

## Polynuclear Nonfused Tetrazole-, 1,3,4-Oxadiazole-, and 1,2,3-Triazole-Containing Systems

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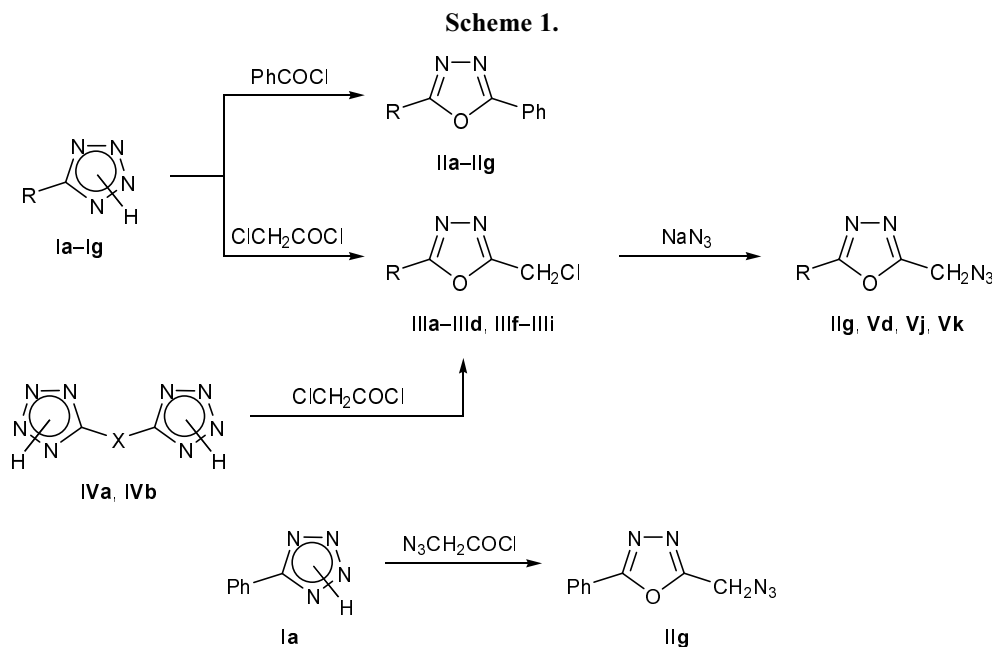
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**Abstract**—Polynuclear nonfused blocks containing 1,2,3-triazole, 1,3,4-oxadiazole, and tetrazole rings were synthesized by reaction of C-substituted tetrazoles with carboxylic acid chlorides, as well as by cycloaddition of 2-azidomethyl-1,3,4-oxadiazoles at the triple bond of acetylenic compounds.

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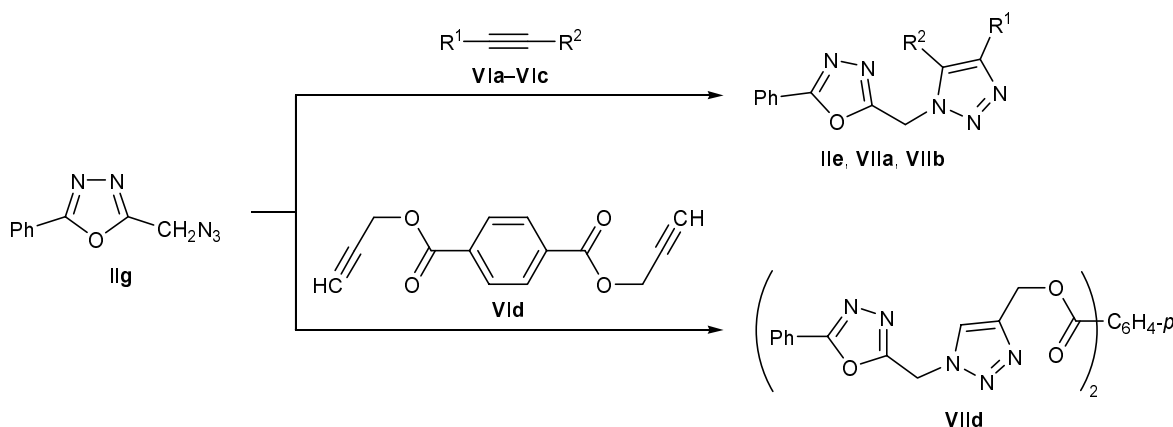
We previously [1–3] described methods for building up polynuclear nonfused tetrazole- and 1,2,3-triazole-containing structures. In continuation of these studies, in the present communication we report on the synthesis of systems including 1,3,4-oxadiazole rings together with triazole and tetrazole fragments. The most convenient route to such systems turned out to be

the transformation of C-substituted tetrazoles into 1,3,4-oxadiazoles by the action of carboxylic acid chlorides. Osipova et al. [4] and Huisgen et al. [5] proposed a mechanism for this transformation; however, in some cases, the failure of tetrazole and C-substituted tetrazoles to react with a number of carboxylic acid chlorides could not be rationalized in terms of the



**I–III, V**, R = Ph (**a**), EtOCOCH<sub>2</sub> (**b**), 2-(5-phenyltetrazol-1-yl)ethyl (**c**), 1,2,3-benzotriazol-1(2)-ylmethyl (**d**), 4-(benzoyloxymethyl)-1*H*-1,2,3-triazol-1-ylmethyl (**e**), 2-phenyl-2*H*-1,2,3-triazol-4-yl (**f**), N<sub>3</sub>CH<sub>2</sub> (**g**), 2-(5-chloromethyl-1,3,4-oxadiazol-2-yl)ethyl (**h**), 4-(5-chloromethyl-1,3,4-oxadiazol-2-yl)phenyl (**i**), 4-(5-azidomethyl-1,3,4-oxadiazol-2-yl)phenyl (**j**), 2-(5-azidomethyl-1,3,4-oxadiazol-2-yl)ethyl (**k**); **IV**, X = CH<sub>2</sub>CH<sub>2</sub> (**a**), *p*-C<sub>6</sub>H<sub>4</sub> (**b**).

Scheme 2.



$\text{R}^1 = \text{R}^2 = \text{MeOCO}$  (a);  $\text{R}^1 = 1H\text{-imidazol-1-ylmethyl}$ ,  $\text{R}^2 = \text{H}$  (b);  $\text{R}^1 = \text{PhC(O)OCH}_2$ ,  $\text{R}^2 = \text{H}$  (c).

proposed mechanism. For example, 5-acylamino-tetrazoles, 5-vinyltetrazole, and 5-cyanomethyltetrazole did not react with various carboxylic acid chlorides. Presumably, 5-vinyltetrazole and 5-cyanomethyltetrazole decomposed under these conditions. The reaction of 5-phenyltetrazole with acryloyl chloride resulted in formation of an unidentified tarry product. These data prompted us to estimate the possibility for converting 5-substituted tetrazoles **Ia–Ig** into the corresponding 1,3,4-oxadiazoles by reaction with benzoyl chloride. The reaction was carried out by heating tetrazoles **Ia–Ig** with excess benzoyl chloride in toluene at 95–105°C. As a result, we isolated in high yields bicyclic compounds **IIa–IIg** containing a 1,3,4-oxadiazole ring with functional (compounds **IIa**, **IIb**, and **IIg**) and heterocyclic substituents (**IIc–IIf**) in position 2 (5) linked through a methylene bridge (Scheme 1).

The IR spectra of compounds **IIa–IIg** contain absorption bands in the region 950–980  $\text{cm}^{-1}$  due to skeletal vibrations of the oxadiazole ring. Bands corresponding to stretching vibrations of the C=N bonds are often overlapped by those belonging to the phenyl substituent.

In order to attach additional rings to the polynuclear system, the most promising was the reaction of tetrazoles with chloroacetyl chloride. In such a way we succeeded in obtaining a series of 1,3,4-oxadiazoles **IIIa–IIId** having a chloromethyl group in position 2 and heteroaromatic substituents on C<sup>5</sup>. Likewise, bis-tetrazole derivatives **IVa** and **IVb** were converted into 1,2-bis(2-chloromethyl-1,3,4-oxadiazol-5-yl)ethane (**IIIh**) and 1,4-bis(2-chloromethyl-1,3,4-oxadiazol-5-yl)benzene (**IIIi**), respectively, by the action of chloroacetyl chloride. The presence of a chloromethyl group

made it possible to append a 1,2,3-triazole ring to oxadiazoles through intermediate 2-azidomethyl-1,3,4-oxadiazoles **IIg**, **Vd**, **Vj**, and **Vk** which were subjected to cycloaddition at the azido group to acetylenic compounds **VIa–VIId** (Scheme 2).

Thus we have synthesized systems **IIe**, **VIIa**, **VIIb**, and **VIIId** containing both oxadiazole and 1,2,3-triazole rings. 1-(5-Phenyl-1,3,4-oxadiazol-2-ylmethyl)-1,2,3-triazol-4-ylmethyl benzoate (**IIe**) was synthesized in two ways: by cycloaddition of 2-azidomethyl-5-phenyl-1,3,4-oxadiazole (**IIg**) to 2-propynyl benzoate (**VIc**) (Scheme 2) and transformation of 1-(tetrazol-5-ylmethyl)-1,2,3-triazol-4-ylmethyl benzoate (**Ie**) by the action of benzoyl chloride.

2-Azidomethyl-1,3,4-oxadiazoles **IIg**, **Vd**, **Vj**, and **Vk** were obtained by nucleophilic replacement of the halogen atom in 2-chloromethyl-1,3,4-oxadiazoles **IIIa–IIId** and **IIIf–IIIi** by azido group under conditions of phase-transfer catalysis using benzyltriethylammonium chloride (BTEAC). 2-Azidomethyl-5-phenyl-1,3,4-oxadiazole (**IIg**) was also synthesized by reactions of 5-azidomethyltetrazole (**Ig**) with benzoyl chloride and of 5-phenyltetrazole (**Ia**) with azidoacetyl chloride.

All azidomethyl-1,3,4-oxadiazoles showed in the IR spectra a clearly defined absorption band at  $\nu$  2120  $\text{cm}^{-1}$ , which is typical of azido group; their <sup>1</sup>H NMR spectra contained signals from protons in the substituent on C<sup>5</sup> and in the methylene bridge ( $\delta$  4.3–5.0 ppm). According to the <sup>1</sup>H NMR data, benzotriazole derivatives **IIId** and **IIIId** were formed as mixtures of two isomers substituted at the N<sup>1</sup> and N<sup>2</sup> atoms. The reason is that initial benzotriazole **Id** is also a mixture of isomers at a ratio of 2:1. However, the isomer ratios

in compounds **IIId** and **IIIId** differed considerably from that intrinsic to **Id** and were approximately 10:12 for **IIId** and 10:1 for **IIIId**, presumably as a result of isomerization accompanying the main reaction.

Polynuclear structures obtained by cycloaddition of azides to acetylene derivatives contain 1,3,4-oxadiazole and 1,2,3-triazole fragments linked together through a methylene bridge. Protons of the bridging methylene group appeared in the  $^1\text{H}$  NMR spectra in the region  $\delta$  6.2–6.4 ppm.

## EXPERIMENTAL

The IR spectra were recorded on a Specord M80 spectrometer from samples dispersed in mineral oil. The  $^1\text{H}$  NMR spectra were measured on a Varian VXR-500S spectrometer (500 MHz) from solutions in acetone- $d_6$  or DMSO- $d_6$ . The progress of reactions was monitored by TLC on Silufol plates using ethyl acetate–hexane (2:3, by volume) as eluent (development under UV light or with iodine vapor).

Initial 5-phenyltetrazole (**Ia**) [6], ethyl 2-(tetrazol-5-yl)acetate (**Ib**) [6], 1-[2-(tetrazol-5-yl)ethyl]tetrazole (**Ic**) [2], 1-(tetrazol-5-ylmethyl)-1,2,3-benzotriazole (**Id**) [2], 1-(tetrazol-5-ylmethyl)-1,2,3-triazol-4-ylmethyl benzoate (**Ie**) [3], 5-(2-phenyl-1,2,3-triazol-4-yl)tetrazole (**If**) [2], 5-azidomethyltetrazole (**Ig**) [2], and 1,2-bis(tetrazol-5-yl)ethane (**IVa**) [6] were prepared by known procedures.

**1,4-Bis(tetrazol-5-yl)benzene (IVb).** A solution of 6.7 g (0.96 mol) of hydroxylamine hydrochloride and 6 g of sodium acetate in 18 ml of water was added at 50°C to a solution of 6 g (44.0 mmol) of terephthalaldehyde in 30 ml of ethanol. The precipitate of the corresponding dioxime was filtered off and dried in air. Yield 6.8 g (93%), mp 209°C; published data [7]: mp 200°C. A mixture of 4 g (24.0 mmol) of terephthalaldehyde dioxime and 10 ml of acetic anhydride was heated for 3 h at 125°C. The mixture was then poured into 100 ml of water, and the needle-shaped crystals were filtered off, washed with water, and dried in air. Yield of terephthalonitrile 2.7 g (87%), mp 223°C (in a sealed capillary); published data [8]: mp 222°C. A suspension of 2.7 g (27.0 mmol) of sodium azide and 2.25 g (42.0 mmol) of ammonium chloride in 15 ml of DMF was heated for 20 min at 90–100°C; the mixture was cooled, 2.3 g (18.0 mmol) of terephthalonitrile was added, and the mixture was heated for 12 h at 100°C and acidified to pH 2 with dilute hydrochloric acid. The precipitate of bis-tetra-

zole **IVb** was filtered off, washed with cold water, and dried in air. Yield 3.4 g (89%), mp 312°C; published data [9]: mp 313°C.

**1-(Prop-2-ynyl)imidazole (VIb).** Imidazole, 5.5 g (0.08 mol), was added under vigorous stirring to a solution of 13.4 g (0.24 mol) of potassium hydroxide in 16 ml of water and 50 ml of acetone. After 15 min, the mixture was cooled to –5°C, 9.9 g (0.084 mol) of 2-propynyl bromide was slowly added dropwise, and the mixture was allowed to warm up to 25°C over a period of 1.5 h. The organic phase was separated, and the aqueous phase was extracted with chloroform. The extract was combined with the organic phase, dried over  $\text{Na}_2\text{SO}_4$ , and evaporated under reduced pressure, and the residue was distilled in a vacuum. Yield 6.7 g (79%), bp 99–101°C (2 mm). IR spectrum:  $\nu(\equiv\text{CH})$  2110  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR spectrum,  $\delta$ , ppm: 3.09 s (1H, CH); 6.96 s, 7.16 s, and 7.64 s (3H, imidazole). Found, %: C 68.07; H 5.48; N 26.57.  $\text{C}_6\text{H}_6\text{N}_2$ . Calculated, %: C 67.92; H 5.66; N 26.41.

**General procedure for the synthesis of 2,5-disubstituted 1,3,4-oxadiazoles.** A suspension of 20.0 mmol of 5-substituted tetrazole **Ia–Ig** and 30.0–50.0 mmol of benzoyl or chloroacetyl chloride in 5–10 ml of toluene was stirred at 95–105°C for 1–5 h (until the initial tetrazole disappeared according to the TLC data). The mixture was poured into a saturated solution of sodium hydrogen carbonate, the mixture was stirred for 30–40 min, and the precipitate was filtered off and recrystallized from ethanol. If the product did not crystallize, it was extracted into diethyl ether or ethyl acetate. The solvent was removed from the extract, and the residue was recrystallized from ethanol or distilled under reduced pressure.

**2,5-Diphenyl-1,3,4-oxadiazole (IIa)** was synthesized from 2 g (13.0 mmol) of 5-phenyltetrazole (**Ia**) and 2.8 g (20.0 mmol) of benzoyl chloride in 5 ml of toluene. Yield 2.7 g, mp 140–141°C [4].

**Ethyl 2-(5-phenyl-1,3,4-oxadiazol-2-yl)acetate (IIb)** was synthesized from 3.0 g (19.0 mmol) of compound **Ib** and 2.8 g (20.0 mmol) of benzoyl chloride in 10 ml of toluene. Yield 3.5 g (83%), mp 64–65°C. IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 1710 (C=O), 1600 ( $\text{C}_6\text{H}_5$ ), 970 (C=N). Found, %: C 62.20; H 5.12; N 11.73.  $\text{C}_{12}\text{H}_{12}\text{N}_2\text{O}_3$ . Calculated, %: C 62.06; H 5.17; N 12.06.

**5-Phenyl-1-[2-(5-phenyl-1,3,4-oxadiazol-2-yl)ethyl]tetrazole (IIc)** was synthesized from 1.0 g (4.0 mmol) of compound **Ic** and 0.84 g (6.0 mmol) of benzoyl chloride in 5 ml of toluene. Yield 0.95 g

(73%), mp 178°C (from alcohol). <sup>1</sup>H NMR spectrum,  $\delta$ , ppm: 3.85 t (2H, CH<sub>2</sub>,  $J = 6.5$  Hz), 5.32 t (2H, CH<sub>2</sub>,  $J = 6.5$  Hz), 7.51–8.09 m (5H, C<sub>6</sub>H<sub>5</sub>). Found, %: C 64.8; H 4.2; N 25.92. C<sub>17</sub>H<sub>14</sub>N<sub>6</sub>O. Calculated, %: C 64.15; H 4.40; N 26.41.

**1(2)-(5-Phenyl-1,3,4-oxadiazol-2-ylmethyl)-1,2,3-benzotriazole (II<sub>d</sub>)** was synthesized from 1.0 g (5.0 mmol) of compound **Id** and 1.4 g (10.0 mol) of benzoyl chloride in 5 ml of toluene. Yield 1.1 g (81%), mp 134–135°C. <sup>1</sup>H NMR spectrum,  $\delta$ , ppm: 1-substituted isomer (45%): 6.43 s (2H, CH<sub>2</sub>), 7.45–8.08 m (4H, C<sub>6</sub>H<sub>4</sub>,  $J = 10.0$  Hz); 2-substituted isomer (55%): 6.42–7.95 m (4H, C<sub>6</sub>H<sub>4</sub>). Found, %: C 65.38; H 3.51; N 25.90. C<sub>15</sub>H<sub>11</sub>N<sub>5</sub>O. Calculated, %: C 64.98; H 3.97; N 25.27.

**1-(5-Phenyl-1,3,4-oxadiazol-2-ylmethyl)-1,2,3-triazol-4-ylmethyl benzoate (II<sub>e</sub>)**. *a.* Compound **IIe** was synthesized from 0.5 g (18.0 mmol) of tetrazole **Ie** and 0.4 g (28.0 mmol) of benzoyl chloride in 5 ml of toluene. Yield 0.25 g (41%), mp 191°C. IR spectrum,  $\nu$ , cm<sup>-1</sup>: 1700 (C=O), 970 (C=N). <sup>1</sup>H NMR spectrum,  $\delta$ , ppm: 5.46 s (2H, CH<sub>2</sub>), 6.13 s (2H, CH<sub>2</sub>), 7.50–7.60 m (5H, C<sub>6</sub>H<sub>5</sub>), 7.99–8.01 m (5H, C<sub>6</sub>H<sub>5</sub>), 8.39 s (1H, triazole). Found, %: C 64.70; H 4.46; N 20.91. C<sub>19</sub>H<sub>15</sub>N<sub>5</sub>O<sub>3</sub>. Calculated, %: C 63.15; H 4.15; N 19.39.

*b.* A solution of 1.0 g (5.0 mmol) of azide **IIg** and 0.8 g (5.0 mmol) of 2-propynyl benzoate (**VIc**) in 10 ml of ethanol was heated for 20 h under reflux (until the initial azide disappeared according to the TLC data). The solvent was evaporated in air, and the residue was recrystallized from alcohol. Yield 1.15 g (64%), mp 191–194°C. The product showed no depression of the melting point on mixing with a sample prepared as described in *a*.

**2-Azidomethyl-5-phenyl-1,3,4-oxadiazole (II<sub>g</sub>)**. *a.* A suspension of 1.1 g (9.0 mmol) of 5-azidomethyltetrazole (**Ig**) and 2.5 g (18.0 mmol) of benzoyl chloride in 5 ml of toluene was slowly heated under stirring to 80°C over a period of 2 h. The mixture turned dark and was treated according to the general procedure. Yield 1.4 g (83%), mp 72–73°C (from ethanol). IR spectrum:  $\nu$ (N<sub>3</sub>) 2115 cm<sup>-1</sup>. <sup>1</sup>H NMR spectrum,  $\delta$ , ppm: 4.85 s (2H, CH<sub>2</sub>), 7.6–8.1 m (5H, C<sub>6</sub>H<sub>5</sub>).

*b.* A mixture of 1.0 g (5 mmol) of oxadiazole **IIIa**, 0.4 g (6 mmol) of sodium azide, 0.1 g of BTEAC, and 5 ml of water was vigorously stirred for 20–30 min at 90–95°C (until the solid phase disappeared). The mixture was cooled to room temperature under continuous stirring, and the light brown precipitate of oxadiazole **IIg** was filtered off. Yield 1.3 g (80%), mp 72–73°C.

*c.* A solution of 11.4 g (96.0 mmol) of thionyl chloride in 20 ml of toluene was added dropwise under stirring at room temperature to a solution of 2.5 g (24.8 mmol) of azidoacetic acid in 20 ml of toluene. The mixture was stirred until hydrogen chloride no longer evolved, excess thionyl chloride was distilled off under reduced pressure, 0.4 g (3.0 mmol) of 5-phenyltetrazole (**Ia**) and 2 ml of toluene were added to the residue, and the mixture was heated for 2 h at 90°C and treated with a saturated solution of sodium hydrogen carbonate. The organic phase was separated, and the aqueous phase was extracted with ethyl acetate. Removal of the solvent left 0.7 g of a crystalline material which was subjected to fractional crystallization from ethanol to isolate 0.2 g (36%) of azidomethyloxadiazole **IIg** with mp 72–73°C. The product showed no depression of the melting point on mixing with samples prepared as described in *a* and *b*.

**2-Chloromethyl-5-phenyl-1,3,4-oxadiazole (III<sub>a</sub>)** was synthesized from 2 g (14.0 mmol) of 5-phenyltetrazole (**Ia**) and 3.6 g (32.0 mmol) of chloroacetyl chloride in 5 ml of toluene at 105°C. Yield 2.5 g (88%), mp 111°C (from ethanol). <sup>1</sup>H NMR spectrum,  $\delta$ , ppm: 5.03 s (2H, CH<sub>2</sub>), 7.63–8.07 m (5H, C<sub>6</sub>H<sub>5</sub>). Found, %: C 55.50; H 3.60; N 14.40. C<sub>9</sub>H<sub>7</sub>ClN<sub>2</sub>O. Calculated, %: C 55.52; H 3.59; N 14.39.

**Ethyl 2-(5-chloromethyl-1,3,4-oxadiazol-2-yl)acetate (III<sub>b</sub>)** was synthesized from 2 g (13.0 mmol) of compound **Ib** and 2.9 g (26.0 mmol) of chloroacetyl chloride in 7 ml of toluene. Yield 1.0 g (43%), oily substance. IR spectrum,  $\nu$ , cm<sup>-1</sup>: 1710 (C=O), 675 (C–Cl). <sup>1</sup>H NMR spectrum,  $\delta$ , ppm: 1.23 t (3H, CH<sub>3</sub>), 4.11 s (2H, CH<sub>2</sub>), 4.18 q (2H, OCH<sub>2</sub>), 4.94 s (2H, CH<sub>2</sub>Cl). Found, %: C 43.55; H 4.75; N 14.31. C<sub>7</sub>H<sub>9</sub>ClN<sub>2</sub>O<sub>3</sub>. Calculated, %: C 41.07; H 4.40; N 13.69.

**1-[2-(5-Chloromethyl-1,3,4-oxadiazol-2-yl)ethyl]-5-phenyltetrazole (III<sub>c</sub>)** was synthesized from 3.7 g (12.0 mmol) of compound **Ic** and 2.8 g (25.0 mmol) of chloroacetyl chloride in 6 ml of toluene. Yield 1.8 g (52%), mp 55–56°C (from ethanol). <sup>1</sup>H NMR spectrum,  $\delta$ , ppm: 3.80 t (2H, CH<sub>2</sub>C), 5.03 s (2H, CH<sub>2</sub>Cl), 5.25 t (2H, CH<sub>2</sub>N), 7.52–8.10 m (5H, C<sub>6</sub>H<sub>5</sub>). Found, %: C 50.10; H 4.21; N 28.15. C<sub>12</sub>H<sub>11</sub>ClN<sub>6</sub>O. Calculated, %: C 49.66; H 3.78; N 28.91.

**1(2)-(5-Chloromethyl-1,3,4-oxadiazol-2-ylmethyl)-1,2,3-benzotriazole (III<sub>d</sub>)** was synthesized from 3 g (15.0 mmol) of compound **Id** and 3.4 g (30.0 mmol) of chloroacetyl chloride in 7 ml of toluene. Yield 2.4 g (65%), mp 121–123°C (from ethanol). <sup>1</sup>H NMR spectrum,  $\delta$ , ppm: 1-substituted

isomer (90%): 6.38 (2H, CH<sub>2</sub>), 7.46–8.05 (4H, C<sub>6</sub>H<sub>4</sub>); 2-substituted isomer (10%): 6.34 (2H, CH<sub>2</sub>), 7.89–7.86 (4H, C<sub>6</sub>H<sub>4</sub>). Found, %: C 48.19; H 3.42; N 27.72. C<sub>10</sub>H<sub>8</sub>ClN<sub>5</sub>O. Calculated, %: C 48.09; H 3.20; N 28.05.

**5-Chloromethyl-2-(2-phenyl-1,3,4-triazol-4-yl)-1,3,4-oxadiazole (III<sub>f</sub>)** was synthesized from 0.8 g (4.0 mmol) of compound **If** and 0.7 g (6.0 mmol) of chloroacetyl chloride in 5 ml of toluene. Yield 0.4 g (41%), mp 144–145°C (from ethanol). <sup>1</sup>H NMR spectrum, δ, ppm: 5.09 s (2H, CH<sub>2</sub>), 7.52–8.18 m (5H, C<sub>6</sub>H<sub>5</sub>), 8.62 s (1H, CH, triazole). Found, %: C 50.02; H 3.15; N 26.07. C<sub>11</sub>H<sub>8</sub>ClN<sub>5</sub>O. Calculated, %: C 50.47; H 3.05; N 26.76.

**2-Azidomethyl-5-chloromethyl-1,3,4-oxadiazole (III<sub>g</sub>)** was synthesized from 1.0 g (8.0 mmol) of 5-azidomethyltetrazole (**Ig**) and 2.0 g (17.0 mmol) of chloroacetyl chloride in 5 ml of toluene (1.5 h at 90–95°C). The mixture was treated for 20 min with a saturated solution of sodium hydrogen carbonate and was extracted with ethyl acetate. The extract was evaporated, and the residue was carefully distilled under reduced pressure (0.5 mm) to isolate 0.2 g of an oily substance. The still residue vigorously decomposed. IR spectrum, ν, cm<sup>-1</sup>: 2120 (N<sub>3</sub>), 825 (C–Cl), 970 (C=N). <sup>1</sup>H NMR spectrum, δ, ppm: 4.17 s (2H, CH<sub>2</sub>Cl), 4.47 s (2H, CH<sub>2</sub>N<sub>3</sub>). Found, %: C 28.45; H 2.53; N 39.24. C<sub>4</sub>H<sub>4</sub>ClN<sub>5</sub>O. Calculated, %: C 27.66; H 2.30; N 40.34.

**1,2-Bis(2-chloromethyl-1,3,4-oxadiazol-5-yl)ethane (III<sub>h</sub>)** was synthesized from 3 g (18.0 mmol) of compound **IVa** and 5.6 g (50.0 mmol) of chloroacetyl chloride. Yield 3.75 g (79%), mp 98–99°C. IR spectrum, ν, cm<sup>-1</sup>: 1085 (C–O), 975 (C=N), 675 (C–Cl). <sup>1</sup>H NMR spectrum, δ, ppm: 4.90 s (4H, 2CH<sub>2</sub>), 3.47 (4H, CH<sub>2</sub>CH<sub>2</sub>). Found, %: C 36.72; H 3.40; N 21.83. C<sub>8</sub>H<sub>8</sub>Cl<sub>2</sub>N<sub>4</sub>O<sub>2</sub>. Calculated, %: C 36.50; H 3.04; N 21.29.

**1,4-Bis(2-chloromethyl-1,3,4-oxadiazol-5-yl)benzene (III<sub>i</sub>)**. A mixture of 3 g (14.0 mmol) of compound **IVb** and 6.3 g (55.8 mmol) of chloroacetyl chloride in 10 ml of toluene was heated for 5 h at 90–100°C. When the initial bis-tetrazole disappeared (TLC), the mixture was treated with a saturated solution of sodium hydrogen carbonate, the precipitate was filtered off, the filtrate was extracted with ethyl acetate, the extract was combined with the precipitate, the solvent was removed under reduced pressure, and the residue was recrystallized from ethanol. Yield 3.2 g (73%), mp 195–197°C (from ethanol). IR spectrum, ν, cm<sup>-1</sup>: 1090 (C–O), 970 (C=N), 680 (C–Cl). <sup>1</sup>H NMR

spectrum, δ, ppm: 5.07 s (4H, 2CH<sub>2</sub>), 8.30 s (4H, C<sub>6</sub>H<sub>4</sub>). Found, %: C 46.72; H 2.63; N 18.37. C<sub>12</sub>H<sub>8</sub>N<sub>4</sub>Cl<sub>2</sub>O<sub>2</sub>. Calculated, %: C 46.30; H 2.57; N 18.00.

**1(2)-(5-Azidomethyl-1,3,4-oxadiazol-2-ylmethyl)-1,2,3-benzotriazole (Vd)**. A suspension of 2.4 g (10.0 mmol) of chloromethylloxadiazole **III<sub>d</sub>**, 0.8 g (12.0 mmol) of sodium azide, and 0.2 g of BTEAC in 10 ml of water was heated for 2 h at 90°C under vigorous stirring. The mixture was cooled and extracted with ethyl acetate, the extract was dried over CaCl<sub>2</sub>, the solvent was distilled under reduced pressure, and the residue was recrystallized from ethanol. Yield 0.6 g (27%), mp 104–106°C. IR spectrum, ν, cm<sup>-1</sup>: 2110 (N<sub>3</sub>), 970 (C=N). <sup>1</sup>H NMR spectrum, δ, ppm: 1-substituted isomer: 4.91 s (2H, CH<sub>2</sub>), 6.38 s (2H, CH<sub>2</sub>), 7.45–8.04 m (4H, C<sub>6</sub>H<sub>4</sub>); 2-substituted isomer: 6.36 s (2H, CH<sub>2</sub>), 7.48–7.86 m (4H, C<sub>6</sub>H<sub>4</sub>).

**Dimethyl 1-(5-phenyl-1,3,4-oxadiazol-2-ylmethyl)-1,2,3-triazole-4,5-dicarboxylate (VII<sub>a</sub>)**. A solution of 1.4 g (7.0 mmol) of azide **Ilg** and 1.0 g (7.0 mmol) of dimethyl acetylenedicarboxylate (**VIa**) in 10 ml of ethanol was heated for 2 h under reflux (until the initial azide disappeared according to the TLC data). The solvent was evaporated in air, and the residue was recrystallized from alcohol. Yield 1.6 g (67%), mp 98–100°C (from ethanol). IR spectrum, ν, cm<sup>-1</sup>: 1720 (C=O), 1590 (C–C<sub>arom</sub>). <sup>1</sup>H NMR spectrum, δ, ppm: 3.93 s and 3.97 s (3H each, CH<sub>3</sub>O), 6.35 (2H, CH<sub>2</sub>), 7.62–8.03 m (5H, C<sub>6</sub>H<sub>5</sub>). Found, %: C 52.63; H 3.45; N 20.75. C<sub>15</sub>H<sub>13</sub>N<sub>3</sub>O<sub>5</sub>. Calculated, %: C 52.47; H 3.79; N 20.40.

**4-(Imidazol-1-ylmethyl)-1-(5-phenyl-1,3,4-oxadiazol-2-ylmethyl)-1,2,3-triazole (VII<sub>b</sub>)** was synthesized from 1.0 g (5.0 mmol) of azide **Ilg** and 0.6 g (6.0 mmol) of 1-(prop-2-ynyl)imidazole (**VIb**) in 10 ml of ethanol. Yield 0.5 g (34%), mp 147–150°C. <sup>1</sup>H NMR spectrum, δ, ppm: 4.85 s (2H, CH<sub>2</sub>), 6.22 s (2H, CH<sub>2</sub>), 6.90–8.23 (3H, CH, imidazole), 7.60–8.05 m (5H, C<sub>6</sub>H<sub>5</sub>). Found, %: C 56.83; H 4.63; N 33.05. C<sub>15</sub>H<sub>13</sub>N<sub>7</sub>O. Calculated, %: C 58.63; H 4.23; N 31.92.

**Bis[1-(5-phenyl-1,3,4-oxadiazol-2-ylmethyl)-1,2,3-triazol-4-ylmethyl] terephthalate (VII<sub>d</sub>)** was synthesized from 1.0 g (5.0 mmol) of azide **Ilg** and 0.4 g (2.0 mmol) of acetylenic diester **VI<sub>d</sub>** in 15 ml of ethanol. Yield 0.34 g (11%), mp 141°C. <sup>1</sup>H NMR spectrum, δ, ppm: 5.5 s (4H, 2CH<sub>2</sub>), 6.2 s (4H, 2CH<sub>2</sub>O), 7.4–8.2 m (10H, 2C<sub>6</sub>H<sub>5</sub>; 4H, C<sub>6</sub>H<sub>4</sub>), 8.4 s (2H, CH, triazole). Found, %: C 58.39; H 3.75; N 22.80. C<sub>32</sub>H<sub>24</sub>N<sub>10</sub>O<sub>6</sub>. Calculated, %: C 59.62; H 3.72; N 21.72.

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