 (3H, s), 3.88 (3H, s)] (8,9-OMe), [6.47 (1H, s), 6.63 (1H, s)] (Ar 7,10-H), 7.25, 7.35 (1H, 2s, NH)
5	$CDCl_3$	[1.45 (3H, s), 1.55 (3H, s)] (3a,10*b*-Me), [1.63-1.78 (1H, m), 2.17-2.27 (1H, m), 2.48-2.62 (1H, m), 2.81-2.96 (1H, m)] (4,4,5,5-H), 2.63 (3H, s, 1-Me), 5.94 (2H, s, OCH_2O), [6.61 (1H, s), 6.88 (1H, s)] (6,10-H)
6a	$CDCl_3$	[1.29 (3H, s), 1.31 (3H, s), 1.42 (3H, s), 1.49 (3H, s), 1.54 (3H, s)] (1,1,10,10,10*a*-Me), [3.15-3.34 (1H, m), 3.38-3.52 (1H, m), 4.00-4.20 (2H, m)] (5,5,6,6-H), 4.07 (1H, s, 11-H)
6b	$CDCl_3$	1.10-2.06 (20H, m, 1,1-$(CH_2)_5$ + 10,10-$(CH_2)_5$), 1.22 (3H, s, 10*a*-Me), 4.02 (1H, s, 11-H)

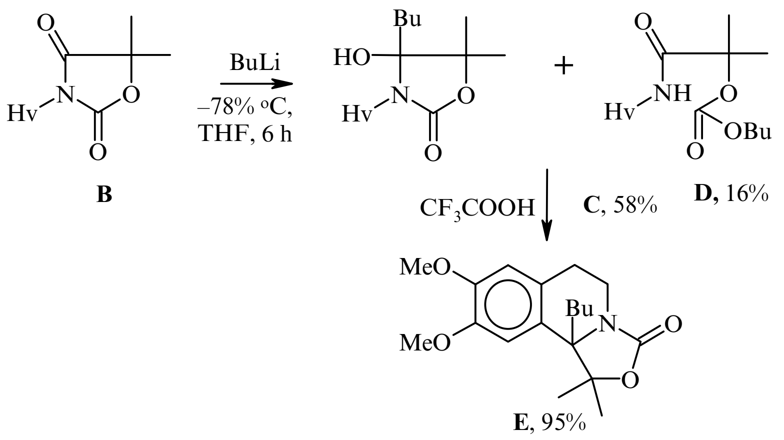


TABLE 2. Constants and Yields of Synthesized Compounds

Compound	IR spectrum, ν, cm^{-1} (group)	R_f, system	mp, °C	Mass spectrum, *m*/*z* (*I*, %)	Yield, %
1d	1720 (CO), 1688 C=CH$_2$)	0.5, *A* twice	82-84	225 (M$^+$ 3.0), 210 (100.0), 184 (9.1), 166 (13.3)	36
1e	1736 (CO), 1688 C=CH$_2$)	0.56, *B*	73-74	262 (M$^+$ 26.5), 148 (47.0), 135 (100.0)	46*
2a	1725 (CO), 3350 (OH)	0.27, *C*	103-105	309 (M$^+$ 1.2), 291 (20.7), 165 (32.1), 164 (100.0), 151 (65.3), 149 (29.5)	89
3a	1740 (CO), 3360 (OH)	0.75, *D*	210-212	316 (M$^+$ 1.0), 197 (24.8), 154 (34.5), 153 (100.0), 135 (22.2), 109 (50.1), 108 (51.0). 96 (61.3), 94 (51.4), 93 (35.1), 92 (45.5)	89
3b	1755 (CO), 3370 (OH)	0.8, *D*	225-227	396 (M$^+$ missing), 378 (2.7), 360 (19.5), 237 (25.4), 194 (68.6), 193 (100.0), 190 (23.2), 153 (21.4), 150 (66.8), 149 (56.8), 148 (64.3), 147 (69.9), 138 (67.6)	93
4a	1755 (CO)	0.43, *C*	132-134	291 (M$^+$ 4.3), 232 (40.5), 206 (12.9), 205 (100.0), 204 (24.4), 190 (26.8), 164 (82.8), 160 (12.4), 93 (11.3), 91 (22.4), 81 (15.1)	93
4b	1745 (CO)	0.5, *C*	100-103	305 (M$^+$ 20.3), 247 (17.5), 246 (71.6), 207 (13.7), 206 (68.0), 205 (100.0), 204 (64.3), 203 (23.3), 202 (10.4), 200 (12.0), 191 (17.2), 190 (72.0)	92
4c	1765 (CO)	0.43, *C*	130-132	331 (M$^+$ 8.1), 316 (28.2), 272 (28.8), 206 (39.2), 205 (100.0), 204 (19.5), 190 (23.8), 80 (2.9)	90
4d	1752 (CO)	0.5, *E* twice	168-170	388 (M$^+$ 4.0), 373 (100.0), 205 (41.1), 190 (21.1), 179 (30.0)	64
5	1732 (CO)	0.5, *C*	135-138	275 (M$^+$ 16.1), 260 (5.0), 200 (100.0), 185 (17.0), 175 (20.2)	100
6a	1735, 1775 (CO), 1650 (C=CH$_2$)	0.78, *D*	235-237	280 (M$^+$ 19.3), 265 (38.9), 177 (14.8), 149 (26.8), 148 (43.4), 135 (15.7)	98
6b	1735, 1775 (CO), 1650 (C=CH$_2$)	0.88, *D*	282-285	360 (M$^+$ missing), 346 (11.6), 345 (51.7), 257 (32.8), 236 (12.3), 235 (56.4), 234 (100.0), 229 (10.7), 191 (12.7), 190 (40.5), 189 (42.8)	94

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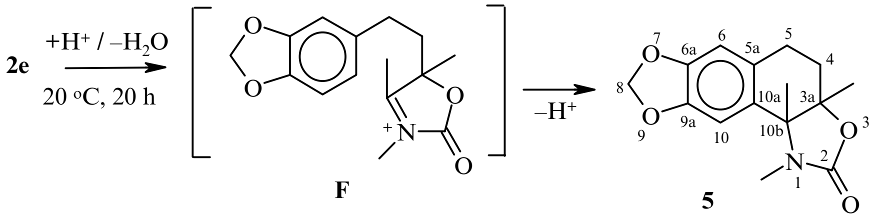
* Calculation based on starting ketone.

Our proposed method has an advantage over the already mentioned approach: the much easier accessibility of the oxazolidinones **2**.

The unisolated oxazolidinone **2e**, synthesized from dioxolanone **1e** and methylamine, under intramolecular amidoalkylation conditions is converted to tetrahydronaphthalene **5** in high yield.

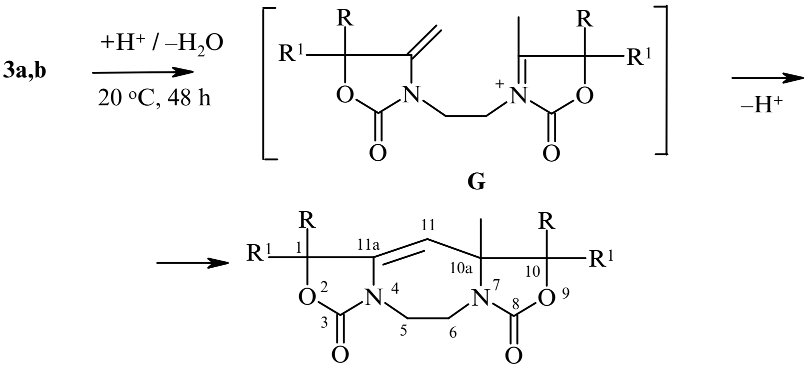


The reaction proceeds through the acyliminium ion **F**. The structure of tetrahydronaphthalene **5** has been proven based on ^{1}H NMR, IR, and mass spectrometry data.

We obtained oxazolidinones **3a,b** by reaction of dioxolanones **1a,c** with ethylenediamine. A linear carbamate structure has been suggested in the literature for the products of this reaction [5], but ^{1}H NMR spectra clearly indicate that the compounds are cyclic. In the ^{1}H NMR spectrum, there are two signals from 4,4'-OH (5.95 ppm and 5.99 ppm for compound **3a**, 5.73 ppm and 5.78 ppm for **3b**) six signals from methyl groups for compound **3a** with chemical shifts no greater than 1.39 ppm (for **3b**, two signals for 4,4'-Me, 1.36 ppm and 1.42 ppm), which is typical of oxazolidinones but not carbamates [1]. The IR spectra show an absorption band for the C=O group. A molecular ion peak is present in the mass spectrum of oxazolidinones **3a**.

By treatment of oxazolidinones **3a,b** with HCOOH, we obtained a novel heterocyclic system: 5,6,10,10*a*-tetrahydro-1*H*-di[1,3]oxazolo[3,4-*d*:4,3-*g*][1,4]diazepine-3,8-dione.

In our opinion, the reaction occurs through an intermediate species **G**, which is formed from the starting oxazolidinone **3**: one oxazolidinone ring undergoes dehydration to the 4-methylene derivative; the second ring is converted to an acyliminium ion, which attacks the enamine π-electron donor double bond of the first ring that is formed.



6a,b

6 a R = R^1 = Me; **b** R+R^1 = $(CH_2)_5$

In the ^{1}H NMR spectrum of diazepines **6a,b**, the methyl group in the 10*b* position has a chemical shift of 1.22 ppm (**6a**) and 1.29 ppm (**6b**); the proton in the 11 position has a chemical shift of 4.02 ppm (**6a**) and 4.07 ppm (**6b**) respectively. In the IR spectrum, we see vibrations of the C=O and C=CH groups. In the mass spectrum of diazepine **6a**, there is a molecular ion peak.

TABLE 3. Elemental Analysis Data

Compound	Empirical formula	Found, % / Calculated, %		
		C	H	N
1d	$C_{12}H_{19}NO_3$	63.90 63.96	8.60 8.52	6.22 6.22
1e	$C_{14}H_{14}O_5$	64.19 64.11	5.40 5.39	—
4a	$C_{16}H_{21}NO_4$	65.93 65.98	7.26 7.22	4.80 4.81
4b	$C_{17}H_{23}NO_4$	66.80 66.89	7.64 7.54	4.62 4.59
4c	$C_{19}H_{25}NO_4$	68.92 68.88	7.51 7.55	4.30 4.23
4d	$C_{22}H_{32}N_2O_4$	67.97 68.00	8.35 8.32	7.20 7.21
5	$C_{15}H_{17}NO_4$	65.43 65.43	6.23 6.24	5.05 5.09
6a	$C_{14}H_{20}N_2O_4$	60.97 59.31	7.04 7.21	10.16 9.99
6b	$C_{14}H_{20}N_2O_4$	66.65 66.67	7.77 7.78	7.80 7.78

EXPERIMENTAL

Dioxolanones **1a-c** were obtained according to the procedure in [6]. The ^{1}H NMR spectra were recorded on a Bruker WM-250; the IR spectra were recorded on a Perkin Elmer 577 (KBr disks); the mass spectra were recorded on a Kartos MS-30 mass spectrometer (direct injection of the sample, energy 70 eV, ionization chamber temperature 250°C). TLC was performed on Silufol UV-254 plates using the systems: chloroform–methanol, 9:1 (*A*), benzene–ethyl acetate, 9:1 (*B*), benzene–ethyl acetate, 1:1 (*C*), ethylacetate–2-propanol–water, 5:3.2:1.9 (*D*), ethanol + 2-3 drops of cyclohexane (*E*).

7,7,9,9-Tetramethyl-4-methylene-1,3-dioxa-8-azaspiro[4.5]decan-2-one (1d). In a one-liter rotary autoclave, the corresponding acetylene alcohol (45 g, 248 mmol) (synthesis of the alcohol is described in [7]), CuBr (4.4 g), NEt_3 (5.5 ml), TEBA (0.4 g), and MeCN (375 ml) were mixed and saturated with CO_2 at 20°C up to an initial pressure of 40 atm. The autoclave was heated for 24 h at 80°C (pressure ~80 atm); after cooling, the mixture was filtered, MeCN was evaporated, and yellowish crystals (19.9 g) were obtained by vacuum sublimation (5 mm Hg).

5-[2-(4-Methyl-5-methylene-1,3-dioxolan-2-on-4-yl)ethyl]-1,3-benzodioxole (1e). 4-(3,4-Methylenedioxyphenyl)-2-butanone (10 g, 52 mmol), 20% methanol KOH solution (20 ml), and liquid NH_3 (300 ml) were loaded into a one-liter rotary autoclave; the mixture was saturated with C_2H_2 under a pressure of 6 atm and held for 36 h. The autoclave was unloaded, NH_3 and C_2H_2 were removed from the reaction mass, water (400 ml) was added, then it was neutralized with 5% H_2SO_4 and extracted with benzene (2×100 ml). Benzene was evaporated and a dark oil (10 g) was obtained. The reaction mass was loaded into a 0.5-liter rotary autoclave and CuBr (1 g), NEt_3 (2 ml), TEBA (0.05 g), and benzene (20 ml) were added together with dry ice (~100 g). The autoclave was heated for 24 h at 80°C and a pressure of ~80 atm. The reaction mass was unloaded from the autoclave and filtered. Benzene was evaporated and the reaction mass was chromatographically purified on a column (diameter 6 cm, 100 g of silica gel Silufol 5/40, solvent – benzene). White crystals (6.3 g) were obtained.

4-Hydroxy-4,4,5-trimethyl-3-[2-(3,4-dimethoxyphenyl)ethyl]oxazolidin-2-one (2a). Homoveratrylamine (2.17 g, 12 mmol) was added to a solution of dioxolanone **1a** (1.66 g, 13 mmol) in CH_2Cl_2 (20 ml). The mixture was held at 20°C for 96 h and then CH_2Cl_2 was distilled off and the material was triturated with 10:3 hexane–benzene mixture (13 ml). The crystals were filtered off and washed with a 2:1 hexane–benzene mixture (2×10 ml). White crystals (3.30 g) were obtained.

N,N'-ethylenedi-(4-hydroxy-4,4,5-trimethyloxazolidin-2-one) (3a). A solution of a 70% aqueous solution of ethylenediamine (1.80 g, 2.58 ml, 30 mmol) and NEt_3 (0.2 ml) in MeCN (5 ml) was added in portions over a period of approximately 5 min to a solution of dioxolanone **1a** (7.81 g, 61 mmol) in MeCN (5 ml), with cooling and stirring (temperature 20-30°C). The solvent was evaporated (60-70°C on a bath) until a paste was formed (about 5-7 ml of liquid was distilled off). Then ether (10 ml) was added, carefully triturating the precipitated crystals; they were filtered off, washed with ether (5 ml), and dried. Yield 8.42 g.

N,N'-Ethylenedi(4-hydroxy-4-methyl-1,3-oxaazaspiro[4.5]decan-2-one) (3b). Obtained similarly to oxazolidinone **3a**: white crystals (1.49 g) were obtained from dioxolanone **1c** (1.35 g, 8.04 mmol) and an ethylenediamine solution (0.24 g, 0.35 ml, 4.02 mmol).

8,9-Dimethoxy-1,1,10*b*-trimethyl-1,5,6,10*b*-tetrahydro[1,3]oxazolo[4,3-*a*]isoquinolin-3-one (4a), 1-Ethyl-8,9-dimethoxy-1,10*b*-dimethyl-1,5,6,10*b*-tetrahydro[1,3]oxazolo[4,3-*a*]isoquinolin-3-one (4b), 8,9-dimethoxy-10*b*-methyl-1,1-pentamethylene-1,5,6,10*b*-tetrahydro[1,3]oxazolo[4,3-*a*]isoquinolin-3-one (4c). A solution of the corresponding dioxolanone **1a-c** (10 mmol) and homoveratrylamine (1.49 g, 10 mmol) in CH_2Cl_2 (15 ml) was allowed to stand for 24 hours at 20°C. CH_2Cl_2 was distilled off and the precipitate was dissolved in 99% CF_3COOH (calculated based on 0.1 g per 3 ml of acid) and then held for 24 hours at 20°C. The acid was distilled off at reduced pressure at 40-60°C. The reaction mixture was dissolved in 100 ml CH_2Cl_2; the residual acid was neutralized with a concentrated soda solution (20 ml) and then washed with a saturated NaCl solution (20 ml) and water (20 ml). The solution was filtered through cotton wool and CH_2Cl_2 was evaporated. An ether–hexane mixture (1:1, 10 ml) was added to the residue. The crystals were separated and washed on the filter with the same mixture. White or slightly cream-colored crystals were obtained: 2.71 g of tetrahydroisoquinoline **4a**, 2.80 g of tetrahydroisoquinoline **4b**, and 2.98 g of tetrahydroisoquinoline **4c** respectively.

Tetrahydroisoquinoline 4d. Obtained similarly to tetrahydroisoquinolines **4a-c** from dioxolanone **1d** (1.25 g, 5 mmol) and homoveratrylamine (0.91 g, 5 mmol) in CH_2Cl_2 (15 ml) (allowed to stand overnight at 20°C). The solvent was evaporated and the material was dried under vacuum, dissolved in CF_3COOH (10 ml), and allowed to stand for 3 days at 20°C. Then the material was purified as in the case of tetrahydroisoquinolines **4a-c**. Yield 1.24 g.

1,3*a*,10*b*-Trimethyl-3*a*,4,5-10*b*-tetrahydro[1,3]oxazolo[4',5':6,7]naphtho[1,2-*d*]oxazol-2(1H)-one (5). Dioxolanone **1e** (0.52 g) in MeCN (3 ml) and 40% aqueous $MeNH_2$ (2 ml) were mixed together at 20°C and allowed to stand overnight. The solvents were distilled off and MeCN (3 ml) was added. The solvent was distilled off again and drying was repeated one more time. The material was dried under vacuum. White crystals (0.61 g) of oxazolidinone **2e** (R_f 0.33, *B*) was obtained. The mixture without preliminary purification was dissolved in CF_3COOH (6 ml) and allowed to stand overnight at 20°C. Acid was distilled off. The reaction mixture was dissolved in CH_2Cl_2 (100 ml) and the residual acid was neutralized with a concentrated soda solution (20 ml). The mixture was washed with a saturated NaCl solution (20 ml) and water (20 ml). The solution was filtered through cotton wool and CH_2Cl_2 was evaporated. The crystals were triturated with ether (1 ml) and hexane (2 ml), the solvent was decanted, and the crystals were dried. White crystals (0.55 g) were obtained.

1,1,10,10,10*a*-Pentamethyl-5,6,10,10*a*-tetrahydro-1*H*-di[1,3]oxazolo[3,4-*d*:4,3-*g*][1,4]diazepine-3,8-dione (6a). Oxazolidinone **3a** (2 g, 6.33 mmol) was dissolved in HCOOH (15 ml) and held for 2 days at 20°C. Acid was distilled off and the reaction mixture was dissolved in CH_2Cl_2 (100 ml). The residual acid was neutralized with a concentrated soda solution (20 ml) and washed with a saturated NaCl solution (20 ml) and water (20 ml). The solution was filtered through cotton wool and CH_2Cl_2 was evaporated. Purification was not required. White crystals (1.73 g) were obtained.

10*a*-Methyl-1,1,10,10-bispentamethylene-5,6,10,10*a*-tetrahydro-1*H*-di[1,3]oxazolo[3,4-*d*:4,3-*g*][1,4]-diazepine-3,8-dione (6b). Obtained similarly to diazepine **6a**: white crystals (1.36 g) were obtained from oxazolidinone **3b** (1.59 g, 4.02 mmol) in HCOOH (15 ml).

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