

1,1,2,2-Tetraaminoethane Derivatives: III. Condensation of 2-(Dinitromethylene)imidazolidine-4,5-diol with Nitrogen-Containing Nucleophiles

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Abstract—Condensation of 1,1-diamino-2,2-dinitroethylene with glyoxal and formaldehyde in water solutions at pH 7–8 gave rise to 2-(dinitromethylene)imidazolidine-4,5-diol and 1,1-diamino-*N,N'*-bis(hydroxymethyl)-2,2-dinitroethylene respectively. Condensation products of 2-(dinitromethylene)imidazolidine-4,5-diol with acetonitrile, benzonitrile, urethane, 3,4-diaminofurazan were isolated. The reaction of 4,5-diacetamido-2-(dinitromethylene)imidazolidine sulfate with water in acetonitrile led to the formation of 2-(dinitromethylene)-5-methyl-1,2,3,3a,4,6a-hexahydroimidazo[4,5-*d*]imidazole. The dehydration of 2-(dinitromethylene)imidazolidine-4,5-diol in a system H_2SO_4 –AcOH provided 2-(dinitromethylene)-2,3-dihydro-1*H*-imidazol-4-ol. 1,1-Diamino-*N,N'*-bis(hydroxymethyl)-2,2-dinitroethylene in sulfuric acid was converted into 4-(dinitromethylene)-1,3,5-oxadiazinane.

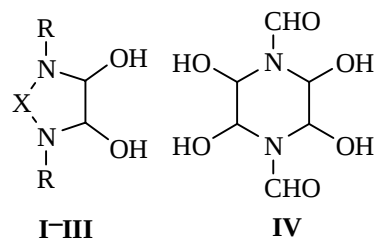
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A known preparation method for 1,1,2,2-tetraaminoethane polycyclic derivatives consists in the condensation of nitrogen-containing nucleophiles in water solutions of acids with products obtained from glyoxal reaction with acylamides, ureas, guanidine, and nitroguanidine in alkaline medium [2–9]. No published data exist on the application of 1,1-diamino-2,2-dinitroethylene, close in structure to the nitroguanidine, to the synthesis of compounds containing the 1,1,2,2-tetraaminoethane fragment.

Three possible reaction types of 1,1-diamino-2,2-dinitroethylene were formerly studied in detail: the nucleophilic substitution of amino group [10], the addition to the double bond, and the electrophilic attack at the amino group and the negatively charged carbon [11]. 1,1-Diamino-2,2-dinitroethylene is a very weak nucleophile that reacts with alkyl bromides at heating exclusively after a preliminary treatment with two equiv of strong bases [12].

Presumably due to low basicity [13] the 1,1-diamino-2,2-dinitroethylene was not involved into the condensation with cyclic bisamidals **I**, **II**, and **IV**, and with 4,5-dihydroxy-2-nitroiminoimidazolidine (**III**) in the concn. HCl; the reaction mixture underwent gradual

tarring, and only the initial 1,1-diamino-2,2-dinitroethylene was isolated.

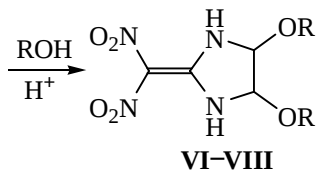
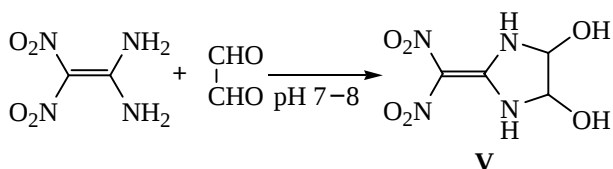


X = CH_2 , R = Ac (**I**), X = CH_2CH_2 , R = Ac (**II**); X = $\text{C}=\text{NNO}_2$, R = H (**III**).

We investigated in this study a reaction of various nitrogen-containing nucleophiles (nitriles, urethane, urea, and diaminofurazan) with 2-(dinitromethylene)imidazolidine-4,5-diol (**V**), a condensation product of 1,1-diamino-2,2-dinitroethylene with glyoxal.

The condensation of 1,1-diamino-2,2-dinitroethylene with glyoxal was carried out in a water solution at pH 7–8. Raising pH to 8–9 resulted in a sharp decrease in the yield of compound **V** caused by its low stability in the alkaline medium. Note that whereas in a weakly alkaline medium derivative **V** was obtained in a good yield, in acid solutions we failed to isolate mono- or disubstituted condensation products.

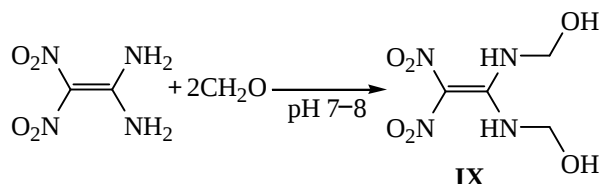
* For Communication II, see [1].



R = OEt (VI), OMe (VII), Ac (VIII).

Compound **V** obtained is stable in acid media, and easily undergoes etherification with alcohols in the presence of sulfuric acid. The boiling of diol **V** in a mixture EtOH–H₂SO₄, 2:1 v/v, and MeOH–H₂SO₄, 2:1, provided diethoxy- and dimethoxyderivatives **VI** and **VII** in 71 and 88% yield respectively.

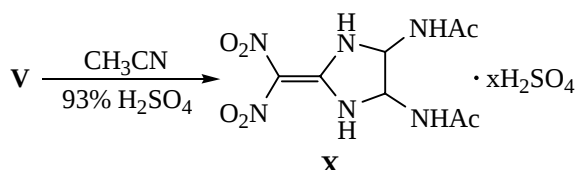
1,1-Diamino-2,2-dinitroethylene reacted with excess formaldehyde in a water solution at pH 7–8 forming 1,1-diamino-*N,N'*-bis(hydroxymethyl)-2,2-dinitroethylene (**IX**).



The attempts to involve dihydroxymethyl derivative **IX** into acylation reaction with acetic anhydride or etherification with alcohols (ethanol, methanol) in the acid medium like diol **V** resulted in formation of 1,1-diamino-2,2-dinitroethylene.

N-alkyl-substituted amides are known to be prepared by Ritter reaction of aliphatic, aromatic, and heterocyclic nitriles with secondary and tertiary alcohols in the presence of protonic acids (85–100% sulfuric acid, phosphoric acid, benzenesulfonic acid, 90% formic acid, and perchloric acid) [14–16].

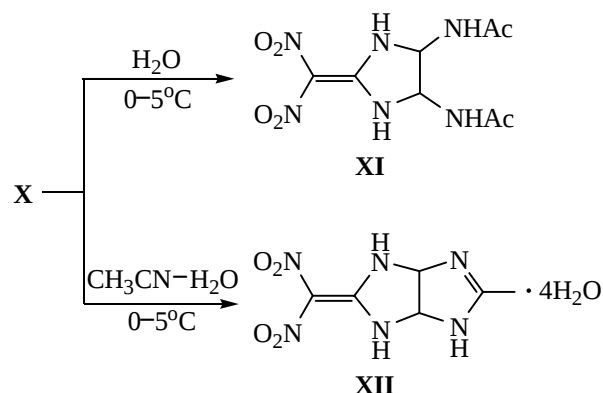
We showed that diol **V** in the presence of 93% sulfuric acid at 0–5°C reacted with acetonitrile. The compound precipitated from the reaction mixture was presumably sulfate of diacetamido derivative **X** insoluble in acetonitrile; the salt was unstable and decomposed at room



temperature within 30 min, in 20–25 h in a refrigerator. Salt **X** can be stored without isolation from the mother liquor at 0–5°C for several weeks.

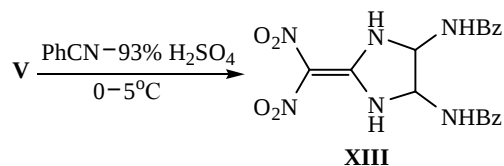
Diacetamido derivative **XI** as a free base was obtained by treating salt **X** with ice water or ethanol in 27% yield.

When the Ritter reaction was carried out in the 100% sulfuric acid and instead of diol **V** its diacetoxymethyl derivative **VIII** was used we failed to isolate diacetamido derivative **XI** by pouring the reaction mixture on ice, apparently, because of the high acidity of the mother liquor where compound **XI** quickly decomposed.



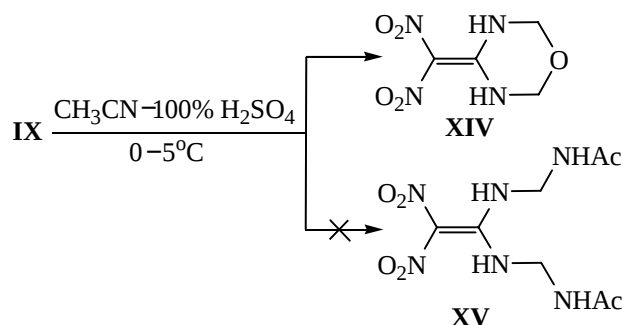
In the course of our studies we found that adding a little water to the suspension of sulfate **X** in acetonitrile at 0–5°C gave rise instead of the expected diacetamido derivative **XI** to compound **XII** in 63% yield. The composition and structure of obtained bicycle **XII** was confirmed by elemental analysis and IR spectrum. Compound **XII** is stable at low temperature (0–5°C) but at storage in an open flask in air it decomposes within a month. Bicycle **XII** is unstable to the action of weakly basic polar solvents (DMSO, DMF) and water. We did not succeed in registering a plausible ¹H NMR spectrum of compound **XII** for it was nearly insoluble in nonpolar solvents and anhydrous carboxylic acids.

Employing other solvents than acetonitrile where compound **XII** was insoluble did not result in conversion of salt **X** into bicycle **XII**: In hydrophobic solvents (ethyl acetate, benzonitrile) diacetamido derivative **XI** was obtained, in hydrophilic solvents (acetone, dioxane) a slow tarring was observed.



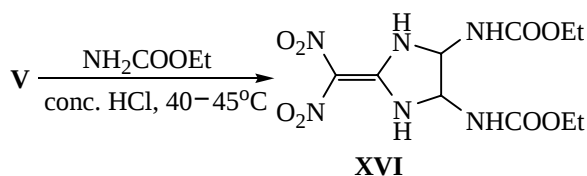
Diol **V** also reacted with benzonitrile in the presence of 93% sulfuric acid. The yield of dibenzamido derivative **XIII** was 24%.

The attempt to carry out the Ritter reaction of acetonitrile with dihydroxymethyl derivative **IX** under similar conditions led to the formation of compound **XIV** in 66% yield, apparently due to insufficient acidity of the medium. At alteration of the ratio 100% H_2SO_4 – CH_3CN from 1:2 to 1:1 (v/v) the cyclic compound **XIV** did not form, but we did not succeed in isolation of the corresponding diacetamido derivative **XV**.



It was shown before that 4,5-dihydroxy-2-nitroimidazolidine (**III**) reacted with urea, thiourea, and diaminofurazan at short (30 min) heating at 80–90°C in 5–20% hydrochloric acid giving the corresponding polycycles [7].

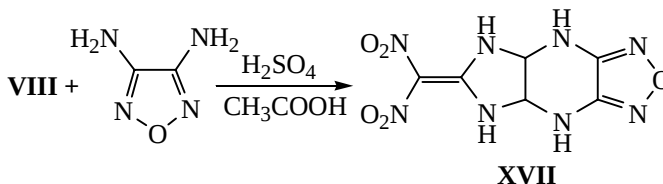
Unlike nitroguanidine derivative **III**, diol **V** at high temperature in acid media quickly decomposed, therefore the condensations were performed at room temperature or slight warming in concn. HCl . The heating at 40–45°C of diol **V** with a double excess of urethane in concn. HCl for 6 h resulted in the formation of bis(ethoxycarbonylamino) derivative **XVI** in 32% yield.



We did not succeed in preparation in a similar way of condensation products of diol **V** with urea or diaminofurazan: The reaction mixture suffered fast decomposition, and only small amount of the initial compound **V** was recovered.

We developed in previous investigations a stepwise procedure for preparation of cyclic and acyclic 1,1,2,2-tetraaminoethane derivatives by intermediate isolation of glyoxal condensation product with acylamides followed by their introducing into reaction with nitrogen-containing nucleophiles in anhydrous environment [1, 17, 18]. Taking into account that obtained bicycle **XII** decomposed very fast in weakly basic polar solvents and

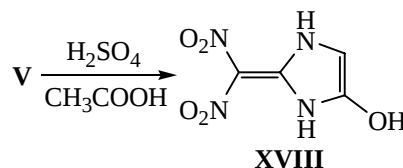
water we assumed that the other polycyclic derivatives of 1,1-diamino-2,2-dinitroethylene behaved similarly. Therefore we studied further the reaction of compound **VIII** with nitrogen-containing nucleophiles (urea, diaminofurazan) in an anhydrous electrophilic medium.



The condensation of acetoxy derivative **VIII** with diaminofurazan was successfully performed at room temperature in a system glacial acetic acid–100% sulfuric acid, 50:1 (v/v). Cyclic compound **XVII** obtained in 35% yield is stable at storage under common conditions, and suffered decomposition in weakly basic polar solvents.

Diacetoxy derivative **VIII** under analogous conditions did not react with urea, *N,N'*-diethylurea, and *O*-tolylurea; in this cases only slow tarring was observed.

The investigation of the reactivity of diol **IX** with respect to nitrogen-containing nucleophiles in a system glacial acetic acid–100% sulfuric acid showed that depending on the acidity of the medium formed either solely oxa derivative **XIV** (100% H_2SO_4 – CH_3COOH , 1:2 v/v), or a mixture of compound **XIV** and 1,1-diamino-2,2-dinitroethylene (100% H_2SO_4 – CH_3COOH , 1:1 v/v).



It is known [7, 19–23] that at the condensation of urea, guanidine, and nitroguanidine with glyoxal in acid media the corresponding hydantoins formed as side products.

We showed that at stirring diol **V** in a mixture glacial acetic acid–100% sulfuric acid, 10:1.5 (v/v), at room temperature for 2 h 2-(dinitromethylene)-2,3-dihydro-1*H*-imidazol-4-ol (**XVIII**) formed in 17% yield. According to IR spectrum, compound **XVIII** in the solid phase is present in an enol form.

Hence the use of 1,1-diamino-2,2-dinitroethylene for the synthesis of cyclic and acyclic derivatives of 1,1,2,2-tetraaminoethane provided a possibility to obtain new, previously unavailable polyfunctional compounds.

EXPERIMENTAL

IR spectra of compounds synthesized were recorded on a spectrophotometer Shimadzu FTIR 8400 (from films or pellets with KBr). ^1H NMR spectra were registered from solutions of compounds in $\text{DMSO}-d_6$ on a spectrometer Bruker WM-400 (400 MHz), internal reference HMDS. Elemental analysis was carried out on an analyzer Hewlett Packard 185B.

2-(Dinitromethylene)imidazolidine-4,5-diol (V). To 40 g (0.27 mol) of 40% water solution of glyoxal neutralized to pH 7–8 was added 100 ml of water and 20 g (0.14 mol) of 1,1-diamino-2,2-dinitroethylene, the mixture was heated to 70°C, and the solution obtained was slowly cooled. The separated precipitate was filtered off, thoroughly washed with water and a little cold ethanol. Yield 26 g (94%), light yellow crystals, mp 174–175°C (decomp.) (ethanol). IR spectrum, cm^{-1} : 3400 (OH), 3300 (NH), 1562 (C=C), 1517 (NO_2), 1448, 1350 (NO_2), 1186 (CO), 1047, 817, 730 (NH). ^1H NMR spectrum, δ , ppm: 5.00 s (2H, CH), 6.55 s (2H, OH), 9.45 s (2H, NH). Found, %: C 23.95; H 3.15; N 27.67. $\text{C}_4\text{H}_6\text{N}_4\text{O}_6$. Calculated, %: C 23.31; H 2.93; N 27.18.

2-(Dinitromethylene)-4,5-diethoxyimidazolidine (VI). To 10 ml of ethanol was added 5 ml of 93% sulfuric acid and 2 g (0.01 mol) of diol V, the mixture was heated to 60°C, and the solution obtained was slowly cooled. The separated precipitate was filtered off and washed with ether. Yield 1.6 g (71%), pale yellow crystals, mp 142–145°C (ethanol). IR spectrum, cm^{-1} : 3387 (NH), 2985 (CH_3), 2939 (OCH_2), 1561 (C=C), 1510 (NO_2), 1450 (CH_3), 1357 (CH_3), 1310 (NO_2), 1218 (COC), 1103, 1064, 1026, 950, 748 (NH). ^1H NMR spectrum, δ , ppm: 1.20 t (6H, CH_3), 3.65 d.q (4H, CH_2 , J 5.1 Hz), 4.90 s (2H, CH), 9.95 s (2H, NH). Found, %: C 36.94; H 5.59; N 21.03. $\text{C}_8\text{H}_{14}\text{N}_4\text{O}_6$. Calculated, %: C 36.64; H 5.38; N 21.37.

4,5-Dimethoxy-2-(dinitromethylene)imidazolidine (VII). *a.* To a solution of 2.5 g (0.02 mol) of dimethyl sulfate in 10 ml of methanol was added 1 ml of 93% sulfuric acid and 2 g (0.01 mol) of diol V, the mixture was heated to 60°C, and the solution obtained was slowly cooled. The separated precipitate was filtered off and washed with ether. Yield 1.7 g (75%), yellow crystals, mp 106–108°C (methanol). IR spectrum, cm^{-1} : 3333 (NH), 2935 (CH_3O), 1589 (C=C), 1527 (NO_2), 1450 (CH_3), 1396 (CH_3), 1339 (NO_2), 1207 (COC), 1114, 1072, 1007, 933, 752 (NH). ^1H NMR spectrum, δ , ppm: 3.40 s (6H, CH_3), 4.80 s (2H, CH), 9.95 s (2H, NH).

Found, %: C 31.02; H 4.64; N 23.59. $\text{C}_6\text{H}_{10}\text{N}_4\text{O}_6$. Calculated, %: C 30.78; H 4.30; N 23.93.

b. To 10 ml of methanol was added 5 ml of 93% sulfuric acid and 2 g (0.01 mol) of diol V, the mixture was heated to 60°C, and the solution obtained was slowly cooled. The separated precipitate was filtered off and washed with ether. Yield 2.0 g (88%), yellow crystals, mp 105–107°C (methanol).

4,5-Diacetoxy-2-(dinitromethylene)imidazolidine (VIII). To 250 ml of acetic anhydride was added 2 g (0.01 mol) of *p*-toluenesulfonic acid and 95 g (0.46 mol) of diol V, the mixture was heated to 40°C till the reaction started, and further the temperature was maintained at 65–70°C. After the end of self-heating the reaction mixture was stirred for 12 h at room temperature, the separated precipitate was filtered off and washed with ethanol and ether. Yield 115.6 g (87%), yellow crystals, mp 159–161°C (decomp.) (acetic acid). IR spectrum, cm^{-1} : 3415 (C=O), 3307 (NH), 3024 (CH_3), 1743 (C=O), 1577 (C=C), 1521 (NO_2), 1460 (CH_3), 1375 (CH_3), 1331 (NO_2), 1209 (CO), 1040, 1003, 977, 750 (NH). ^1H NMR spectrum, δ , ppm: 1.95 s (6H, CH_3), 6.20 s (2H, CH), 9.95 s (2H, NH). Found, %: C 34.00; H 4.09; N 19.91. $\text{C}_8\text{H}_{10}\text{N}_4\text{O}_8$. Calculated, %: C 33.11; H 3.47; N 19.31.

***N,N'*-Bis(hydroxymethyl)-1,1-diamino-2,2-dinitroethylene (IX).** To 90 g (1.00 mol) of 33% formaldehyde neutralized to pH 7–8 was added 15 g (0.10 mol) of 1,1-diamino-2,2-dinitroethylene, the mixture was heated to 50–60°C, the solution obtained was acidified to pH 4 and then stirred at room temperature for 7 days. The separated precipitate was filtered off and washed with ethanol and ether. Yield 13 g (61%), pale yellow crystals, mp 258–260°C (decomp.). IR spectrum, cm^{-1} : 3402 (OH), 3244 (NH), 2954 (CH_2), 1596 (C=C), 1504 (NO_2), 1450 (CH_2), 1392, 1361 (NO_2), 1250, 1150 (CO), 1041, 752 (NH). ^1H NMR spectrum, δ , ppm: 4.35–4.95 m (4H, CH_2), 6.05–6.65 m (2H, OH), 9.40–10.55 m (2H, NH). Found, %: C 23.73; H 4.15; N 26.41. $\text{C}_4\text{H}_8\text{N}_4\text{O}_6$. Calculated, %: C 23.08; H 3.87; N 26.92.

4,5-Diacetamido-2-(dinitromethylene)imidazolidine (XI). To 20 ml of acetonitrile was slowly added 10 ml of 93% sulfuric acid maintaining the rate of addition so as to conserve the reaction temperature below 0–5°C. Then 4 g (0.02 mol) of diol V was added, the mixture was stirred for 2 h at 0–5°C, precipitated salt X was filtered off, washed with 10 ml of acetonitrile and at once charged by small portions into 50 ml of water cooled to 0–5°C. The reaction mixture was stirred at this

temperature for 30 min, the separated precipitate was filtered off and thoroughly washed with water and ethanol. Yield 1.5 g (27%), bright yellow powder, mp > 300°C (decomp.). Decomposes in polar solvents (DMSO, DMF) within 1 h. IR spectrum, cm^{-1} : 3288 (NH), 3168 (C–N, CH_3), 1630 (C=O), 1578 (NO_2), 1552 (NO_2), 1488 (CH_3), 1389 (CH_3), 1336 (NO_2), 1246 (C–N), 1157, 1007, 744 (NH). ^1H NMR spectrum, δ , ppm: 2.10 s (6H, CH_3), 7.20 s (2H, CH), 10.50 s (2H, NH), 13.20 C (2H, NH). Found, %: C 34.01; H 4.98; N 28.70. $\text{C}_8\text{H}_{12}\text{N}_6\text{O}_6$. Calculated, %: C 33.34; H 4.20; N 29.16. ^1H NMR spectrum of sulfate **X** was identical to the ^1H NMR spectrum of diacetamido derivative **XI**. IR spectrum of compound **X**, cm^{-1} : 2760 (NH_2^+), 1658 (C=O), 1574 (C=C, NH_2^+), 1516 (NO_2), 1369 (CH_3), 1320 (NO_2 , sulfate), 1218 (C–N, sulfate), 1172, 1068, 1006, 980, 887.

2-(Dinitromethylene)-5-methyl-1,2,3,3a,4,6a-hexahydroimidazo[4,5-d]imidazole (XII). To 20 ml of acetonitrile was slowly added 10 ml of 93% sulfuric acid maintaining the rate of addition so as to conserve the reaction temperature below 0–5°C. Then 4 g (0.02 mol) of diol **V** was added, the mixture was stirred for 2 h at 0–5°C, the separated precipitate was filtered off, washed with 10 ml of acetonitrile, and immediately it was dispersed in 70 ml of acetonitrile. To the reaction mixture cooled to 0–5°C was slowly added at vigorous stirring an amount of water (about 10 ml) sufficient for complete dissolving salt **X**. After maintaining the reaction mixture for 30 min at 0–5°C the separated precipitate was filtered off and washed with acetonitrile and ether. Yield 3.5 g (63%), pale yellow powder, mp 100–101°C (decomp.). Decomposes in polar solvents (DMSO, DMF) and in water. IR spectrum, cm^{-1} : 3548 (NH), 3286 (NH), 3024 (CH_3), 1759 (C=N), 1574 (C=C), 1516 (NO_2), 1442 (CH_3), 1365 (CH_3 , NO_2), 1203 (C–N), 1045, 879, 760 (NH). Found, %: C 24.43; H 5.22; N 27.43. $\text{C}_6\text{H}_8\text{N}_6\text{O}_4 \cdot 4\text{H}_2\text{O}$. Calculated, %: C 24.00; H 5.37; N 27.99.

4,5-Dibenzamido-2-(dinitromethylene)imidazolidine (XIII). To 25 ml of benzonitrile was slowly added 20 ml of 93% sulfuric acid maintaining the rate of addition so as to conserve the reaction temperature below 0–5°C. Then 5 g (0.024 mol) of diol **V** was added, the mixture was stirred for 3 h at 0–5°C, then it was poured on ice, diluted with 50 ml of ethanol, and stirred at room temperature for 30 min. The separated precipitate was filtered off and thoroughly washed with boiling ethanol. Yield 2.4 (24%), bright yellow powder, mp > 300°C (decomp.). Decomposes in polar solvents (DMSO, DMF)

within 1 h. IR spectrum, cm^{-1} : 3325 (NH), 3170 (C–N), 1643 (C=O, CH_{arom}), 1550 (C=C, NO_2), 1473 (C=C), 1350 (NO_2), 1242 (C–N), 1157, 1080, 1010, 950, 825 (CH), 740 (NH). ^1H NMR spectrum, δ , ppm: 7.40 s (2H, CH), 7.45–7.75 m (6 H_{arom}), 7.80–8.25 m (4 H_{arom}), 10.95–11.90 m (2H, NH), 12.75–13.30 m (2H, NH). Found, %: C 52.99; H 4.42; N 19.85. $\text{C}_{18}\text{H}_{16}\text{N}_6\text{O}_6$. Calculated, %: C 52.43; H 3.91; N 20.38.

4-(Dinitromethylene)-1,3,5-oxadiazinane (XIV). To 10 ml of acetonitrile was slowly added 5 ml of 93% sulfuric acid maintaining the rate of addition so as to conserve the reaction temperature below 0–5°C. Then 1 g (0.005 mol) of compound **IX** was added, the mixture was stirred for 6 h at 0–5°C, and slowly poured on ice. The separated precipitate was filtered off and thoroughly washed with water and a small quantity of alcohol and ether. Yield 0.6 g (66%), bright yellow powder, mp 208–210°C (decomp.). IR spectrum, cm^{-1} : 3260 (NH), 2896 (OCH_2), 1597 (C=C), 1516 (NO_2), 1458 (CH_2), 1346 (NO_2), 1165 (COC), 1126, 972, 879, 748 (NH). ^1H NMR spectrum, δ , ppm: 5.05 d (4H, CH_2 , J 1.4 Hz), 10.20 s (2H, NH). Found, %: C 25.60; H 3.48; N 29.23. $\text{C}_4\text{H}_6\text{N}_4\text{O}_5$. Calculated, %: C 25.27; H 3.18; N 29.47.

2-(Dinitromethylene)-4,5-bis(ethoxycarbonylamino)imidazolidine (XVI). To 10 ml of concn. HCl was added 4.5 g (0.05 mol) of urethane and 2 g (0.01 mol) of diol **V**, the mixture was stirred for 6 h at 40–45°C, the precipitate was filtered off, thoroughly washed with water and boiling ethanol. Yield 1.1 g (32%), bright yellow powder, mp > 300°C (decomp.). Decomposes in polar solvents (DMSO, DMF) within 1 h. IR spectrum, cm^{-1} : 3282 (NH), 3166 (C–N), 2962 (CH_2 , CH_3), 1701 (C=O), 1654 (C=O), 1558 (C=C), 1523 (NO_2), 1473 (CH_3), 1435 (CH_2), 1388 (CH_3), 1346 (NO_2), 1245 (C–N), 1157 (C–O), 1072, 1010, 956, 840 (CH), 745 (NH). ^1H NMR spectrum, δ , ppm: 1.25 t (6H, CH_3 , J 6.5 Hz), 4.20 q (4H, CH_2 , J 6.5 Hz), 7.05 s (2H, CH), 9.95 s (2H, NH), 13.40 s (2H, NH). Found, %: C 35.10; H 4.87; N 24.01. $\text{C}_{10}\text{H}_{16}\text{N}_6\text{O}_8$. Calculated, %: C 34.49; H 4.63; N 24.13.

6-(Dinitromethylene)-4a,5,6,7,7a,8-hexahydroimidazo[4,5-b]furazano[3,4-e]pyrazine (XVII). To a mixture of 50 ml of glacial acetic acid and 1 ml of 100% sulfuric acid was added 0.7 g (0.007 mol) of diaminofurazan and 2 g (0.007 mol) of compound **VIII**, the mixture was stirred for 4 h at room temperature, the separated precipitate was filtered off and thoroughly washed with acetic acid and ether. Yield 1.0 g (35%),

dark orange powder, mp 276–280°C (decomp.). Decomposes in polar solvents (DMSO, DMF, acetone), insoluble in water. IR spectrum, cm^{-1} : 3340 (NH), 1574 (C=C, C=N–O), 1512 (NO_2), 1439 (N–O), 1357 (CH, NO_2), 1207 (N–O), 1064 (heterocycle), 844 (heterocycle), 752 (NH). Found, %: C 24.05; H 3.94; N 36.53. $\text{C}_6\text{H}_6\text{N}_8\text{O}_5 \cdot 2\text{H}_2\text{O}$. Calculated, %: C 23.54; H 3.29; N 36.60.

2-(Dinitromethylene)-2,3-dihydro-1H-imidazol-4-ol (XVIII). To a mixture of 10 ml of glacial acetic acid and 1.5 ml of 100% sulfuric acid was added 2 g (0.01 mol) of diol **V**, the mixture was stirred for 2 h at room temperature, the separated precipitate was filtered off and thoroughly washed with acetic acid and acetone. Yield 0.3 g (17%), pale yellow powder, mp > 300°C (decomp.). IR spectrum, cm^{-1} : 3344 (NH, OH), 1573 (C=C), 1519 (NO_2), 1454, 1361 (CH, NO_2), 1307, 1207 (OH), 1153, 1037, 864, 752 (NH). ^1H NMR spectrum, δ , ppm: 5.70 s (2H, CH_2), 9.85 s (2H, NH). Found, %: C 26.07; H 2.73; N 29.17. $\text{C}_4\text{H}_4\text{N}_4\text{O}_5$. Calculated, %: C 25.54; H 2.14; N 29.79.

REFERENCES

1. Sizova, E.V., Sizov, V.V., and Tselinskii, I.V., *Zh. Org. Khim.*, 2007, vol. 43, p.599.
2. Dagley, I.J. and Flippen-Anderson, J.L., *Aust. J. Chem.*, 1994, vol. 47, p. 2033.
3. Ramakrishnan, V.T., Vedachalam, M., and Boyer, J.H., *Heteroatom Chem.*, 1991, vol. 2, no. 6, p. 669.
4. Ramakrishnan, V.T., Vedachalam, M., and Boyer, J.H., *Heteroatom Chem.*, 1991, vol. 2, no. 2, p. 313.
5. Vedachalam, M. and Boyer, J.H., *Heteroatom Chem.*, 1993, vol. 4, no. 1, p. 85.
6. Ramakrishnan, V.T., Vedachalam, M., Boyer, J.H., Dagley, I.J., Flippen-Anderson, J.L., Nelson, K.A., Adolph, H.G., Gilardi, R., and George, C., *J. Org. Chem.*, 1991, vol. 56, no. 10, p. 3413.
7. Terpigorev, A.N., Rudakova, S.B., *Zh. Org. Khim.*, 1998, vol. 34, no. 7, p. 1078.
8. Pagoria, P.F., Lee, G.S., Mitchell, A.R., and Schmidt, R.D., *Termochimica Acta*, 2002, vol. 384, p. 187.
9. Sheremet'ev, A.B. and Yudin, I.A., *Usp. Khim.*, 2003, vol. 72, no. 1, p. 93.