ISSN 1070-4280, Russian Journal of Organic Chemistry, 2007, Vol. 43, No. 4, pp. 596–601. © Pleiades Publishing, Ltd., 2007.
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Derivatives of 1,1,2,2-Tetraaminoethane: II.* Condensation of 4,5-Diacetoxy-1,3-diacetylimidazolidine and 2,3-Diacetoxy-1,4-diacetylpiperazine with Nitrogen-Containing Nucleophiles

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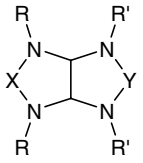
Received May 11, 2006

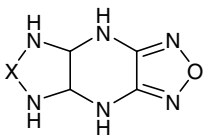
Abstract—Reactions of 4,5-diacetoxy-1,3-diacetylimidazolidine and 2,3-diacetoxy-1,4-diacetylpiperazine with acetamide and ethyl carbamate gave 1,3-diacetyl-4,5-bis(acetylamino)imidazolidine, 1,4-diacetyl-2,3-bis(acetylamino)piperazine, 1,3-diacetyl-4,5-bis(ethoxycarbonylamino)imidazolidine, and 1,4-diacetyl-2,3-bis(ethoxycarbonylamino)piperazine, respectively. Condensation products of 4,5-diacetoxy-1,3-diacetylimidazolidine and 2,3-diacetoxy-1,4-diacetylpiperazine with urea, furazan-3,4-diamine, and 4-phenylfurazan-3-amine were isolated.

DOI: 10.1134/S1070428007040185

In the preceding communication [1] we described a stepwise procedure for the synthesis of acyclic *N*,*N*′,*N*″,*N*‴-tetraacyl-substituted derivatives of ethane-1,1,2,2-tetraamine. The procedure included intermediate isolation of the condensation products of glyoxal with amides, followed by treatment with nitrogen-containing nucleophiles in anhydrous medium [1]. While continuing studies in this line, we presumed that an analogous approach can be applied to the synthesis of cyclic derivatives having a 1,1,2,2-tetraaminoethane fragment. According to published data [2–4], such compounds can be obtained by condensation of nitrogen-containing nucleophiles with the condensation products of bis-amides with glyoxal in aqueous solutions of acids. For example, the condensation of 4,5-dihydroxyimidazolidine-1,3-dicarbaldehyde and 2,3-dihydroxypiperazine-1,4-dicarbaldehyde with urea in hydrochloric acid gave hexahydroimidazo[4,5-*d*]imidazol-2(1*H*)-one (**Ia**) and 2,5,7,9-tetrahydro-2,5,7,9-tetraazabicyclo[4.3.0]nonan-8-one (**Ib**), respectively, which were isolated as the corresponding hydrochlorides [2, 3]. Likewise, furazano[3,4-*b*]pyrazine derivatives **IIa** and **IIb** were synthesized [4]. The condensation of 1,3-diacetylimidazolidine-4,5-diyl diacetate (**V**) with *N*,*N*′-methylenedi(acetamide) in acetonitrile, catalyzed by *p*-toluenesulfonic acid is the only example of the synthesis of cyclic compounds having a 1,1,2,2-tetraaminoethane fragment in anhydrous medium. The yield of the resulting 2,4,6,8-tetraacetyl-2,4,6,8-tetraazabicyclo[3.3.0]octane (**Ic**) was 58% [5].



Ia–Ic



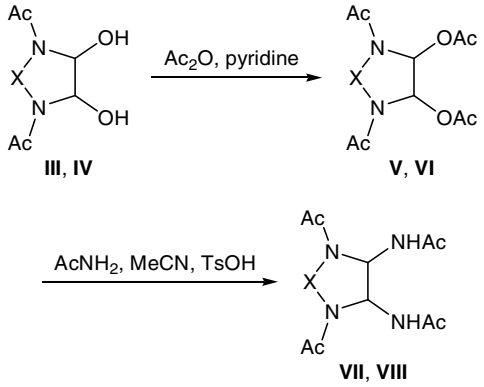
IIa, **IIb**

I, Y = C=O, R = R′ = H, X = CH_2 (**a**), CH_2CH_2 (**b**); X = Y = CH_2, R = R′ = Ac (**c**); **II**, X = CH_2 (**a**), CH_2CH_2 (**b**).

In the present work we examined reactions of 1,3-diacetylimidazolidine-4,5-diyl diacetate (**V**) and 1,4-diacetylpiperazine-2,3-diyl diacetate (**VI**) with various nitrogen-centered nucleophiles, including primary amides, ethyl carbamate, ureas, and low-basic amines of the furazan series, in anhydrous medium. By condensation of imidazolidine **V** with acetamide in boiling acetonitrile in the presence of a catalytic amount of *p*-toluenesulfonic acid we obtained bis(acetylamino)imidazolidine **VII** in 45% yield (Scheme 1). We succeeded in slightly raising the yield of **VII** (to 61%) using boron trifluoride–ether complex as catalyst. However, we failed to isolate the corresponding bis(acetylamino) derivative **VIII** in the reaction of piperazine **VI** with acetamide under analogous conditions, for the process was accompanied by strong tarring.

* For communication I, see [1].

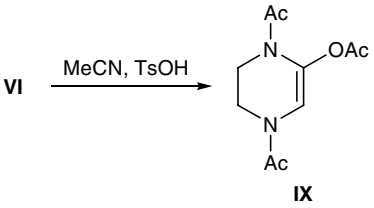
Scheme 1.



III, **V**, **VII**, X = CH_2; **IV**, **VI**, **VIII**, X = CH_2CH_2.

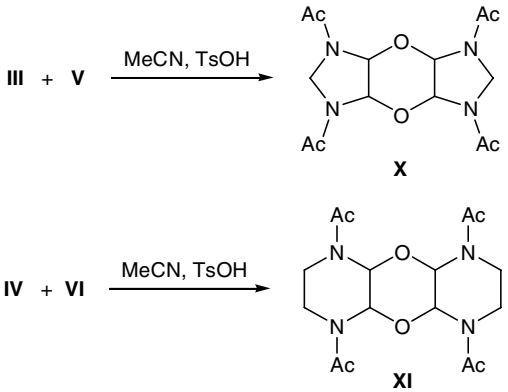
We also found that heating of piperazine **VI** in acetonitrile in the presence of a catalytic amount of *p*-toluenesulfonic acid over a period of 1–2 min leads to partial deacetoxylation of the initial compound to give monoacetoxy derivative **IX** (TLC) which can be isolated from the reaction mixture in 38% yield (Scheme 2).

Scheme 2.



Taking into account that compound **IX** in aprotic solvents in the presence of *p*-toluenesulfonic acid undergoes fast tarring, we made an attempt to synthesize bis(acetylamino) derivative **VIII** under milder conditions. When the reaction was carried out at room temperature, we isolated compound **VIII** in 10–15% yield.

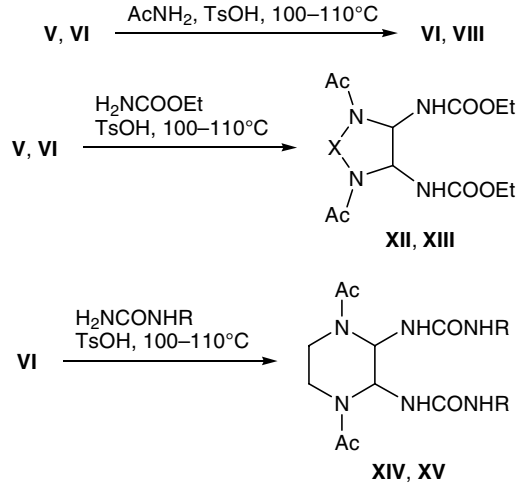
Scheme 3.



We examined the reactivity of dihydroxy- and diacetoxyimidazolidine and -piperazine derivatives **III**, **V** and **IV**, **VI** with respect to each other and found that heating of their mixtures in acetonitrile in the presence of *p*-toluenesulfonic acid as catalyst results in the formation of the corresponding cyclic diethers **X** and **XI** in 31 and 23% yield, respectively (Scheme 3). We failed to synthesize compounds **X** and **XI** by heating diacetoxyimidazolidine **V** or diacetoxypiperazine **VI** in acetonitrile under analogous conditions.

We previously showed [1] that 1,2-diacetoxy-1,2-bis(acetylamino)ethanes successfully react with acetamide and ethyl carbamate on heating for 30 min at 100–110°C in the presence of *p*-toluenesulfonic acid under solvent-free conditions. Following an analogous procedure, we synthesized the corresponding bis(acetylamino) and bis(ethoxycarbonylamino) derivatives of imidazolidine (**VII**, **VIII**) and piperazine (**XII**, **XIII**) in satisfactory yields (45–65%; Scheme 4).

Scheme 4.

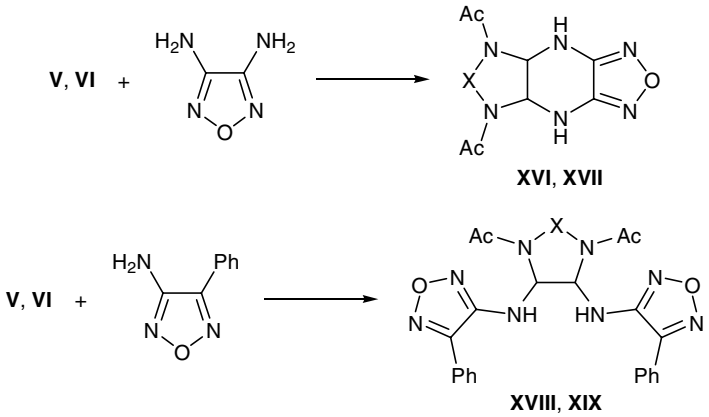


XII, X = CH_2; **XIII**, X = CH_2CH_2; **XIV**, R = H; **XV**, R = *o*-MeC_6H_4.

Piperazine **VI** reacted with excess urea and *N*-(*o*-tolyl)urea under catalysis by *p*-toluenesulfonic acid to give 54 and 52% of the corresponding disubstitution products **XIV** and **XV**, respectively. Our attempts to obtain analogous derivatives of imidazolidine **V** were unsuccessful: the reaction was accompanied by vigorous decomposition.

Imidazolidine **V** and piperazine **VI** behaved similarly to 1,2-diacetoxy-1,2-bis(acylamino)ethane [1] in reactions with amines of the furazan series, whose basicity approaches that of acetamide and ethyl carbamate. The condensations readily occurred in aceto-

Scheme 5.



XVI, **XVIII**, X = CH_2; **XVII**, **XIX**, X = CH_2CH_2.

nitrile at room temperature in the presence of a catalytic amount of *p*-toluenesulfonic acid. By reactions of compounds **V** and **VI** with furazan-2,3-diamine we obtained cyclic derivatives **XVI** and **XVII** in quantitative yields. The reactions of imidazolidine **V** and piperazine **VI** with 4-phenylfurazan-3-amine gave the corresponding disubstitution products **XVIII** and **XIX** in about 90% yield (Scheme 5).

The structure of the newly synthesized compounds was confirmed by ^{1}H and IR spectroscopy and elemental analysis (see Experimental).

EXPERIMENTAL

The IR spectra were recorded on a Shimadzu FTIR 8400 spectrometer from samples prepared as thin films or KBr pellets. The ^{1}H NMR spectra were measured on a Bruker WM-400 spectrometer (400 MHz) relative to hexamethyldisiloxane as internal reference. The elemental compositions were determined on a Hewlett–Packard HP 185B CHN analyzer. Thin-layer chromatography was performed on Sorbfil PTSKh-P-V-UF plates using acetone as eluent; spots were visualized under UV light.

1,3-Diacetylimidazolidine-4,5-diol (**III**) was synthesized as described in [6] and was recrystallized from ethanol, mp 176–177°C. 1,3-Diacetylimidazolidine-4,5-diyl diacetate (**V**) was synthesized by the procedure reported in [5] and was recrystallized from ethanol, mp 147–148°C.

1,4-Diacetylpiperazine-2,3-diol (IV). *N*,*N*′-Ethylenedi(acetamide), 5.0 g (0.035 mol), was added to 6.2 g (0.044 mol) of 40% aqueous glyoxal, and the mixture was adjusted to pH 8–9 by adding solid Na_2CO_3 or K_2CO_3 and was stirred for several days at room temperature. The precipitate was filtered off and washed with cold propan-2-ol. Yield 6.3 g (90%), mp 107–112°C (from acetonitrile). IR spectrum, ν, cm^{-1}: 3465 (OH), 2938 (CH_3, CH_2), 2890 (CH), 1628 (C=O), 1456 (CH_2), 1440 (CH_3), 1365 (CH_3), 1340 (CH), 1092 (C–O). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.05 d (6H, CH_3, J = 8.2 Hz), 2.90– 3.15 m (1.5H, CH_2), 3.30–3.60 m (1H, CH_2), 3.80–4.05 m (1.5H, CH_2), 5.00–5.60 m (2H, OH), 5.75–6.10 m (2H, CH). Found, %: C 47.85; H 6.25; N 13.73. $C_8H_{14}N_2O_4$. Calculated, %: C 47.52; H 6.98; N 13.85.

1,4-Diacetylpiperazine-2,3-diyl diacetate (VI). Compound **IV**, 2.0 g (0.01 mol), was slowly added to a mixture of 10 ml of pyridine or triethylamine and 5 ml of acetic anhydride, maintaining the temperature below 40–50°C. The mixture was stirred for a short time at that temperature, cooled, and left overnight in a refrigerator. The precipitate was filtered and washed with ethyl acetate. Yield 1.5 g (53%), mp 120–121°C (from ethyl acetate). IR spectrum, ν, cm^{-1}: 2934 (CH_3, CH_2), 2885 (CH), 1747 (C=O), 1674 (C=O), 1456 (CH_2), 1425 (CH_3), 1380 (CH_3), 1328 (CH), 1290 (C–O), 1086 (C–O). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.95–2.20 m (12H, CH_3), 2.75–3.20 m (1.5H, CH_2), 3.25–3.80 m (1H, CH_2), 4.15–4.40 m (1.5H, CH_2), 6.50 d (2H, CH, J = 92.3 Hz). Found, %: C 50.94; H 7.01; N 10.03. $C_{12}H_{18}N_2O_6$. Calculated, %: C 50.35; H 6.34; N 9.79.

***N*,*N*′-(1,3-Diacetylimidazolidine-4,5-diyl)diacetamide (VII).** *a*. A solution of 10.0 g (0.037 mol) of imidazolidine **V**, 4.3 g (0.073 mol) of acetamide, and 0.2 g (1.2 mmol) of *p*-toluenesulfonic acid in 50 ml of acetonitrile was heated for 48 h under reflux. The precipitate was filtered off, washed with boiling ethanol, and dried at 80°C. Yield 4.5 g (45%), mp 251°C (from

aqueous ethanol). IR spectrum, ν, cm^{-1}: 3273 (NH), 3033 (CH_3), 2937 (CH_2), 2890 (CH), 2808 (CH_2), 1666 (C=O), 1525 (CN, NH), 1410 (CH_3, CH_2), 1325 (CH, CH_3), 1278 (CNH), 713 (NH). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 1.85 d (6H, CH_3, J = 10.7 Hz), 2.05 d (6H, CH_3, J = 10.7 Hz), 4.65– 5.05 m (2H, CH_2), 4.5 d (2H, CH, J = 7.1 Hz), 8.20–8.80 m (2H, NH). Found, %: C 49.13; H 6.97; N 20.49. $C_{11}H_{18}N_4O_4$. Calculated, %: C 48.88; H 6.71; N 20.73.

b. Three drops of boron trifluoride–ether complex were added to a solution of 10.0 g (0.037 mol) of imidazolidine **V** and 4.3 g (0.073 mol) of acetamide in 50 ml of chloroform, and the mixture was heated for 72 h under reflux. The precipitate was filtered off, washed with chloroform, and dried at 80°C. Yield 6.5 g (61%), mp 251–252°C.

***N*,*N′*-(1,4-Diacetylpiperazine-2,3-diyl)diacetamide (VIII).** A solution of 3.0 g (0.010 mol) of piperazine **VI**, 1.5 g (0.025 mol) of acetamide, and 0.2 g (1.2 mmol) of *p*-toluenesulfonic acid in 30 ml of acetonitrile or chloroform was stirred for 7 days at room temperature. The precipitate was filtered off, washed with acetonitrile, and dried at 80°C. Yield 0.3 g (10%) (in acetonitrile), 0.45 g (15%) (in chloroform); mp 270–272°C (from aqueous ethanol). IR spectrum, ν, cm^{-1}: 3269 (NH), 3026 (CH_3), 2926 (CH_2), 2885 (CH), 2788 (CH_2), 1635 (C=O), 1533 (CN, NH), 1423 (CH_3, CH_2), 1323 (CH, CH_3), 1279 (CNH), 706 (NH). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 1.80–1.90 m (6H, CH_3), 2.00–2.10 m (6H, CH_3), 2.75–3.00 m (2H, CH_2), 3.60–4.25 m (2H, CH_2), 5.45–5.95 m (2H, CH), 8.30–8.90 m (2H, NH). Found, %: C 49.64; H 6.85; N 19.34. $C_{12}H_{20}N_4O_4$. Calculated, %: C 50.69; H 7.09; N 19.71.

1,4-Diacetyl-1,4,5,6-tetrahydropyrazin-2-yl acetate (IX). *p*-Toluenesulfonic acid, 0.1 g (0.6 mmol), was added to a solution of 5.0 g (0.017 mol) of piperazine **VI** in 5–7 ml of acetonitrile, and the mixture was heated to 80°C, immediately cooled, and left overnight in a refrigerator. The precipitate was filtered off, washed with ice-cold acetonitrile, and dried at room temperature. Yield 1.5 g (38%), mp 104–105°C. IR spectrum, ν, cm^{-1}: 3014 (CH), 2939 (CH_2, CH_3), 1780 (C=O), 1635 (C=O, C=C), 1456 (CH_2), 1406 (CH_3), 1350 (CH_3), 1242 (C–O), 840 (C=CH). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 2.10 d (6H, CH_3, J = 10.0 Hz), 2.17 s (3H, CH_3), 3.50–3.78 m (4H, CH_2), 6.67 d (1H, CH, J = 65.0 Hz). Found, %: C 53.22; H 5.96; N 12.52. $C_{10}H_{14}N_2O_4$. Calculated, %: C 53.09; H 6.24; N 12.38.

1,3,5,7-Tetraacetyloctahydro[1,4]dioxino-[2,3-*d*:5,6-*d′*]diimidazole (X). Imidazolidine **III**, 0.7 g (3.6 mmol), and *p*-toluenesulfonic acid, 0.06 g (0.36 mmol), were added to a solution of 1.0 g (3.6 mmol) of imidazolidine **V** in 25 ml of acetonitrile. The mixture was heated for 8 h under reflux, the solvent was distilled off under reduced pressure, and the residue was recrystallized from ethanol. Yield 0.4 g (31%), mp >300°C (decomp., from ethanol). IR spectrum, ν, cm^{-1}: 2995 (CH_3), 2943 (CH_2), 2881 (CH), 1662 (C=O), 1415 (CH_3, CH_2), 1338 (CH, CH_3), 1186 (COC), 1113 (COC). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 2.00–2.20 m (12H, CH_3), 4.55–5.15 m (4H, CH_2), 5.60–5.85 m (2H, CH). Found, %: C 49.05; H 6.45; N 16.61. $C_{14}H_{20}N_4O_6$. Calculated, %: C 49.41; H 5.92; N 16.46.

1,4,5,8-Tetraacetyldecahydro-9,10-dioxa-1,4,5,8-tetraazaanthracene (XI). Piperazine **IV**, 0.7 g (3.5 mmol), and *p*-toluenesulfonic acid, 0.06 g (0.36 mmol), were added to a solution of 1.0 g (3.5 mmol) of piperazine **VI** in 25 ml of acetonitrile. The mixture was heated for 8 h under reflux, and the precipitate was filtered off and washed with boiling ethanol. Yield 0.25 g (23%), mp >300°C (from water). IR spectrum, ν, cm^{-1}: 2970 (CH_3), 2937 (CH_2), 2883 (CH), 1668 (C=O), 1404 (CH_3, CH_2), 1333 (CH, CH_3), 1194 (COC), 1117 (COC). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 1.80–2.20 m (12H, CH_3), 3.35–4.20 m (8H, CH_2), 5.00–5.70 m (2H, CH). Found, %: C 50.41; H 6.03; N 14.32. $C_{16}H_{24}N_4O_6 \cdot H_2O$. Calculated, %: C 49.73; H 6.78; N 14.50.

Condensations of 1,3-diacetylimidazolidine-4,5-diyl diacetate (V) and 1,4-diacetylpiperazine-2,3-diyl diacetate (VI) with acetamide, ethyl carbamate, urea, and *N*-(*o*-tolyl)urea (*general procedure*)**.** A mixture of 0.1 mol of imidazolidine **V** or piperazine **VI** and 0.4 mol of acetamide, ethyl carbamate, urea, or *N*-(*o*-tolyl)urea was thoroughly ground in a mortar and heated to 100–110°C, 0.005 mol of *p*-toluenesulfonic acid was added to the melt, and the mixture was stirred for 30 min at that temperature, cooled, and washed with acetone (to remove excess acetamide), diethyl ether (to remove ethyl carbamate), or boiling ethanol (to remove ureas).

***N*,*N′*-(1,3-Diacetylimidazolidine-4,5-diyl)diacetamide (VII).** Yield 67%, mp 251–252°C (from aqueous ethanol).

Diethyl (1,3-diacetylimidazolidine-4,5-diyl)dicarbamate (XII). Yield 73%, mp 212–216°C (from propan-2-ol). IR spectrum, ν, cm^{-1}: 3269 (NH), 3059 (CH_3), 2985 (CH_3), 2936 (CH_2), 2904 (CH), 2779

(CH_2), 1717 (C=O), 1654 (C=O), 1541 (C=O), 1410 (CH_3, CH_2), 1370 (CH_3), 1337 (CH), 1178 (C–O). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.15–1.25 m (6H, CH_3), 1.90–2.10 m (6H, CH_3), 4.00–4.15 m (4H, CH_2), 4.60–4.95 m (2H, CH_2), 5.30–5.45 m (2H, CH), 7.70–8.40 m (2H, NH). Found, %: C 47.87; H 7.11; N 17.35. $C_{13}H_{22}N_4O_6$. Calculated, %: C 47.27; H 6.71; N 16.96.

***N*,*N*′-(1,4-Diacetylpiperazine-2,3-diyl)diacetamide (VIII).** Yield 45%, mp 271–272°C (from aqueous ethanol).

Diethyl (1,4-diacetylpiperazine-2,3-diyl)dicarbamate (XIII). Yield 62%, mp 219–220°C (from propan-2-ol). IR spectrum, ν, cm^{-1}: 3254 (NH), 3047 (CH_3), 2989 (CH_3), 2943 (CH_2), 2910 (CH), 2763 (CH_2), 1724 (C=O), 1647 (C=O), 1533 (C=O), 1425 (CH_3, CH_2), 1375 (CH_3), 1329 (CH), 1180 (C–O). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.15–1.30 m (6H, CH_3), 1.95–2.15 m (6H, CH_3), 2.75–2.95 m (1.5H, CH_2), 3.30–3.55 m (1.5H, CH_2), 4.00–4.20 m (5H, CH_2), 5.30–6.00 m (2H, CH), 7.70–8.45 m (2H, NH). Found, %: C 49.23; H 7.85; N 16.49. $C_{14}H_{24}N_4O_6$. Calculated, %: C 48.83; H 7.02; N 16.27.

***N*,*N*″-(1,4-Diacetylpiperazine-2,3-diyl)diurea (XIV).** Yield 54%, mp 243–244°C (from aqueous ethanol). IR spectrum, ν, cm^{-1}: 3298 (NH), 3026 (CH_3), 2935 (CH_2), 2891 (CH), 2794 (CH_2), 1680 (C=O), 1632 (C=O), 1533 (C=O), 1427 (CH_3, CH_2), 1360 (CH_3), 1329 (CH). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.00–2.25 m (6H, CH_3), 2.70 d (2H, CH_2, J = 11.4 Hz), 4.25 d (2H, CH_2, J = 11.4 Hz), 5.40 d (2H, CH, J = 11.4 Hz), 5.60 s (4H, NH_2), 7.10 d (2H, NH, J = 8.7 Hz). Found, %: C 40.13; H 7.05; N 27.78. $C_{10}H_{18}N_6O_4 \cdot H_2O$. Calculated, %: C 39.47; H 6.62; N 27.62.

***N*,*N*″-(1,4-Diacetylpiperazine-2,3-diyl)bis(3-*o*-tollylurea) (XV).** Yield 52%, mp 244–245°C. IR spectrum, ν, cm^{-1}: 3308 (NH), 2979 (CH_2), 2930 (CH_3), 2879 (CH), 1705 (CH), 1620 (C=O), 1589 (C=C), 1545 (C=O), 1485 (C=C), 1456 (C=C), 1429 (CH_3, CH_2), 1369 (CH_3), 1329 (CH), 758 (CH). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.20 s (6H, CH_3), 2.30 s (6H, CH_3), 2.80 d (2H, CH_2, J = 14.8 Hz), 4.30 d (2H, CH_2, J = 14.8 Hz), 5.60 d (2H, CH, J = 12.5 Hz), 6.80–6.90 m (2H, H_{arom}), 7.00–7.15 m (4H, H_{arom}), 7.65–7.75 m (2H, H_{arom}), 7.75–7.95 m (4H, NH). Found, %: C 62.07; H 6.01; N 18.27. $C_{24}H_{30}N_6O_4$. Calculated, %: C 61.79; H 6.48; N 18.01.

Condensations of 1,3-diacetylimidazolidine-4,5-diyl diacetate (V) and 1,4-diacetylpiperazine-2,3-diyl diacetate (VI) with furazan-3,4-diamine and 4-phenylfurazan-3-amine (*general procedure*). Furazan-3,4-diamine, 0.01 mol, or 4-phenylfurazan-3-amine, 0.02 mol, and *p*-toluenesulfonic acid, 0.001 mol, were added to a solution of 0.01 mol of imidazolidine **V** or piperazine **VI** in 15 ml of acetonitrile at room temperature. The mixture was stirred for 8 h at room temperature, and the precipitate was filtered off, washed with boiling ethanol, and dried at 50–60°C.

5,7-Diacetyl-4,4a,6,7,7a,8-hexahydroimidazo[4,5-*b*][1,2,5]oxadiazolo[3,4-*e*]pyrazine (XVI). Yield 90%, mp 200–202°C (from aqueous ethanol). IR spectrum, ν, cm^{-1}: 3267 (NH), 3057 (CH_3), 2937 (CH_2), 2899 (CH), 1660 (C=O), 1616 (C=N–O), 1402 (CH_3, CH_2, N–O), 1352 (CH_3), 1352 (CH), 1038 (furazan), 860 (furazan). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.00–2.20 m (6H, CH_3), 4.80–5.30 m (2H, CH_2), 5.40–5.85 m (2H, CH), 6.70–7.20 m (2H, NH). Found, %: C 40.57; H 4.83; N 31.43. $C_9H_{12}N_6O_3 \cdot H_2O$. Calculated, %: C 40.00; H 5.22; N 31.10.

5,8-Diacetyl-4,4a,7,8,8a,9-hexahydro-2-oxa-1,3,4,5,8,9-hexaazacyclopenta[*b*]naphthalene (XVII). Yield 95%, mp 218–220°C (from aqueous ethanol). IR spectrum, ν, cm^{-1}: 3332 (NH), 3018 (CH_3), 2933 (CH_2), 2887 (CH), 1660 (C=O), 1620 (C=N–O), 1425 (CH_3, CH_2, N–O), 1359 (CH_3), 1325 (CH), 1053 (furazan), 842 (furazan). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.00–2.30 m (6H, CH_3), 2.80–3.00 m (2H, CH_2), 3.70– 4.40 m (2H, CH_2), 5.30–6.05 m (2H, CH), 6.60–7.20 m (2H, NH). Found, %: C 42.79; H 6.12; N 29.99. $C_{10}H_{14}N_6O_3 \cdot H_2O$. Calculated, %: C 42.25; H 5.67; N 29.56.

1,3-Diacetyl-4,5-bis(4-phenylfurazan-3-ylamino)imidazolidine (XVIII). Yield 89%, mp 247–248°C (from ethanol). IR spectrum, ν, cm^{-1}: 3281 (NH), 3043 (CH, CH_3), 2937 (CH_2), 2889 (CH), 1640 (C=O, C=N–O, C=C), 1574 (C=C), 1485 (C=C), 1448 (C=C), 1402 (CH_3, CH_2, N–O), 1348 (CH_3), 1328 (CH), 1034 (furazan), 889 (furazan). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.00–2.20 m (6H, CH_3), 4.85–5.20 m (2H, CH_2), 5.50–5.70 m (2H, CH), 7.10–7.60 m (6H, H_{arom}, and 2H, NH), 7.65–7.80 m (4H, H_{arom}). Found, %: C 58.01; H 4.59; N 23.38. $C_{23}H_{22}N_8O_4$. Calculated, %: C 58.22; H 4.67; N 23.62.

1,4-Diacetyl-2,3-bis(4-phenylfurazan-3-ylamino)piperazine (XIX). Yield 89%, mp 209–210°C (from acetonitrile). IR spectrum, ν, cm^{-1}: 3246 (NH), 3008 (CH, CH_3), 2941 (CH_2, CH), 1657 (C=O), 1633 (C=N–O, C=C), 1574 (C=C), 1460 (C=C), 1448 (C=C), 1421 (CH_3, CH_2, N–O), 1367 (CH_3), 1329 (CH), 1037 (furazan), 885 (furazan). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.00–2.20 m (6H, CH_3), 2.95–3.05 m (1.5H,

CH_2), 3.45–3.65 m (1H, CH_2), 4.15–4.25 m (1.5H, CH_2), 5.55–6.15 m (2H, CH), 6.90–7.40 (2H, NH), 7.50–7.60 m (6H, H_{arom}), 7.65–7.80 m (4H, H_{arom}). Found, %: C 59.39; H 4.89; N 22.94. $C_{24}H_{24}N_8O_4$. Calculated, %: C 59.01; H 4.95; N 22.94.

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