

SHORT
COMMUNICATIONS

Derivatives of 1,1,2,2-Tetraaminoethane. Condensation of 1,2-Diacetoxy-1,2-bis(ethoxycarbonylamino)ethane and 1-Acetoxy-1,2,2-tris(ethoxycarbonylamino)ethane with Nitrogen-Containing Nucleophiles

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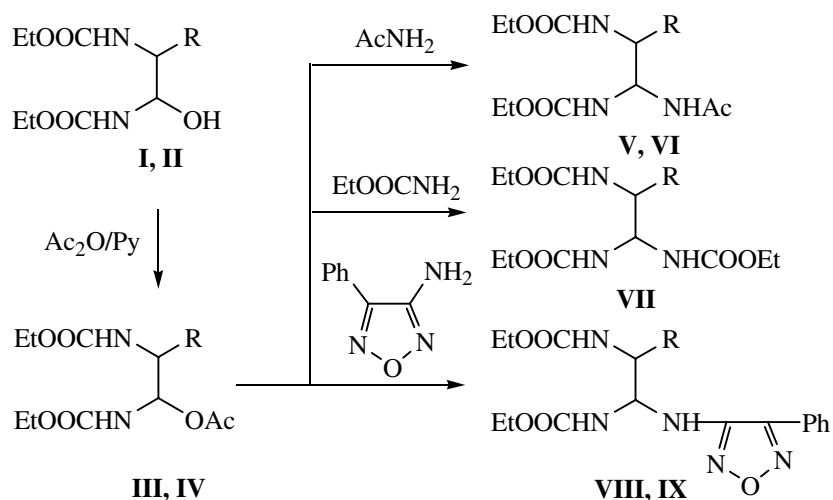
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We formerly established that N,N',N'',N'''-tetraacyl derivatives of 1,1,2,2-tetraaminoethane can be obtained from 1,2-diacetoxy-1,2-bis(acylamino)ethanes and nitrogen-containing nucleophiles in anhydrous medium [1]. In the present study a possibility is demonstrated to apply a similar approach to the synthesis of substituted 1,1,2,2-tetraaminoethanes by an example of a condensation of 1,2-diacetoxy-1,2-bis(ethoxycarbonylamino)ethane (**III**) and 1-acetoxy-1,2,2-tris(ethoxycarbonylamino)ethane (**IV**) with acetamide, urethane, and low-basic amines of the furazan series (diaminofurazan and 4-phenyl-3-furazanylamine).

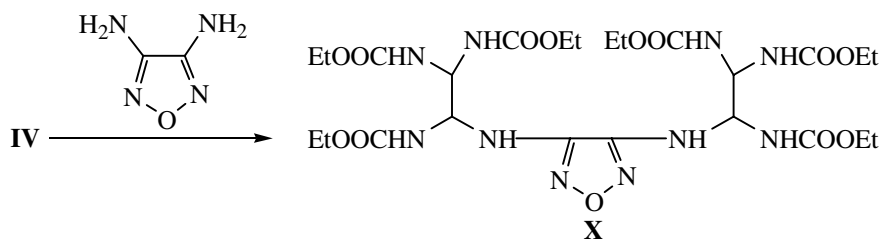
Heating of 1 mol of compounds **III** and **IV** with excess acetamide or urethane (4 mol) without solvent for 20 min at 100–110°C under acid catalysis with *p*-toluenesulfonic acid (0.1 mol) led to the formation of the corresponding bis(acetylamino) derivatives **V** and **VI** in 50–60% yield and 1,1,2,2-tetrakis(ethoxycarbonylamino)ethane (**VII**) in 90–95% yield.

The condensations with the low-basic amines of the furazan series were carried out in acetonitrile at room temperature in the presence of a catalytic amount of *p*-toluenesulfonic acid. Bis- and tris(ethoxycarbonylamino)ethanes **III** and **IV** readily reacted with 4-phenyl-



R = OH (**I**), OAc (**III**), NHAc (**V**), NHCOOEt (**II**, **IV**, **VI**, **VII**, **IX**), 4-phenyl-3-furazanylamino (**VIII**).

Scheme.



3-furazanylamine providing the corresponding derivatives **VIII** and **IX** in quantitative yields.

The reaction of monoacetoxy derivative **IV** with 1 equiv of diaminofurazane gave rise instead of expected monosubstituted product to disubstituted compound **X** in high yield (91%) (see scheme).

In contrast to 1,2-diacetoxy-1,2-bis(acylamino)ethanes [1] 1,2-diacetoxy-1,2-bis(ethoxycarbonylamino)ethane (**III**) does not form with diaminofurazan the corresponding bicyclic compound. In the course of reaction a gradual tarring was observed, and we succeeded in separation of only a little of 1,1,2,2-tetrakis(ethoxycarbonylamino)ethane (**VII**) (10%).

Initial 1,2-dihydroxy-1,2-bis(ethoxycarbonylamino)ethane (**I**) and 1-hydroxy-1,2,2-tris(ethoxycarbonylamino)ethane (**II**) were prepared by procedure [2] in 41 and 53% yield respectively. Their physicochemical characteristics and ^1H NMR spectra are in agreement with the published data [2].

General procedure of condensation of 1,2-diacetoxy-1,2-bis(ethoxycarbonylamino)ethane (I) and 1-acetoxy-1,2,2-tris(ethoxycarbonylamino)ethane (II) with acetamide and urethane. A thoroughly ground in a mortar mixture of 0.1 mol of compound **I** or **II** and 0.4 mol of acetamide or urethane 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 20 min. The reaction mixture was cooled, and the residue was washed from excess acetamide with acetone or from urethane with ether.

1,2-Diacetoxy-1,2-bis(ethoxycarbonylamino)ethane (III). mp 155–156°C. ^1H NMR spectrum (DMSO- d_6), δ , ppm: 1.20 t (6H, CH_3 , J 10.5 Hz), 1.95 s (6H, CH_3), 4.05 q (4H, CH_2 , J 5.5 Hz), 6.20 d (2H, CH, J 12.0 Hz), 7.95 s (2H, NH). Found, %: C 44.87; H 6.74; N 8.47. $\text{C}_{12}\text{H}_{20}\text{N}_2\text{O}_8$. Calculated, %: C 45.00; H 6.29; N 8.75.

1-Diacetoxy-1,2,2-tris(ethoxycarbonylamino)ethane (IV). mp 172–174°C. ^1H NMR spectrum

(DMSO- d_6), δ , ppm: 1.20 t (6H, CH_3 , J 10.5 Hz), 1.95 d (3H, CH_3 , J 42.1 Hz), 4.05 q (4H, CH_2 , J 5.5 Hz), 4.95–5.95 m (2H, CH), 6.70–7.90 m (2H, NH). Found, %: C 44.47; H 6.87; N 12.37. $\text{C}_{13}\text{H}_{23}\text{N}_3\text{O}_8$. Calculated, %: C 44.70; H 6.64; N 12.03.

1,2-Di(acetylamino)-1,2-bis(ethoxycarbonylamino)ethane (V). mp 240–241°C (240°C [1]).

1-Acetylamino-1,2,2-tris(ethoxycarbonylamino)ethane (VI). mp 237–239°C (decomp.). ^1H NMR spectrum (DMSO- d_6), δ , ppm: 1.20 t (6H, CH_3 , J 10.5 Hz), 1.80 s (3H, CH_3), 4.00 d (6H, CH_2 , J 10.5 Hz), 4.75–5.50 m (2H, CH), 6.05–7.20 m (3H, NH), 7.80 s (1H, NH). Found, %: C 44.21; H 6.34; N 15.89. $\text{C}_{13}\text{H}_{24}\text{N}_4\text{O}_7$. Calculated, %: C 44.82; H 6.94; N 16.08.

1,1,2,2-Tetrakis(ethoxycarbonylamino)ethane (VII). mp 277–279°C (276–278°C [2], 274–276°C [3]). ^1H NMR spectra of compounds **V** and **VII** are identical to the published ones [1–3].

General procedure of condensation of 1,2-diacetoxy-1,2-bis(ethoxycarbonylamino)ethane (I) and 1-acetoxy-1,2,2-tris(ethoxycarbonylamino)ethane (II) with diaminofurazan and 4-phenyl-3-furazanylamine. To a solution of 0.01 mol of compound **I** or **II** in 15 ml of acetonitrile was added at room temperature 0.01 mol of diaminofurazan or 0.02 mol of 4-phenyl-3-furazanylamine, and 0.001 mol of *p*-toluenesulfonic acid. The reaction mixture was stirred at room temperature for 8 h, the precipitate was filtered off, washed with boiling ethanol, and dried at 50–60°C.

1,2-Bis(4-phenyl-3-furazanylamino)-1,2-di(ethoxycarbonylamino)ethane (VIII). mp 234–237°C. ^1H NMR spectrum (DMSO- d_6), δ , ppm: 1.20 t (6H, CH_3 , J 10.5 Hz), 4.00 q (4H, CH_2 , J 5.5 Hz), 6.45 s (2H, CH), 6.30 s (2H, NH), 6.70–7.10 m (2H, NH), 7.50–7.60 m (6H_{arom}), 7.65–7.80 m (4H_{arom}). Found, %: C 55.57; H 4.99; N 21.88. $\text{C}_{24}\text{H}_{26}\text{N}_8\text{O}_6$. Calculated, %: C 55.17; H 5.02; N 21.44.

2-(4-Phenyl-3-furazanylamino)-1,1,2-tris(ethoxycarbonylamino)ethane (IX). mp 213–215°C (decomp.). ^1H NMR spectrum (DMSO- d_6), δ , ppm: 1.10–1.25 m

(9H, CH₃), 3.75–4.05 m (6H, CH₂), 5.15–5.45 m (2H, CH), 6.20 d (1H, NH, *J* 10.5 Hz), 6.50–7.20 m (3H, NH), 7.45–7.60 m (3H_{arom}), 7.65–7.75 m (2H_{arom}). Found, %: C 50.92; H 5.89; N 18.28. C₁₉H₂₆N₆O₇. Calculated, %: C 50.66; H 5.82; N 18.66.

***N,N'*-Furazan-3,4-diylbis[*N*¹,*N*²,*N*²-tris(ethoxy-carbonyl)ethane-1,1,2,2-tetramine] (X).** mp 233–235°C (decomp.) (ethanol). ¹H NMR spectrum (DMSO-*d*₆), δ, ppm: 1.20 t (18H, CH₃, *J* 10.5 Hz), 4.00 q (12H, CH₂, *J* 2.5 Hz), 4.75–5.75 m (4H, CH), 6.35–7.35 m (8H, NH). Found, %: C 42.16; H 5.98; N 20.35. C₂₄H₄₂N₁₀O₁₃. Calculated, %: C 42.48; H 6.24; N 20.64.

¹H NMR spectra were registered on a spectrometer Bruker WM-400 (400 MHz), solvent DMSO-*d*₆, internal reference HMDS. Elemental analysis was carried out on a CHN-analyzer Hewlett Packard 185B.

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