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Derivatives of 1,1,2,2-Tetraaminoethane: I. Condensation of 1,2-Diacetoxy-1,2-bis(acylamino)ethanes with Nitrogen-Containing Nucleophiles

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Abstract—Reaction of 1,2-diacetoxy-1,2-bis(acylamino)ethanes with acetamide and urethane gave rise to 1,2-bis-(acetylamino)-1,2-bis(acylamino)ethanes and 1,2-bis(acylamino)-1,2-bis(ethoxycarbonylamino)ethanes respectively. Condensation products were isolated of reactions between 1,2-diacetoxy-1,2-bis-(acylamino)ethanes with acetonitrile, diaminofurazan, and 4-phenylfurazan-3-ylamine.

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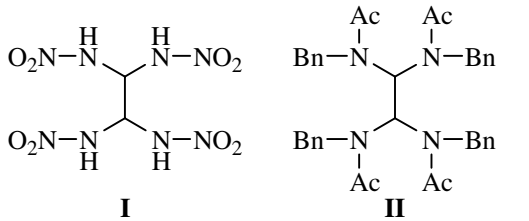
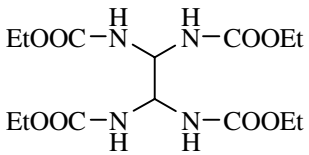
Nowadays the information on acyclic derivatives of 1,1,2,2-tetraaminoethane is very poor notwithstanding the simplicity of their structure. 1,1,2,2-Tetraaminoethane proper and also its *N,N'*,*N''*,*N'''*-tetraalkyl derivatives were not described in the literature. Only three representatives are known of this class compounds: 1,1,2,2-tetrakis(nitroamino)ethane (**I**) obtained by hydrolysis of 1,3,4,6-tetranitroglycoluril [1–3], *N,N'*,*N''*,*N'''*-tetrabenzyl-1,1,2,2-tetrakis-(acetylamino)ethane (**II**) isolated in 4% yield as a result of *N,N'*,*N''*,*N'''*-tetrabenzyl-2,4,6,8-tetraazabicyclo[3,3,0]octane hydrogenation [4], and 1,1,2,2-tetrakis(ethoxycarbonylamino)ethane (**III**) prepared by urethane condensation with glyoxal [5, 6].

One of the possible synthetic routes to 1,1,2,2-tetraaminoethane is the condensation of nitrogen-containing nucleophiles with 1,2-bis(acylamino)-1,2-ethanediols **IV** that are easily obtained from primary and secondary amides and glyoxal in a weakly basic medium [7–11] (Scheme 1).



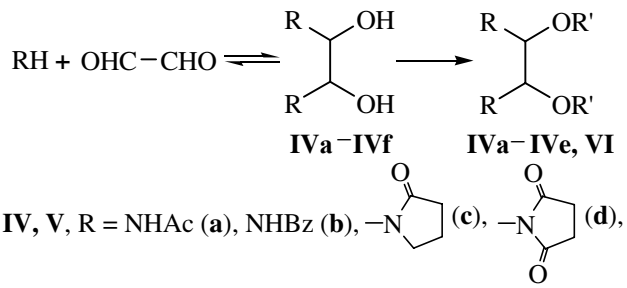
I

II



III

Scheme 1.



It was noted that whereas in a weakly basic media diols **IV** were formed in good yield, in the acid medium it was impossible to isolate the condensation products [7, 9]. Urethane is an exception for its heating with aqueous glyoxal in a 10% hydrochloric acid leads to the formation both of 1,1,2-tris(ethoxycarbonylamino)ethan-2-ol and 1,1,2,2-tetrakis(ethoxycarbonylamino)ethane (**III**). The latter formed in 30% yield [6].

The procedure used for condensation of urethane with glyoxal is not suitable for the most amides due to their low hydrolytic stability in the hydrochloric acid. Therefore we studied the reaction of primary amides (acetamide,

benzamide, chloroacetamide), and also of urethane with 1,2-bis(acylamino)-1,2-diols **IV** and their acetoxy derivatives **V** in anhydrous environment.

The corresponding condensations performed in aprotic solvents (acetonitrile, DMF) under acid catalysis with *p*-toluenesulfonic acid only in a single case of diacetoxy derivative **Va** resulted in isolation of 1,1,2,2-tetrakis-(acetylamino)ethane (**VIIa**), although in a very low yield (5%). The higher acidity of the reaction system or increased temperature led only to fast tarring both in this and all other cases.

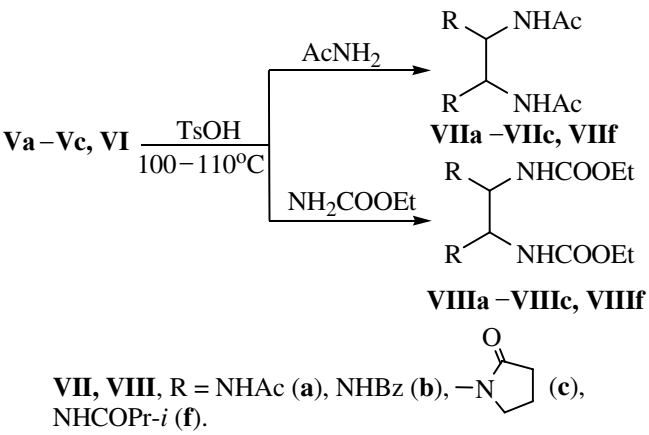
At the same time the use as solvent excess amide (or urethane) made it possible to synthesize the derivatives of tetraaminoethane **VII** and **VIII** in yields from 30 to 70%.

It was established that the condensation of 1,2-diacetoxy-1,2-bis(acylamino)ethanes **Va–Vc** with acetamide and urethane occurred successfully at heating without solvent for 30 min at 100–110°C under acid catalysis with *p*-toluenesulfonic acid (Scheme 2). The introducing into the reaction dimethoxy derivative **VI** under analogous conditions permitted isolation of compounds **VIIf** and **VIIIf** in respective yields 42 and 56%.

The study of the effect of the process parameters on the yield of compounds **VII** and **VIII** revealed that raising the temperature by 20–30°C sharply decreased the yield of target products because of the fast tarring. The increase than twice in the amount of catalyst used more resulted in significant reduction in the yield of derivatives **VII** and **VIII** by the same reason.

We failed to carry out the condensation of compounds **Va–Vc** with chloroacetamide and benzamide, less basic than acetamide and urethane, and also to involve into the reaction with acetamide and urethane less active

Scheme 2.



diacetoxyethylenediamides **Vd** and **Ve** under more rigid conditions (150–160°C); no expected derivatives of tetraaminoethane were obtained, and only gradual tarring was observed under the given conditions.

N-Alkyl-substituted amides are known to be obtained by Ritter reaction of aliphatic, aromatic, and heterocyclic nitriles with secondary and tertiary alcohols in the presence of strong acids (85–100% sulfuric acid, phosphoric acid, benzenesulfonic acid, 90% formic acid, perchloric acid) [12–14].

We demonstrated that diol **IVe** in the presence of 90% sulfuric acid at 0–5°C reacted with acetonitrile forming target compound **VIIe** in 85% yield (Scheme 3). The attempts to involve into the Ritter reaction diols **IVa–IVc** under similar conditions failed to give the corresponding tetraacylaminoethanes **VIIa–VIIc** apparently due to the hydrolysis of initial and/or intermediate compounds.

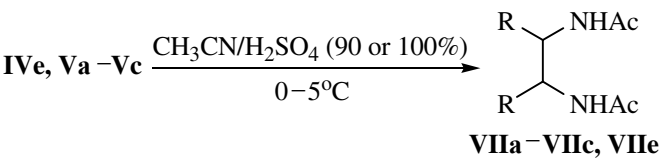
We established that a reaction in 100% sulfuric acid with diacetoxy derivatives **Va–Vc** instead of diols **IVa–IVc** provided target compounds **VIIa–VIIc** in 70–80% yield. In the course of these studies we found that the reagents ratio H_2SO_4(100%)/CH_3CN essentially affected the yield of the final tetrakis(acylamino) derivatives **VIIa–VIIc** : By increasing the ratio H_2SO_4(100%)/CH_3CN from 1:15 to 2:3 (by volume) the yield of compounds **VIIa–VIIc** as expected grew (from 50 to 80%).

The investigation of the reactivity of diacetoxy derivatives **V** with respect to other nitrogen-containing nucleophiles revealed the ease of compounds **V** condensation with low-basic amines from a furazan seies similar in the basicity to the acetamide and urethane.

The reaction of compounds **Va–Vc** with diaminofurazan under mild conditions (at room temperature in acetonitrile in the presence of a catalytic quantity of *p*-toluenesulfonic acid) provided cyclic derivatives of tetraaminoethane **Xa–Xc** in quantitative yield (Scheme 4). Diacetoxy derivatives **Va–Vc** under analogous conditions reacted with 4-phenylfurazan-3-ylamine giving the corresponding disubstituted compounds **IXa–IXc** in nearly 90% yield.

Consequently, the application of a stepwise procedure to the preparation of tetraaminoethane derivatives

Scheme 3.



(through an intermediate isolation of the products of glyoxal condensation with amides followed by their reaction with nitrogen-containing nucleophiles in anhydrous medium) made it possible to obtain a wide range of previously inaccessible polyfunctional compounds.

The structure and composition of all first synthesized compounds were confirmed by ^{1}H NMR and IR spectroscopy, and also by elemental analyses (physicochemical characteristics are reported in EXPERIMENTAL).

EXPERIMENTAL

IR spectra of compounds synthesized were recorded on a spectrometer Shimadzu FTIR 8400 (from films or pellets with KBr). ^{1}H NMR spectra were registered on Bruker WM-400 instrument (400 MHz), internal reference HMDS. Elemental analysis was carried out on a CHN-analyzer Hewlett Packard 185B.

1,2-Bis(acylamino)-1,2-ethanediols IV. General procedure [7, 11]. To 0.5 mol of 40% aqueous glyoxal was added 1 mol of amide (solid or dissolved in 50–100 ml of water), pH of the reaction mixture was adjusted to 8–9 by adding solid Na_2CO_3 or 20% solution of NaOH, and the mixture was stirred at room temperature for several days. The separated precipitate was filtered off, washed with a little water, and dried at 70–80°C.

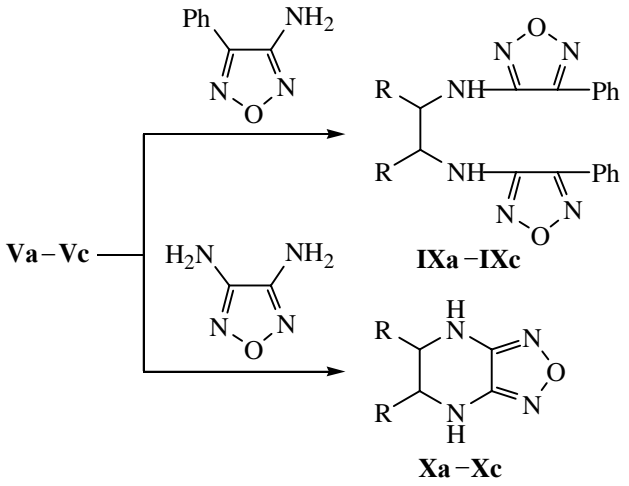
1,2-Bis(acetylamino)-1,2-ethanediol (IVa). Yield 91%, mp 165–166°C (ethanol–water). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.85 s (6H, CH_3), 5.04 d (2H, CH, *J* 4.2 Hz), 5.60 s (2H, OH), 7.80 d (2H, NH, *J* 4.2 Hz). Found, %: C 40.67; H 7.16; N 15.59. $C_6H_{12}N_2O_4$. Calculated, %: C 40.91; H 6.87; N 15.90.

1,2-Bis(benzoylamino)-1,2-ethanediol (IVb). Yield 89%, mp 168–169°C (ethanol–water). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 5.35–5.60 m (2H, CH), 7.35–7.60 m ($6H_{arom}$), 7.75–8.05 m ($4H_{arom}$), 8.50–8.75 m (2H, NH). Found, %: C 63.53; H 5.84; N 9.67. $C_{16}H_{16}N_2O_4$. Calculated, %: C 63.99; H 5.37; N 9.93.

1,2-Bis(2-oxopyrrolidin-1-yl)-1,2-ethanediol (IVc). Yield 90%, mp 190–191°C (ethanol–water). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.80–2.10 m (4H, CH_2), 2.10–2.35 m (4H, CH_2), 3.35–3.55 m (4H, CH_2), 5.20 s (2H, OH), 5.80 s (2H, CH). Found, %: C 52.98; H 7.36; N 12.05. $C_{10}H_{16}N_2O_4$. Calculated, %: C 52.62; H 7.07; N 12.27.

1,2-Bis(2,5-dioxopyrrolidin-1-yl)-1,2-ethanediol (IVd). Yield 80%, mp 182–183°C (ethanol–water). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.65 s (8H, CH_2), 6.05 s (2H, CH), 6.40 s (2H, OH). Found, %: C 47.03; H 4.97; N 11.08. $C_{10}H_{12}N_2O_6$. Calculated, %: C 46.88; H 4.72; N 10.93.

Scheme 4.



1,2-Bis(chloroacetylamino)-1,2-ethanediol (IVe). Yield 92%, mp 138–144°C (decomp.) (DMF). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 4.06 q (4H, CH_2, *J* 8.0 Hz), 4.97 d (2H, CH, *J* 6.1 Hz), 6.90–7.55 m (2H, OH), 8.45 d (2H, NH, *J* 6.9 Hz). Found, %: C 29.87; H 4.62; N 11.58. $C_6H_{10}Cl_2N_2O_4$. Calculated, %: C 29.41; H 4.11; N 11.43.

1,2-Bis(isobutyrylamino)-1,2-ethanediol (IVf). yield 87%, mp 145–146°C (ethanol–water). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.00–1.15 m (12H, CH_3), 2.25–2.45 m [2H, $CH(CH_3)_2$], 4.98–5.40 m (2H, CH), 5.50–6.40 m (2H, OH), 6.70–8.50 m (2H, NH). Found, %: C 51.34; H 9.05; N 12.36. $C_{10}H_{20}N_2O_4$. Calculated, %: C 51.71; H 8.68; N 12.06.

Acylation of 1,2-bis(acylamino)-1,2-ethanediols IVa–d. General procedure. To a mixture of 0.8 mol of triethylamine or pyridine and 0.4 mol of acetic anhydride was carefully added at vigorous stirring 0.1 mol of diol **IVa–IVd** maintaining the temperature below 50–60°C. After short stirring at this temperature the reaction mixture was cooled and left overnight in a refrigerator. The separated precipitate was filtered off, washed with cold ethanol, and dried at 70–80°C.

1,2-Bis(acetylamino)-1,2-diacetoxyethane (Va). Yield 86%, mp 175–177°C (ethanol–water). IR spectrum, cm^{-1}: 3269 (NH), 3069 (CN, CH_3), 1751 (C=O), 1676 (C=O), 1558 (CN, NH), 1375 (CH_3), 1330 (CH), 1243 (CNH, CO), 692 (NH). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.94 d (12H, CH_3, *J* 19.2 Hz), 6.40 d (2H,

CH, *J* 7.7 Hz), 8.50 d (2H, NH, *J* 7.7 Hz). Found, %: C 45.93; H 6.40; N 10.42. $C_{10}H_{16}N_2O_6$. Calculated, %: C 46.15; H 6.20; N 10.76.

1,2-Diacetoxy-1,2-bis(benzoylamino)ethane (Vb). Yield 84%, mp 153–155°C (ethane). IR spectrum, cm^{-1}: 3292 (NH), 3063 (CN, CH_3), 1740 (C=O), 1661 (C=O), 1603 (C=C), 1534 (CN, NH), 1490 (C=C), 1372 (CH_3), 1330 (CH), 1221 (CNH, CO), 804 (CH), 694 (NH). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.85– 2.05 m (6H, CH_3), 6.65–6.85 m (2H, CH), 7.45–7.55 m (6H_{arom}), 7.80–8.00 m (4H_{arom}), 8.80–9.35 m (2H, NH). Found, %: C 62.76; H 5.84; N 7.62. $C_{20}H_{20}N_2O_6$. Calculated, %: C 62.49; H 5.24; N 7.29.

1,2-Diacetoxy-1,2-bis(2-oxopyrrolidin-1-yl)-ethane (Vc). Yield 65%, mp 138–144°C. IR spectrum, cm^{-1}: 2990 (CH_2), 2900 (CH), 1755 (C=O), 1680 (C=O), 1417 (CH_2, CH_3), 1370 (CH, CH_3), 1227 (CO), 804 (CH). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.80–2.00 m (4H, CH_2), 2.05 d (6H, CH_3, *J* 13.3 Hz), 2.15–2.25 m (4H, CH_2), 3.25–3.45 m (4H, CH_2), 6.55 d (2H, CH, *J* 13.3 Hz). Found, %: C 53.47; H 6.29; N 9.02. $C_{14}H_{20}N_2O_6$. Calculated, %: C 53.84; H 6.45; N 8.97.

1,2-Diacetoxy-1,2-bis(2,5-dioxopyrrolidin-1-yl)-ethane (Vd). Yield 72%, mp 255–258°C (decomp.). IR spectrum, cm^{-1}: 2995 (CH_2), 2937 (CH), 1759 (C=O), 1716 (C=O), 1429 (CH_2, CH_3), 1367 (CH, CH_3), 1217 (CO), 818 (CH). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.05 d (6H, CH_3, *J* 26.7 Hz), 2.65 d (8H, CH_2, *J* 26.7 Hz), 7.05 d (2H, CH, *J* 53.3 Hz). Found, %: C 49.76; H 4.91; N 8.54. $C_{14}H_{16}N_2O_8$. Calculated, %: C 49.41; H 4.74; N 8.23.

1,2-Diacetoxy-1,2-bis(chloroacetylamino)ethane (Ve). To 50 ml of acetic anhydride was added 5 g (0.02 mol) of diol **IVe** and several drops of sulfuric acid, the reaction mixture was heated at 50–60°C and stirred at this temperature for 1 h, then it was cooled and poured into water. The separated precipitate was filtered off, washed with water, and dried at 70–80°C. Yield 5.6 g (83%), mp 160–161°C (decomp.) (DMF). IR spectrum, cm^{-1}: 3223 (NH), 3074 (CN), 2883 (CH), 1680 (C=O), 1562 (CN, NH), 1421 (CH_2Cl, CH_3), 1352 (CH, CH_3), 1280 (CH_2Cl), 1230 (CO), 1217 (CNH), 689 (NH). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.05 s (6H, CH_3), 4.05 s (4H, CH_2), 6.45 d (2H, CH, *J* 14.3 Hz). Found, %: C 36.78; H 4.68; N 8.61. $C_{10}H_{14}Cl_2N_2O_6$. Calculated, %: C 36.49; H 4.29; N 8.51.

1,2-Bis(isobutyrylamino)-1,2-dimethoxyethane (VI). To a solution of 5.4 g (0.04 mol) of dimethyl sulfate in 50 ml of methanol was added 5.0 g (0.02 mol) of diol **IVf**, the reaction mixture was heated at reflux for 1 h, cooled, left overnight in a refrigerator, and the separated precipitate was filtered off. Yield 4.2 g (75%), mp 172–174°C (2-propanol). IR spectrum, cm^{-1}: 3269 (NH), 3069 (CN, CH_3), 2966 (OCH_3), 1652 (C=O), 1552 (CN, NH), 1464 (CH_3), 1386 (CH_3), 1320 (CH), 1232 (CNH, CO), 1174 (CH_3), 1115 (COC), 725 (NH). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.00–1.15 m (12H, CH_3), 2.30–2.50 m [2H, $CH(CH_3)_2$], 3.20 s (6H, OCH_3), 4.90 d (2H, CH, *J* 7.7 Hz), 7.80 d (2H, NH, *J* 7.7 Hz). Found, %: C 55.59; H 8.96; N 10.83. $C_{12}H_{24}N_2O_4$. Calculated, %: C 55.36; H 9.29; N 10.76.

Condensation of 1,2-diacetoxy-1,2-bis(acylamino)ethanes Va–Vc and 1,2-bis(isobutyrylamino)-1,2-dimethoxyethane (VI) with acetamide and urethane. General procedure. A mixture of 0.1 mol of compound **Va–Vc** (or **VI**) and 0.4 mol of acetamide (or urethane) preliminary thoroughly ground in a mortar was melted at 100–110°C, then 0.005 mol of *p*-toluenesulfonic acid was added to the melt, and the mixture was stirred at the same temperature for 30 min. The reaction mixture was cooled, and the residue was washed from excess acetamide with acetone or from urethane with ether.

1,1,2,2-Tetrakis(acetylamino)ethane (VIIa). Yield 30%, mp > 300°C (water). IR spectrum, cm^{-1}: 3284 (NH), 3132 (CN), 3030 (CH_3), 1664 (C=O), 1570 (CN, NH), 1446 (CH_3), 1371 (CH_3), 1273 (CNH), 750 (NH). ^{1}H NMR spectrum (CF_3COOD), δ, ppm: 1.75 s (12H, CH_3), 5.75 s (2H, CH), 7.70 s (2H, NH). Found, %: C 46.83; H 7.16; N 21.73 $C_{10}H_{18}N_4O_4$. Calculated, %: C 46.50; H 7.03; N 21.69.

1,2-Bis(acetylamino)-1,2-bis(benzoylamino)-ethane (VIIb). Yield 30%, mp > 300°C (water). IR spectrum, cm^{-1}: 3273 (NH), 3115 (CN, CH_3), 1740 (C=O), 1649 (C=O), 1603 (C=C), 1556 (CN, NH), 1491 (C=C), 1436 (CH_3), 1371 (CH_3), 1340 (CH), 1226 (CNH, CO), 802 (CH), 716 (NH). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.85–2.00 m (6H, CH_3), 5.50– 5.95 m (2H, CH), 7.40–7.60 m (6H_{arom}), 7.70–8.10 m (4H_{arom}), 8.35–8.70 m (2H, NH). Found, %: C 62.68; H 5.48; N 14.17. $C_{20}H_{22}N_4O_4$. Calculated, %: C 62.82; H 5.80; N 14.65.

1,2-Bis(acetylamino)-1,2-bis(2-oxopyrrolidin-1-yl)ethane (VIIc). Yield 63%, mp 281–283°C. IR spectrum, cm^{-1}: 3300 (NH), 3061 (CN), 2968 (CH_2), 2898 (CH), 1663 (C=O), 1547 (CN, NH), 1433 (CH_2, CH_3), 1364 (CH, CH_3), 1286 (CNH), 794 (CH), 680 (NH). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.45–1.65 m

(4H, CH_2), 1.65–2.00 m (6H, CH_3), 2.05–2.30 m (4H, CH_2), 3.15–3.50 m (4H, CH_2), 5.60–6.00 m (2H, CH), 7.60–8.45 m (2H, NH). Found, %: C 54.25; H 6.85; N 17.93. $C_{14}H_{22}N_4O_4$. Calculated, %: C 54.18; H 7.14; N 18.05.

1,2-Bis(acetylamino)-1,2-bis(isobutyrylamino)-ethane (VIIf). Yield 42%, mp > 300°C (water), insoluble in DMSO. IR spectrum, cm^{-1}: 3287 (NH), 3132 (CN, CH_3), 1663 (C=O), 1566 (CN, NH), 1470 (CH_3), 1373 (CH_3), 1323 (CH), 1238 (CNH, CO), 1176 (CH_3), 732 (NH). Found, %: C 55.63; H 8.02; N 16.98. $C_{14}H_{26}N_4O_4$. Calculated, %: C 55.49; H 8.34; N 17.42.

1,2-Bis(acetylamino)-1,2-bis(ethoxycarbonyl-amino)ethane (VIIIa). Yield 53%, mp 240°C (ethanol–water). IR spectrum, cm^{-1}: 3292 (NH), 3122 (CN), 2984 (CH_3, CH_2), 1693 (C=O), 1655 (C=O), 1558 (CN, NH), 1528 (C=O), 1437 (CH_3, CH_2), 1371 (CH_3), 1329 (CH), 1260 (CNH), 1176 (CO), 802 (CH), 736 (NH). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.15–1.25 m (6H, CH_3), 1.80 s (6H, CH_3), 3.90–4.05 m (4H, CH_2), 5.20– 5.45 m (2H, CH), 6.90 s (2H, NH), 7.75 s (2H, NH). Found, %: C 45.11; H 5.97; N 17.22 $C_{12}H_{22}N_4O_6$. Calculated, %: C 45.28; H 6.97; N 17.60.

1,2-Bis(benzoylamino)-1,2-bis(ethoxycarbonyl-amino)ethane (VIIIb). Yield 69%, mp 260–262°C (ethanol–water). IR spectrum, cm^{-1}: 3285 (NH), 2983 (CN, CH_3, CH_2), 1697 (C=O), 1647 (C=O), 1603 (C=C), 1550 (CN, NH), 1491 (C=C), 1458 (CH_3, CH_2), 1370 (CH_3), 1344 (CH), 1256 (CNH, CO), 802 (CH), 694 (NH). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.05–1.30 m (6H, CH_3), 3.90–4.10 m (4H, CH_2), 5.55–5.95 m (2H, CH), 6.55–7.10 m (2H, NH), 7.30–7.65 m ($6H_{arom}$), 7.70–7.95 m ($4H_{arom}$), 8.40–8.50 m (2H, NH). Found, %: C 60.07; H 5.59; N 12.85. $C_{22}H_{26}N_4O_6$. Calculated, %: C 59.72; H 5.92; N 12.66.

1,2-Bis(2-oxopyrrolidin-1-yl)-1,2-bis(ethoxy-carbonylamino)ethane (VIIIc). Yield 81%, mp 223–225°C. IR spectrum, cm^{-1}: 3233 (NH), 3064 (CN), 2987 (CH_3, CH_2), 1664 (C=O), 1560 (CN, NH), 1489 (C=O), 1439 (CH_3, CH_2), 1389 (CH_3), 1366 (CH), 1234 (CNH), 1165 (CO), 783 (CH), 681 (NH). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.15–1.25 m (6H, CH_3), 1.75–2.00 m (4H, CH_2), 2.05–2.30 m (4H, CH_2), 3.25–3.50 m (2H, CH_2), 3.85–4.05 m (4H, CH_2), 5.65 c (2H, CH), 7.65 C (2H, NH). Found, %: C 52.37; H 6.76; N 15.52. $C_{16}H_{26}N_4O_6$. Calculated, %: C 51.88; H 7.08; N 15.13.

1,2-Bis(isobutyrylamino)-1,2-bis(ethoxy-carbonylamino)ethane (VIIIf). Yield 56%, mp 268–269°C (water), insoluble in DMSO. IR spectrum, cm^{-1}: 3292 (NH), 2980 (CN, CH_3, CH_2), 1697 (C=O), 1666 (C=O), 1554 (CN, NH), 1446 (CH_3, CH_2), 1371 (CH_3), 1334 (CH), 1248 (CNH, CO), 783 (CH), 691 (NH). Found, %: C 49.81; H 8.23; N 15.80. $C_{16}H_{30}N_4O_6$. Calculated, %: C 51.32; H 8.08; N 14.96.

1,1,2,2-Tetrakis(acylamino)ethanes VIIa–e. Ritter reaction. *a*. To 20 ml of acetonitrile was slowly added 20 ml of 90% sulfuric acid maintaining the temperature below 0–5°C. At the end of addition into the reaction mixture was introduced 0.020 mol of diol **IVd** or **IVe**, the mixture was stirred for 1.5 h at 0–5°C, and then it was poured on ice. The separated precipitate was filtered off and thoroughly washed with water.

1,2-Bis(acetylamino)-1,2-bis(chloroacetyl-amino)ethane (VIIe). Yield 84%, mp >300°C (DMF). IR spectrum, cm^{-1}: 3288 (NH), 3122 (CN), 3028 (CH_3), 2958 (CH_2), 1668 (C=O), 1558 (CN, NH), 1419 (CH_2), 1373 (CH_3), 1261 (CNH, CH_2Cl), 694 (NH). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.80 s (6H, CH_3), 4.05 s (4H, CH_2), 5.60–5.70 m (2H, CH), 8.05–8.20 m (2H, NH), 8.25–8.40 m (2H, NH). Found, %: C 36.40; H 4.63; N 16.89 $C_{10}H_{16}Cl_2N_4O_4$. Calculated, %: C 36.71; H 4.93; N 17.12.

b. To 15 ml of acetonitrile at 0–5°C was slowly added while stirring 10 ml of 100% sulfuric acid. At the end of addition into the reaction mixture cooled to –5°C was introduced 0.015 mol of diol **Va–Vc**. The solution obtained was left overnight in a refrigerator, then it was poured on ice. The separated precipitate was filtered off and thoroughly washed with water. Yields of compounds, %: 81 (**VIIa**), 70 (**VIIb**), 67 (**VIIc**).

Condensation of 1,2-diacetoxy-1,2-bis(acyl-amino)ethanes Va–Vc with diaminofurazan and 4-phenylfurazan-3-ylamine. *General procedure*. To a suspension of 0.01 mol of reagent **Va–Vc** in 15 ml of acetonitrile was added at room temperature 0.01 mol of diaminofurazan (or 0.02 mol of 4-phenylfurazan-3-ylamine), 0.001 mol of *p*-toluenesulfonic acid, and 3 drops of DMSO. The reaction mixture was vigorously stirred for 36 h at room temperature, then the precipitate was filtered off, washed with boiling ethanol, and dried at 50–60°C.

1,2-Bis(acetylamino)-1,2-bis(4-phenylfurazan-3-ylamino)ethane (IXa). Yield 93%, mp 224–226°C (decomp.). IR spectrum, cm^{-1}: 3271 (NH), 3058 (CH_3), 1656 (C=O, C=N, CH), 1593 (CH), 1519 (C=N, NH), 1472 (CC), 1448 (CH_3), 1375 (CH_3), 1263 (CNH), 800 (CH), 696 (NH). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.75–1.90 m (6H, CH_3), 5.20–5.75 m (2H, CH),

6.30– 6.60 m (2H, NH), 7.50–7.65 m ($6H_{arom}$), 7.65–7.75 m ($4H_{arom}$), 7.90–8.15 m (2H, NH). Found, %: C 57.24; H 5.01; N 23.91. $C_{22}H_{22}N_8O_4$. Calculated, %: C 57.14; H 4.79; N 24.23.

1,2-Bis(benzoylamino)-1,2-bis(4-phenylfurazan-3-ylamino)ethane (IXb). Yield 91%, mp 215–218°C (decomp.). IR spectrum, cm^{-1}: 3285 (NH), 1641 (C=O, C=N, CH), 1593 (CH), 1524 (C=N, NH), 1489 (CC), 1265 (CNH), 800 (CH), 692 (NH). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 6.00–6.20 m (2H, CH), 6.35–6.60 m (2H, NH), 7.35–7.65 m ($6H_{arom}$), 7.65–7.80 m ($4H_{arom}$), 8.50–8.70 m (2H, NH). Found, %: C 65.88; H 4.79; N 19.40 $C_{22}H_{22}N_8O_4$. Calculated, %: C 65.52; H 4.47; N 19.10.

1,2-Bis(2-oxopyrrolidin-1-yl)-1,2-bis(4-phenylfurazan-3-ylamino)ethane (IXc). Yield 73%, mp 232–235°C (decomp.). IR spectrum, cm^{-1}: 3248 (NH), 3055 (CH_2), 1664 (C=O, C=N, CH), 1593 (CH), 1548 (C=N, NH), 1419 (CH_2), 1290 (CNH), 773 (CH), 692 (NH). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 1.80–2.00 m (4H, CH_2), 2.10–2.30 m (4H, CH_2), 3.00–3.15 m (2H, CH_2), 3.40–3.55 m (2H, CH_2), 5.80–5.85 m (2H, CH), 6.85– 7.25 m (2H, NH), 7.35–7.60 m ($6H_{arom}$), 7.65–7.75 m ($4H_{arom}$). Found, %: C 61.10; H 4.95; N 22.03 $C_{26}H_{26}N_8O_4$. Calculated, %: C 60.69; H 5.09; N 21.78.

(4,5,6,7-Tetrahydro[1,2,5]oxadiazolo[3,4-*b*]-pyrazine-5,6-diyl)diacetamide (Xa). Yield 83%, mp 165–166°C (decomp.). IR spectrum, cm^{-1}: 3292 (NH), 3061 (CH_3), 1660 (C=O, C=N), 1516 (C=N, NH), 1436 (CH_3), 1375 (CH_3), 1284 (CNH), 705 (NH). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 1.70–1.95 m (6H, CH_3), 5.00–5.55 m (2H, CH), 6.30–6.90 m (2H, NH), 7.10–8.25 m (2H, NH). Found, %: C 39.87; H 5.64; N 34.25. $C_8H_{12}N_6O_3$. Calculated, %: C 40.00; H 5.04; N 34.98.

(4,5,6,7-Tetrahydro[1,2,5]oxadiazolo[3,4-*b*]-pyrazine-5,6-diyl)dibenzamide (Xb). Yield 94%, mp 230–232°C (decomp.). IR spectrum, cm^{-1}: 3323 (NH), 3030 (CH_3), 1650 (C=O, C=N, CH), 1582 (CH), 1514 (C=N, NH), 1485 (CC), 1446 (CH_3), 1334 (CH_3), 1280 (CNH), 830 (CH), 711 (NH). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 5.45–6.25 m (2H, CH), 7.15–7.55 m ($6H_{arom}$), 7.55–7.80 m ($4H_{arom}$), 7.80–8.00 m (2H, NH), 8.45– 9.10 m (2H, NH). Found, %: C 59.02; H 4.24; N 22.76. $C_{18}H_{16}N_6O_3$. Calculated, %: C 59.34; H 4.43; N 23.06.

(4,5,6,7-Tetrahydro[1,2,5]oxadiazolo[3,4-*b*]-pyrazine-5,6-diyl)dipyrrolidin-2-one (Xc). Yield 92%, mp 168–171°C (decomp.) (ethanol–water). IR spectrum, cm^{-1}: 3317 (NH), 3062 (CH_2), 1678 (C=O, C=N, CH), 1569 (CH, C=N, NH), 1488 (CC), 1419 (CH_2), 1288 (CNH), 837 (CH), 651 (NH). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 1.60–2.00 m (4H, CH_2), 2.05–2.35 m (4H, CH_2), 2.80–3.50 m (4H, CH_2), 5.45– 5.70 m (2H, CH), 6.65–7.20 m (2H, NH). Found, %: C 46.61; H 6.21; N 27.19. $C_{12}H_{16}N_6O_3 \cdot H_2O$. Calculated, %: C 46.45; H 5.85; N 27.08.

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