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Polynuclear Nonfused Bis(1,3,4-oxadiazole)-Containing Systems

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Abstract—Nonfused bis-1,3,4-oxadiazoles were synthesized by reaction of 5-substituted mono- and bis-tetrazoles with mono- and dicarboxylic acid chlorides. The results of kinetic studies showed that the transformation of tetrazoles into 1,3,4-oxadiazoles is accelerated by 1 to 2 orders of magnitude on addition of a catalytic amount of dimethylformamide, triethylamine, or pyridine.

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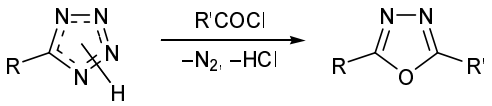
We previously [1] synthesized nonfused polynuclear systems containing 1,3,4-oxadiazole rings by reaction of 5-substituted tetrazoles with carboxylic acid chlorides (Scheme 1). In the present work we extended this procedure to the synthesis of various (including previously inaccessible) nonfused bis-1,3,4-oxadiazoles. Interest in such systems remains persistently strong due to their luminescent properties and the possibility of using them as scintillators [2–4]; in addition, some nonfused bis-1,3,4-oxadiazole derivatives exhibit biological activity [5]. The classical method of synthesis of 1,3,4-oxadiazoles via cyclization of *N*,*N*′-diacylhydrazines is not free from a number of disadvantages; in some cases, it cannot be used to obtain binuclear systems. On the other hand, thermolysis of *N*-acyltetrazoles [6] formed by reaction of carboxylic acid chlorides with 5-substituted tetrazoles is a convenient method for the preparation of 2,5-disubstituted 1,3,4-oxadiazoles, as well as bis-1,3,4-oxadiazoles.

Scheme 1.

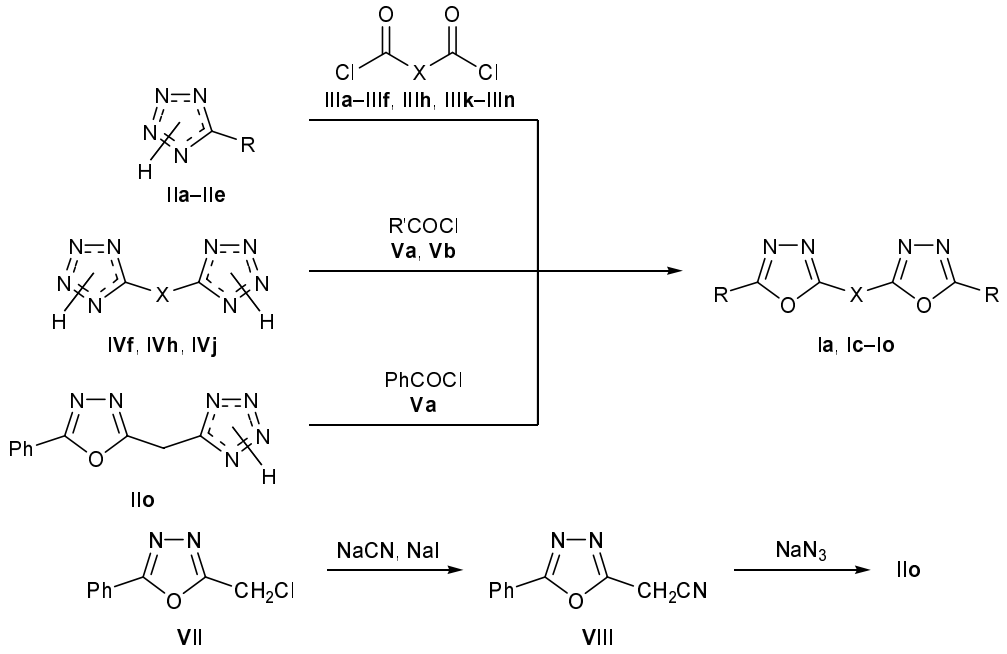


Bis-1,3,4-oxadiazoles **Ia** and **Ic**–**Io** were synthesized from tetrazoles **IIa**–**IIe** and the corresponding dicarboxylic acid dichlorides **IIIa**–**IIIi** and **IIIk**–**IIIn**, as well as by reaction of bis-tetrazoles **IVf**, **IVh**, and **IVj** with monocarboxylic acid chlorides **Va** and **Vb** (Scheme 2). Bis(2-phenyl-1,3,4-oxadiazol-5-yl)methane (**Io**) was obtained by reaction of 5-(5-phenyl-1,3,4-oxadiazol-2-ylmethyl)tetrazole (**IIo**) with benzoyl chloride, for the corresponding bis-tetrazole is difficultly accessible [1]. Tetrazole **IIo** was prepared in turn by cyanation of 2-chloromethyl-5-phenyl-1,3,4-oxadiazole (**VII**), followed by treatment of (5-phenyl-1,3,4-oxadiazol-2-yl)acetonitrile (**VIII**) with sodium azide (Scheme 2).

By reactions of phenyltetrazole **IIa** with terephthaloyl dichloride (**IIIh**) and of 1,4-bis(tetrazol-5-yl)benzene (**IVh**) with benzoyl chloride we synthesized in high yield 1,4-bis(5-phenyl-1,3,4-oxadiazol-2-yl)benzene which is used as standard scintillator (POPOP). Systems containing other unsaturated bridging groups between oxadiazole rings, e.g., compounds **Ij**–**Il**, also show visually observable luminescence upon irradiation with UV light in the λ range from 200 to 300 nm. Like compound **VII**, structures **Ig** and **Ii** having a chloromethyl group at the oxadiazole ring may be used as key intermediates for further appending heterocyclic fragments to build up polyazole chains [1].

We have found that addition of a catalytic amount of an amine to the reaction mixture strongly accelerates the transformation of 5-substituted tetrazoles into 1,3,4-oxadiazoles by the action of acyl chlorides (Scheme 1), the yield of the target product remaining unchanged. We performed a kinetic study of the reaction of 5-phenyltetrazole with benzoyl chloride (R = R' = Ph) in *p*-xylene at 100°C in the absence and in the presence of DMF, triethylamine, and pyridine (2 vol %). The reaction rate was measured by the volume of gaseous nitrogen evolved during the process. From the kinetic curves shown in figure we calculated

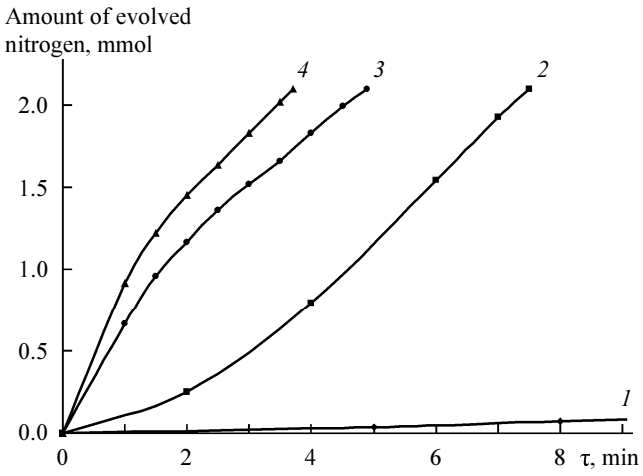
Scheme 2.



X = bond, R = Ph (**a**), $ClCH_2$ (**b**), $EtOCOCH_2$ (**c**), 1*H*-benzotriazol-1-yl (**d**), 4-phenyl-1*H*-1,2,3-triazol-1-yl (**e**); X = CH_2CH_2, R = Ph (**f**), $ClCH_2$ (**g**); X = 1,4-C_6H_4, R = Ph (**h**), $ClCH_2$ (**i**); R = Ph, X = 4-$C_6H_4C_6H_4$-4' (**j**), HC=CH (**k**), C≡C (**l**), 1-butyl-1*H*-1,2,3-triazole-4,5-diyl (**m**), 1-benzyl-1*H*-1,2,3-triazole-4,5-diyl (**n**), CH_2 (**o**).

the initial rates of gas evolution (see table). In the presence of amine, the gas evolution process begins immediately after mixing the reactants at 100°C (no induction period is observed; see figure), and the rate of gas evolution depends on the amine nature (see table).

The catalytic effect of amine may be rationalized in terms of accessibility of the unshared electron pair on the nitrogen atom, which increases in the series DMF < Et_3N < Py in keeping with steric and electronic effects.

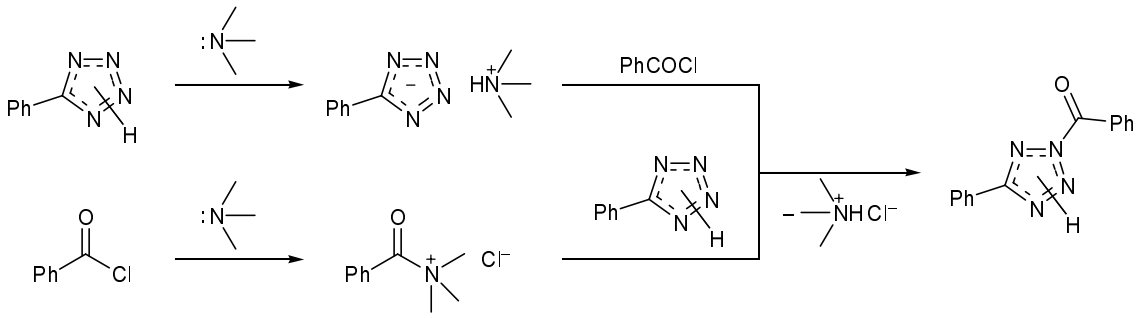


Kinetic curves for gas evolution in the reaction of 5-phenyltetrazole with benzoyl chloride (*1*) in the absence of a catalyst and in the presence of (*2*) DMF, (*3*) triethylamine, and (*4*) pyridine.

Osipova et al. [6] proposed a mechanism including initial N-acylation of the tetrazole ring with subsequent elimination of nitrogen molecule and 1,3,4-oxadiazole ring closure. Taking this scheme into account, we concluded that catalysis by amines should contribute most to the rate of the first stage, i.e., formation of *N*-acyltetrazole. Therefore, we propose two alternative mechanisms of catalysis, which involve activation of either tetrazole ring to electrophilic attack or carboxylic acid chloride to nucleophilic attack (Scheme 3). The question as to which of these mechanisms is operative will be the subject of our further studies.

An analogous but weaker catalytic effect of amines was observed in the reactions of 5-substituted tetrazoles with imidoyl chlorides to give 3,4,5-trisubstituted 1,2,4-triazoles, which were presumed to follow a similar mechanism [7]. The initial rate of the reaction of 5-phenyltetrazole with *N*-phenylbenzimidoyl chloride in *p*-xylene at 100°C in the presence of pyridine increased by a factor of only 2.8 relative to the rate of the noncatalytic reaction. The addition of a catalytic amount of amine makes it possible to reduce the temperature in the reactions of tetrazoles with carboxylic acid chlorides. However, the reaction of 5-vinyltetra-

Scheme 3.



zole with benzoyl chloride under these conditions led to the formation of polymeric products which were difficult to identify, while the desired 2-vinyl-1,3,4-oxadiazoles cannot be isolated [1]. We succeeded in synthesizing 2-vinyl-5-phenyl-1,3,4-oxadiazole in two steps [6]: (1) acylation of 5-vinyltetrazole with benzoyl chloride under conditions of phase-transfer catalysis at room temperature and (2) thermolysis of the benzoyltetrazole thus formed at 95–110°C.

EXPERIMENTAL

The ^{1}H and ^{13}C NMR spectra were recorded from solutions in acetone-d_6 or DMSO-d_6 on a Varian VXR-500S spectrometer (500 and 126 MHz, respectively). The IR spectra were obtained on a Specord M80 instrument from samples dispersed in mineral oil. The elemental compositions were determined on a FLASH EA 1112 Series CHN analyzer. The progress of reactions was monitored by TLC on Silufol plates using ethyl acetate–hexane (2:3) as eluent; development with UV light or iodine vapor.

The kinetic studies were performed by volumetry. A solution of 1.9 g (14 mmol) of benzoyl chloride in 3.0 ml (catalytic reaction) or 3.1 ml (noncatalytic reaction) of *p*-xylene, heated to 100°C, was quickly added to a suspension of 1 g (7 mmol) of 5-phenyltetrazole (**IIe**) in 2.9 ml of *p*-xylene containing (catalytic reaction) 0.1 ml of DMF, triethylamine, or pyridine and maintained at 100°C. The reaction vessel was capped, and the mixture was continuously stirred, the volume of liberated nitrogen being measured at definite time intervals.

The initial compounds were synthesized by known methods: 5-phenyltetrazole (**IIa**) [8], ethyl (tetrazol-5-yl)acetate (**IIc**) [8], 1-(tetrazol-5-ylmethyl)benzotriazole (**IId**) [9], 5-(4-phenyl-1,2,3-triazol-1-ylmethyl)-tetrazole (**IIe**) [9], 1,2-bis(tetrazol-5-yl)ethane (**IVf**) [8], 1,4-bis(tetrazol-5-yl)benzene (**IVh**) [1], 2-chloromethyl-5-phenyl-1,3,4-oxadiazole (**VII**) [1], oxalyl chloride (**IIIa**) [10], succinyl chloride (**IIIf**) [11], terephthaloyl chloride (**IIIh**) [12], and fumaroyl chloride (**IIIk**) [13].

5-Chloromethyltetrazole. Anhydrous aluminum chloride, 14.7 g (110 mmol), was dissolved on stirring and cooling in 100 ml of THF, 19.5 g (300mmol) of sodium azide was added, and the mixture was heated to 50–60°C over a period of 1.5–2 h. The mixture was then cooled to room temperature, 8.0 g (106 mmol) of 2-chloroacetonitrile was added, and the mixture was heated for 20–25 h at 60–70°C. The progress of the reaction was monitored by TLC following disappearance of chloroacetonitrile. When the reaction was complete, the solvent was distilled off, the residue was treated with dilute hydrochloric acid to pH 2, and the mixture was repeatedly extracted with diethyl ether. The extract was dried over calcium chloride and evaporated in air, and the residue was recrystallized from chloroform. Yield 89%, mp 88°C (from $CHCl_3$). ^{1}H NMR spectrum, δ, ppm: 5.06 s (2H, CH_2). Found, %: C 20.13; H 2.50; N 47.18. $C_2H_3ClN_4$. Calculated, %: C 20.27; H 2.55; N 47.27.

4,4'-Bis(tetrazol-5-yl)biphenyl (IVj). Biphenyl-4,4'-diamine, 4,45 g (27 mmol) was treated with 50 ml of dilute (1:3) hydrochloric acid. The resulting suspension was cooled to 0–3°C, and a solution of 7.5 g (108 mmol) of sodium nitrite in 50 ml of water, cooled to the same temperature, was added dropwise under

Initial rates of gas evolution (r_0) in the reaction of 5-phenyltetrazole with benzoyl chloride

Catalyst	$r_0 \cdot 10^4$, mol/min	Relative initial rate, r_0(cat.)/r_0
–	0.07	1.0
DMF	1.00	14.3
Triethylamine	7.00	100.0
Pyridine	9.00	128.6

continuous stirring at such a rate that the temperature did not exceed 5°C. The mixture was neutralized with sodium carbonate, and a suspension of 2.7 g (30 mmol) of freshly prepared copper(I) cyanide in 20 ml of toluene was added. The mixture was kept for 10–12 h at room temperature, heated to 60–70°C until gaseous products no longer evolved, cooled, and treated with toluene. The extract was evaporated, and the dry residue was washed with excess aqueous ammonia to remove residual copper compounds and treated with diethyl ether. The extract was dried over $CaCl_2$, and the solvent was distilled off. Yield of biphenyl-4,4'-dicarbonitrile 36%, mp 190–200°C. ^{13}C NMR spectrum, δ_C, ppm: 118.3 (2C, CN), 112.2 ($2C^{i}$), 128.2 ($4C^{m}$), 132.9 ($4C^{o}$), 143.4 ($2C^{p}$).

A mixture of 1.3 g (20 mmol) of sodium azide, 1.1 g (20 mmol) of ammonium chloride, and 12 ml of DMF was stirred for 30–40 min at 80–90°C, 1 g (5 mmol) of biphenyl-4,4'-dicarbonitrile was added, and the mixture was stirred for 20 h at that temperature, the progress of the reaction being monitored by TLC. The solvent was distilled off, the residue was treated with dilute hydrochloric acid to pH 2, and the precipitate was filtered off, washed with water, and dried in air. Yield of bis-tetrazole **IVj** 70%, mp 325–328°C (decomp.). ^{13}C NMR spectrum, δ_C, ppm: 124.5 (C^1, $C^{1'}$), 128.6 (C^2, $C^{2'}$, C^3, $C^{3'}$, C^5, $C^{5'}$, C^6, $C^{6'}$), 142.3 (C^4, $C^{4'}$), 156.1 (2C, tetrazole). Found, %: C 58.58; H 3.02; N 38.88. $C_{14}H_{10}N_8$. Calculated, %: C 57.93; H.47; N 38.60.

5-(5-Phenyl-1,3,4-oxadiazol-2-ylmethyl)tetrazole (IIo). Sodium iodide (preliminarily calcined for 1–1.5 h at 120–140°C), 0.3 g (2.1 mmol), was added to a solution of 3 g (15 mmol) of oxadiazole **III** in 15 ml of acetone. The mixture was heated for 30–40 min under reflux, 1.2 g (24 mmol) of sodium cyanide was added, and the mixture was heated for 3–3.5 h under reflux. The solvent was distilled off, the residue was treated with excess water, and the precipitate was filtered off and recrystallized from acetone. Yield of (5-phenyl-1,3,4-oxadiazol-2-yl)acetonitrile (**VIII**) 87%, mp 186–188°C (from acetone). ^1H NMR spectrum, δ, ppm: 4.4 (2H, CH_2), 7.5–7.6 m (5H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 33(1C, CH_2), 117 (1C, CN), 129–134 (6C, Ph). Found, %: C 65.29; H 3.72; N 22.33. $C_{10}H_7N_3O$. Calculated, %: C 64.86; H 3.78; N 22.70.

A mixture of 1.6 g (25 mmol) of sodium azide and 1.3 g (25 mmol) of ammonium chloride in 15 ml of DMF was stirred for 30–35 min at 80–90°C. The mixture was cooled to room temperature, 3.0 g (16 mmol) of oxadiazole **VIII** was added, and the mixture was heated for 20–25 h at 90–100°C, the conversion of nitrile **VIII** being monitored by TLC. When the reaction was complete, the solvent was distilled off, the residue was treated with dilute hydrochloric acid to pH 2, and the precipitate was filtered off and recrystallized from alcohol. Yield 74%, mp 340°C (from EtOH). ^{13}C NMR spectrum, δ_C, ppm: 40.0 (CH_2), 123–133 m (C_6H_5), 162 (tetrazole), 164 (C^5, oxadiazole), 172 (C^2, oxadiazole). Found, %: C 52.00; H 3.62; N.33. $C_{10}H_8N_6O$. Calculated, %: C 52.63; H 3.53; N 36.83.

Bis-1,3,4-oxadiazoles (*general procedure*). *a*. A suspension of 20 mmol of the corresponding tetrazole and 5–7 mmol of dicarboxylic acid dichloride in 5 ml of *p*-xylene was stirred at 90–120°C until nitrogen no longer evolved. The mixture was poured into a saturated solution of sodium hydrogen carbonate, the resulting mixture was stirred for 30–40 min, and the precipitate was filtered off and recrystallized from ethanol or DMF.

b. A suspension of 20 mmol of the corresponding bis-tetrazole, 50–60 mmol of carboxylic acid chloride, and 0.1 ml of DMF, triethylamine, or pyridine in 5 ml of *p*-xylene was stirred at 90–120°C until nitrogen no longer evolved. The product was then isolated as described above in *a*.

2,2'-Bi(5-phenyl-1,3,4-oxadiazole) (Ia) was synthesized from 5-phenyltetrazole (**IIa**) and oxalyl chloride (**IIIa**) at 100–110°C. Yield 75%, mp 270–272°C (from EtOH); published data [14]: mp 272–273°C. ^{13}C NMR spectrum, δ_C, ppm: 129–132 m ($2C_6H_5$), 154 (C^5), 163 (C^2). Found, %: C 66.27; H 3.33; N 19.0. $C_{16}H_{10}N_4O_2$. Calculated, %: C 66.20; H 3.47; N 19.30.

Diethyl 2,2'-bi(1,3,4-oxadiazol-5-ylacetate) (Ic) was obtained from ethyl (tetrazol-5-yl)acetate (**IIc**) and oxalyl chloride (**IIIa**) at 100–110°C. Yield 70%, mp 105–108°C (from EtOH). ^{13}C NMR spectrum, δ, ppm: 14 (CH_3), 62 (CH_2), 175 (CO), 164 (C^5), 167 (C^2). Found, %: C 47.06; H 4.62; N 17.81. $C_{12}H_{14}N_4O_6$. Calculated, %: C 46.45; H 4.52; N 18.06.

2,2'-Bi[5-(benzotriazol-1-ylmethyl)-1,3,4-oxadiazole] (Id) was synthesized from compound **IId** and oxalyl chloride (**IIIa**) at 95–110°C. Yield 70%, mp 170°C (from EtOH). ^{13}C NMR spectrum, δ_C, ppm: 42.6 (CH_2), 120–133 (C_6H_4), 154.6 (C^5), 163.1 (C^2). Found, %: C 54.57; H 2.48; N 34.46. $C_{18}H_{12}N_{10}O_2$. Calculated, %: C 54.00; H 3.00; N 35.00.

2,2'-Bi[5-(4-phenyl-1,2,3-triazol-1-ylmethyl)-1,3,4-oxadiazole] (Ie) was synthesized from compound **IIe** and oxalyl chloride (**IIIa**) at 90–100°C. Yield 72%, mp 144–146°C (from EtOH). ^{13}C NMR spectrum, δ_C, ppm: 43 (CH_2), 129.5–133.5 (C_6H_5), 126.7 (CH, triazole), 139.2 (C, triazole), 154.3 (C^5, oxadiazole), 163.7 (C^2, oxadiazole). Found, %: C 57.81; H 3.28; N 31.56. $C_{22}H_{14}N_{10}O_2$. Calculated, %: C 58.67; H 3.11; N 31.11.

1,2-Bis(5-phenyl-1,3,4-oxadiazol-2-yl)ethane (If). *a*. Compound **If** was synthesized from 5-phenyltetrazole (**IIa**) and succinyl chloride (**IIIf**) at 80–90°C. Yield 79%, mp 204–208°C (from DMF). ^{1}H NMR spectrum, δ, ppm: 3.58 s (4H, CH_2CH_2), 7.57–8.01 m (10H, H_{arom}). Found, %: C 67.86; H 4.23; N 18.1. $C_{18}H_{14}N_4O_2$. Calculated, %: C 67.91; H 4.43; N 17.60.

b. From 1,2-bis(tetrazol-5-yl)ethane (**IVf**) and benzoyl chloride (**Va**) at 100–110°C. Yield 76%, mp 207–209°C (from DMF). ^{1}H NMR spectrum, δ, ppm: 3.58 s (4H, CH_2CH_2), 7.57–8.01 m (10H, H_{arom}).

1,2-Bis(5-chloromethyl-1,3,4-oxadiazol-2-yl) ethane (Ig). *a.* From 5-chloromethyltetrazole (**IIb**) and succinyl chloride (**IIIf**) at 80–100°C. Yield 84%, mp 97–99°C (from EtOH). ^{1}H NMR spectrum, δ, ppm: 3.47 s (4H, CH_2CH_2), 4.90 s (4H, CH_2Cl). Found, %: C 36.72; H 3.40; N 21.83. $C_8H_8Cl_2N_4O_2$. Calculated, %: C 36.50; H 3.04; N 21.29.

b. From 1,2-bis(tetrazol-5-yl)ethane (**IVf**) and chloroacetyl chloride (**Vb**) at 90–95°C. Yield 75%, mp 98–99°C (from EtOH). ^{1}H NMR spectrum, δ, ppm: 3.47 s (4H, CH_2CH_2), 4.90 s (4H, CH_2Cl).

1,4-Bis(5-phenyl-1,3,4-oxadiazol-2-yl)benzene (Ih). *a.* From 5-phenyltetrazole (**IIa**) and terephthaloyl chloride (**IIIh**) at 100–110°C. Yield 73%, mp 232–234°C (from DMF). ^{1}H NMR spectrum, δ, ppm: 7.5–7.9 (10H, C_6H_5), 8.3 s (4H, C_6H_4). Found, %: C 71.50; H 3.85; N 15.37. $C_{22}H_{14}N_{10}O_2$. Calculated, %: C 72.13; H 3.82; N 15.30.

b. From 1,4-bis(tetrazol-5-yl)benzene (**IVh**) and benzoyl chloride (**Va**) at 110–120°C. Yield 82%, mp 233–235°C (from DMF). A sample of **Ih** prepared as described in *a* showed no depression of the melting point on mixing with a commercial sample of POPOP.

1,4-Bis(5-chloromethyl-1,3,4-oxadiazol-2-yl)benzene (Ii). *a.* From 5-chloromethyltetrazole (**IIb**) and terephthaloyl chloride (**IIIh**) at 80–100°C. Yield 84%, mp 195–197°C (from EtOH). ^{1}H NMR spectrum, δ, ppm: 4.90 s (4H, CH_2Cl). Found, %: C 46.72; H 2.63; N 18.37. $C_{12}H_8Cl_2N_4O_2$. Calculated, %: C 46.30; H 2.57; N 18.00.

b. From 1,4-bis(tetrazol-5-yl)benzene (**IVh**) and chloroacetyl chloride (**Vb**) at 80–90°C. Yield 82%, mp 196–197°C (from EtOH). ^{1}H NMR spectrum, δ, ppm: 5.07 s (4H, CH_2Cl), 8.30 s (4H, C_6H_4).

4,4'-Bis(5-phenyl-1,3,4-oxadiazol-2-yl)biphenyl (Ij) was obtained from biphenyl **IVj** and benzoyl chloride (**Va**) at 120–130°C. Yield 74%, mp 267–270°C (from DMF). ^{13}C NMR spectrum, δ_C, ppm: 126.4–131.6 m (10C, $2C_6H_4$; 12C, $2C_6H_5$), 141.8 (C^4, $C^{4'}$, $2C_6H_4$), 165.0 (C^5), 174.9 (C^2). Found, %: C 77.0; H 3.83; N.98. $C_{28}H_{18}N_4O_2$. Calculated, %: C 76.01; H 4.10; N 12.66.

1,2-Bis(5-phenyl-1,3,4-oxadiazol-2-yl)ethene (Ik) was obtained from 5-phenyltetrazole (**IIa**) and fumaroyl chloride (**IIIk**) at 80–100°C. Yield 77%, mp 290–293°C (DMF). Found, %: C 67.68; H 3.78; N 17.82. $C_{18}H_{12}N_4O_2$. Calculated, %: C 68.35; H 3.80; N 17.72.

1,2-Bis(5-phenyl-1,3,4-oxadiazol-2-yl)ethyne (Il). Acetylenedicarboxylic acid, 2 g (17 mmol), was added to a mixture of 5 g (25 mmol) of phthaloyl chloride and 0.5 g of anhydrous zinc chloride. On heating under reduced pressure (50 mm) the mixture foamed. A fraction boiling in the range from 100 to 120°C (50 mm), 3.5 g, was collected; it contained acetylenedicarboxylic acid dichloride (**IIIl**).

Dichloride **IIIl**, 1 g (6.6 mmol), was added to a suspension of 3 g (20 mmol) of 5-phenyltetrazole (**IIa**) in 10 ml of *p*-xylene containing 0.2 ml of DMF. The mixture was heated at 110–120°C until nitrogen no longer evolved, and the product was isolated according to the general procedure. Yield of **Il** 74%, mp 195–197°C (from DMF–EtOH). ^{13}C NMR spectrum, δ_C, ppm: 115.1 (2C, C≡), 122.4–132.1 ($2C_6H_5$), 160.2 ($2C^5$), 165.0 ($2C^2$). Found, %: C 68.00; H 3.24; N 18.06. $C_{18}H_{10}N_4O_2$. Calculated, %: C 68.79; H 3.18; N 17.83.

1-Butyl-4,5-bis(5-phenyl-1,3,4-oxadiazol-2-yl)-1,2,3-triazole (Im). A solution of 5 g (50 mmol) of butyl azide in 5 ml of acetone was added dropwise to a solution of 5.4 g (47 mmol) of acetylenedicarboxylic acid in 10 ml of acetone, and the temperature rose from 25 to 32°C. The mixture was left to stand for 12 h, heated to 50°C, and kept for 3 h at that temperature, the solvent was distilled off, and the residue was recrystallized from water. We thus obtained 7.2 g (72.3%) of 1-butyl-1,2,3-triazole-4,5-dicarboxylic acid with mp 129°C (from H_2O).

A solution of 6.1 ml (60 mmol) of thionyl chloride in 5 ml of chloroform was added dropwise under stirring to a suspension of 6.5 g (30 mmol) of 1-butyl-1,2,3-triazole-4,5-dicarboxylic acid in 30 ml of chloroform containing 5 drops of DMF. After 1 h, the mixture was heated to 50–60°C and was kept for 10 h at that temperature. The solvent and excess thionyl chloride were distilled off, and the residue was recrystallized from chloroform to obtain 4.2 g of dark crystalline 1-butyl-1,2,3-triazole-4,5-dicarbonyl dichloride with mp 125°C (decomp.).

5-Phenyltetrazole (**IIa**), 5.8 g (40 mmol), was dispersed in 10 ml of *p*-xylene, and 0.1 ml of pyridine and 4.2 g (16 mmol) of 1-butyl-1,2,3-triazole-4,5-dicarbonyl dichloride were added. The mixture was stirred at 100°C until gaseous products no longer evolved, poured into a saturated solution of sodium hydrogen carbonate, stirred for 30–40 min, and extracted with ethyl acetate. The extract was dried over $CaCl_2$, the solvent was distilled off, and the residue was recrystallized from alcohol. Yield 65%, mp 145–147°C (from EtOH). ^{1}H NMR spectrum, δ, ppm: 0.8 t (3H, CH_3), 1.22 m (2H, CH_2), 1.90 (2H, CH_2), 4.45 (2H, CH_2N), 7.5–8.7 m (10H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 13.6 (1C, CH_3), 20.1 (1C, CH_2), 32.7 (1C, CH_2), 50.8 (1C, CH_2), 124.7–132.7 (12C, $2C_6H_5$), 134.1 and 140.0 (2C, triazole), 159.4 ($2C^5$, oxadiazole), 164.5 ($2C^2$, oxadiazole). Found, %: C 63.0; H 4.15; N 23.72. $C_{22}H_{19}N_7O_2$. Calculated, %: C 63.91; H 4.63; N 23.72.

1-Benzyl-4,5-bis(5-phenyl-1,3,4-oxadiazol-2-yl)-1,2,3-triazole (In). A solution of 22.7 g (171 mmol) of benzyl azide in 7.5 ml of acetone was added dropwise to a solution of 10 g (90 mmol) of acetylenedicarboxylic acid in 23 ml of acetone; the mixture warmed up to 40°C, and the temperature was maintained at 40°C by external cooling. When the exothermic reaction was over, the mixture was left to stand for 12 h, and the precipitate was filtered off and recrystallized from alcohol. Yield of 1-benzyl-1,2,3-triazole-4,5-dicarboxylic acid 21 g (94.4%), mp 183–186°C; published data [15]: mp 184°C.

A solution of 7.1 g (60 mmol) of thionyl chloride in 5 ml of chloroform was added dropwise to a suspension of 5.0 g (20 mmol) of 1-benzyl-1,2,3-triazole-4,5-dicarboxylic acid in 25 ml of chloroform containing 4 drops of DMF. The mixture was stirred for 12 h at 23–25°C, and the solvent and excess thionyl chloride were distilled off. The residue, 7.2 g, was a dark oily substance which contained 1-benzyl-1,2,3-triazole-4,5-dicarbonyl dichloride (**IIIn**); it was used in the next stage without additional purification.

5-Phenyltetrazole (**Va**), 8.8 g (60 mmol), was dispersed in 10 ml of *p*-xylene, and 0.1 ml of DMF and 7.2 g (25 mmol) of dichloride **IIIn** in 5 ml of *p*-xylene were added. The mixture was heated at 70–80°C until gas evolution ceased, and the product was isolated as described above for compound **Im**. Yield of **In** 68%, mp 212°C (from EtOH). Found, %: C 67.73; H 3.96; N 21.87. $C_{25}H_{15}N_7O_2$. Calculated, %: C 67.42; N 3.37; H 22.02.

Bis(5-phenyl-1,3,4-oxadiazol-2-yl)methane (IIo) was synthesized from 5-(5-phenyl-1,3,4-oxadiazol-2-ylmethyl)tetrazole (**IIo**) and benzoyl chloride (**Va**) at 100–110°C. Yield 75%, mp 230–232°C (from DMF). Found, %: C 66.37; H 3.86; N 19.05. $C_{17}H_{12}N_4O_2$. Calculated, %: C 67.10; H 3.95; N 18.42.

2-Ethenyl-5-phenyl-1,3,4-oxadiazole. A solution of 7.25 g (52 mmol) of benzoyl chloride in 150 ml of methylene chloride was added under vigorous stirring to a suspension of 5 g (52 mmol) of 5-vinyltetrazole, 2.9 g (52 mmol) of potassium hydroxide, and 1 g of tetrabutylammonium chloride in 100 ml of water. The mixture was stirred for 8 h at room temperature, the organic phase was separated and diluted with 200 ml of toluene, and methylene chloride was distilled off on a rotary evaporator (by the end, under slightly reduced pressure). The remaining toluene solution was heated at 95–100°C until gaseous products no longer evolved, and the residue was distilled under reduced pressure. Yield 4 g (45%), bp 122°C (1 mm), n_D^{20} = 1.5885. IR spectrum, ν, cm^{-1}: 1650 (C=C), 1590 (Ph), 1210 (–O–). ^{1}H NMR spectrum, δ, ppm: 5.90 d (1H, $=CH_2$, *trans*), 6.38 d (1H, CH_2, *cis*), 6.60 m (1H, CH=), 7.2–7.6 m (5H, H_{arom}).

REFERENCES

1. Vereshchagin, L.I., Petrov, A.V., Proidakov, A.G., Pokatilov, F.A., Smirnov, A.I., and Kizhnyaev, V.N., *Russ. J. Org. Chem*., 2006, vol. 42, p. 912.
2. Krasovitskii, B.M. and Bolotin, B.M., *Organicheskie lyuminofory* (Organic Luminophores), Leningrad: Khimiya, 1976.
3. Popova, N.A., Yushko, E.G., Krasovitskii, B.M., Minkin, V.I., Lyubarskaya, A.E., and Gol'berg, M.L., *Khim. Geterotsikl. Soedin*., 1983, no. 1, p. 26.
4. Knyazhanskii, M.I., Gilyanovskii, P.V., and Osipov, O.A., *Khim. Geterotsikl. Soedin*., 1977, no. 11, p. 1455.

5. Shaban, M.A.E., Nasr, A.Z., and El-Badry, S.M., *J. Islamic Acad. Sci*. 1991, vol. 4, p. 184.
6. Osipova, T.F., Koldobskii, G.I., and Ostrovskii, V.A., *Zh. Org. Khim*., 1984, vol. 20, p. 2468.
7. Huisgen, R., Sauer, J., and Seidel, M., *Chem. Ber*., 1960, vol. 93, p. 2885.
8. Finnegan, W., Henry, R., and Lofquist, R., *J. Am. Chem. Soc*., 1958, vol. 80, p. 3908.
9. Verkhozina, O.N., Vereshchagin, L.I., Kizhnyaev, V.N., Rokhin, A.V., and Smirnov, A.I., *Russ. J. Org. Chem*., 2003, vol. 39, p. 1792.
10. Kul'berg, L.M., *Sintezy organicheskikh preparatov dlya neorganicheskogo analiza* (Syntheses of Organic Reagents for Inorganic Analysis), Moscow: Goskhimizdat, 1947, p. 364.
11. *Weygand–Hilgetag Organisch-chemische Experimentierkunst*, Hilgetag, G. and Martini, A., Eds., Leipzig: Johann Ambrosius Barth, 1964, 3rd ed. Translated under the title *Metody eksperimenta v organicheskoi khimii*, Moscow: Khimiya, 1968, p. 234.
12. *Condensation Monomers*, Stille, J.K. and Campbell, T.W., Ed., New York: Wiley, 1972. Translated under the title *Monomery dlya polikondensatsii*, Moscow: Mir, 1976, p. 395.
13. Kyrides, L.P., Allen, C.F.H., and Pingert, F.P., *Organic Syntheses*, Horning, E.C., Ed., New York: Wiley, 1955, collect. vol. 3, p. 422.
14. Taber, R.L. and Boyd, T., *J. Heterocycl. Chem*. 1972, vol. 9, p. 393.
15. Wiley, R.H., *J. Org. Chem*., 1956, vol. 21, p. 190.