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# Synthesis of Polynuclear Nonfused Azoles

**O. N. Verkhozina, V. N. Kizhnyaev, L. I. Vereshchagin, A. V. Rokhin, and A. I. Smirnov**

*Institute of Petrochemical and Coal-Chemical Synthesis, Irkutsk State University, ul. Lermontova 126, P.O. Box 4020, Irkutsk, 664033 Russia*
*e-mail: kizhnyaev@chem.isu.ru*

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**Abstract**—Polynuclear blocks consisting of nonfused heterocycles of the azole series, connected through methylene bridges, were synthesized by successive addition of azole units via cycloaddition of organic azides to the triple bond of *N*-(2-propynyl)azoles, as well as via reaction of azide ion at the cyano group of cyanomethylazoles. Initial *N*-(2-propynyl)azoles were prepared by reaction of 2-propynyl bromide with 1,2,3-triazoles, benzotriazole, and tetrazoles; cyanomethylazoles were obtained by alkylation of azoles with chloroacetonitrile. An analogous scheme was used to add heterocyclic units to 2-phenyl-1,2,3-triazole-4-carbonitrile. In this case, the first two heterocyclic units are linked through the ring carbon atom.

The chemistry of polynuclear systems has been reviewed in [1] in sufficient detail. We previously demonstrated [2] the possibility of synthesizing nonfused polynuclear triazole- and tetrazole-containing systems. In continuation of these studies, in the present work we examined a version of synthesis of nonfused polynuclear blocks consisting of heterocyclic units of the azole series, which are linked through methylene bridges. The procedure is based on alkylation of azoles with 2-propynyl bromide or chloroacetonitrile, followed by cycloaddition of organic or inorganic azides to the triple bond of the alkylation product. As a result, an additional triazole or tetrazole ring is built up.

For this purpose, a number of *N*-(2-propynyl)- and *N*-cyanomethylazoles were synthesized. As a rule, the alkylation was performed with preliminarily prepared potassium or sodium salts of azoles. Despite some similarity of the alkylation processes, the reactions with different azoles required different conditions. 4-Nitro-*N*-(2-propynyl)-1,2,3-triazole (**Ia**) was obtained from 2-propynyl bromide and 4-nitro-1,2,3-triazole (**IIa**) potassium salt. By contrast, the alkylation of 5-phenyltetrazole (**IIb**) and benzotriazole (**IIc**) with 2-propynyl bromide was more successful than the corresponding triethylammonium salts were used. The reaction gives a mixture of isomeric products. In some cases, we succeeded in isolating particular isomers by fractional crystallization or by column chromatography on aluminum oxide.

Unsuccessful attempts to effect cyanomethylation of unsubstituted tetrazole and 5-phenyltetrazole (**IIb**) with chloroacetonitrile were reported previously [3]. However, by reaction of ammonium salts of azoles **IIb**, **IIc**, and **III** with chloroacetonitrile we obtained mixtures of isomeric cyanomethylazoles **IVa**, **IVb**, and **V** in satisfactory yields (Scheme 1). In some cases, the fraction of one (minor) isomer was so small that it was lost during the isolation procedure. Nevertheless, some individual isomers were isolated by fractional crystallization or column chromatography.

The $^1$H NMR spectra of 2-propynylazoles **Ia**–**Ic** contain signals at δ 2.6–3.3 ppm from the terminal acetylenic proton. In the δ region 8–9 ppm we observed two signals from protons of the triazole ring in isomer **Ia**. According to the data of [4], the signal from the triazole ring proton of the 1,4-isomer is located in a weaker field than that of the corresponding 1,5-isomer. The chemical shifts of the methylene protons in both propynyl- and cyanomethylazoles range from 5.5 to 6.5 ppm; these protons appear as two signals from isomeric azoles.

4-Phenyl-1,2,3-triazol-1-ylacetonitrile (**VI**) was synthesized by cycloaddition of azidoacetonitrile (**VII**) to phenylacetylene. It should be noted that the IR spectra of all prepared *N*-cyanomethylazoles, regardless of the position of the cyanomethyl group, lack absorption band typical of the C≡N bond. The spectral pattern does not change in going to nonpolar

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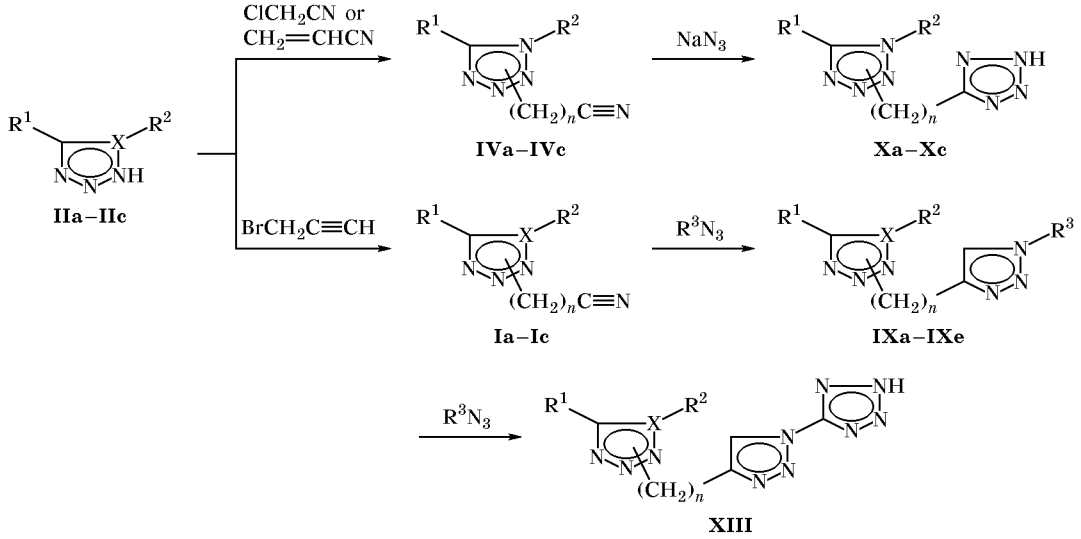
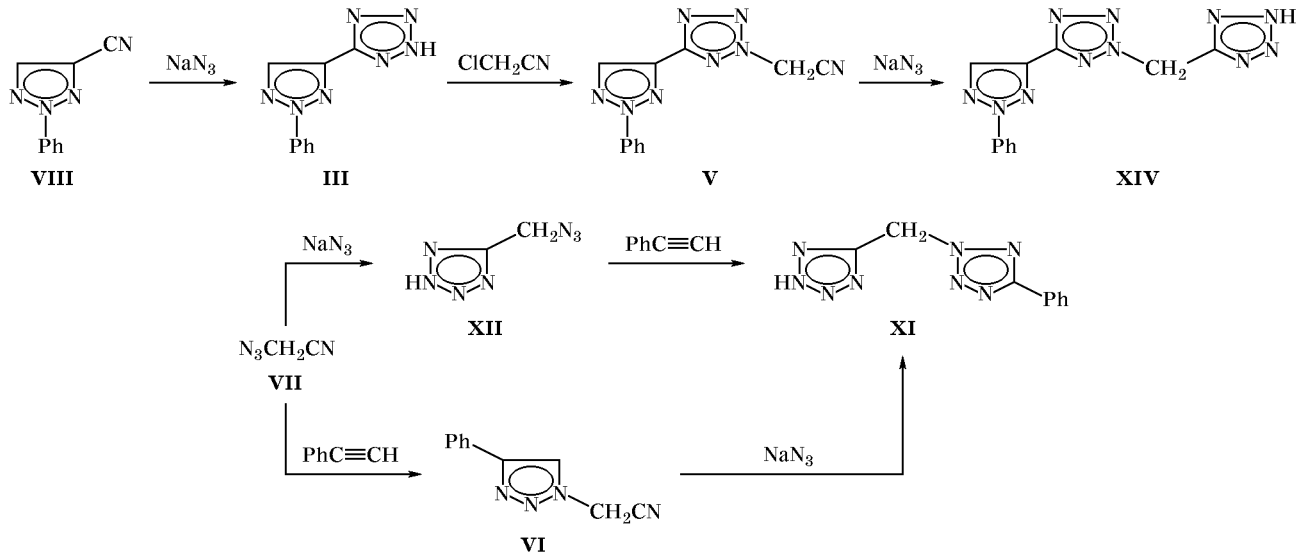
**Scheme 1.**




**I**, **II**, $XR^2$ = CH, $R^1$ = $NO_2$ (**a**); $XR^2$ = N, $R^1$ = Ph (**b**); X = C, $R^1R^2$ = benzo (**c**); **IV**, $XR^2$ = N, $R^1$ = Ph, *n* = 1 (**a**), X = C, $R^1R^2$ = benzo, *n* = 1 (**b**); $XR^2$ = N, $R^1$ = Ph, *n* = 2 (**c**); **IX**, $XR^2$ = CH, $R^1$ = $NO_2$, $R^3$ = Ph (**a**); $XR^2$ = CH, $R^1$ = $NO_2$, $R^3$ = Bzl (**b**); X = C, $R^1R^2$ = benzo, $R^3$ = Bzl (**c**); $XR^2$ = N, $R^1$ = Ph, $R^3$ = $CH_2CN$ (**d**); $XR^2$ = N, $R^1$ = Ph, $R^3$ = Bzl (**e**); **XIII**, $XR^2$ = N, $R^1$ = Ph.

**Scheme 2.**




solvents, though the $^{13}C$ NMR spectra contain the corresponding carbon signal. On the other hand, the IR spectra of compounds where the cyano group is attached to carbon atom, e.g., as in 2-phenyl-1,2,3-triazole-4-carbonitrile (**VIII**), or is separated from the ring by two methylene groups, as in 3-(5-phenyltetrazol-2-yl)propionitrile (**IVc**), contain a strong absorption band at 2250 $cm^{-1}$, which belongs to the cyano group. Presumably, this is the result of prototropic rearrangement like $CH_2-C\equiv N \rightleftarrows CH=C=NH$ in the *N*-cyanomethyl fragment. In any case, this problem requires additional study. Polynuclear blocks were built up by successive addition of azole units via cycloaddition of an organic azide to the triple bond of *N*-(2-propynyl)azoles **Ia**–**Ic**, as well as via reaction of sodium azide at the C≡N bond of cyanoazoles **IV**–**VI**, **VIII**, and **IXd** (Schemes 1, 2). The reactions of azides with propynylazoles were carried out in boiling ethanol or toluene. The products were compounds **IXa**–**IXe** whose molecules consist of two

heterorings bridged by a methylene group. Depending on the initial propynylazole, structures containing two triazole rings (compounds **IXa**–**IXc**) and two different heterocycles (**III**, **Xa**, **XI**) were obtained. The addition of 5-azidomethyltetrazole (**XII**) to phenylacetylene afforded 5-(4-phenyl-1,2,3-triazol-1-ylmethyl)tetrazole (**XI**). Propynylazole **Ib** reacted with azidoacetonitrile (**VII**) to give 2-[4-(5-phenyltetrazol-2-ylmethyl)-1,2,3-triazol-1-yl]acetonitrile (**IXd**). The presence in the latter of a cyanomethyl group makes it possible to add new azole rings. On the other hand, the reaction of propynylazoles with aromatic azides is a dead end from the veiwpoint of further addition of heterocyclic units. In this case, only bicyclic compounds **IXa**–**IXc** and **IXe** were formed. The products contain no NH moiety; therefore, they cannot be brought into further alkylation. The reaction of sodium or ammonium azide with cyanoazoles **IV**–**VI**, **VIII**, and **IXd** leads to formation of new heterocycles possessing a proton at the ring nitrogen atom. These products are capable of undergoing alkylation, and hence one more heterocyclic unit can be attached to the existing polynuclear block. As a result, we obtained structures **XIII** and **XIV** which include a sequence of three heterocycles.

Initial azidoacetonitrile (**VII**) was synthesized from chloroacetonitrile and sodium azide under conditions of phase-transfer catalysis (in the presence of benzyltriethylammonium chloride). Compound **VII** is a highly inflammable substance which requires careful handling. Azole **XII** was prepared from nitrile **VII** and sodium azide.

## EXPERIMENTAL

The IR spectra were recorded on a Specord M80 instrument from samples dispersed in mineral oil. The $^1$H and $^{13}$C NMR spectra were recorded on a Bruker VXR-500S spectrometer at 500 and 125.6 MHz, respectively 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) as eluent; spots were detected under UV light or by treatment with iodine vapor. Compounds **IVc** [3], **IIa** [5], and **IIb** [2] were synthesized by known methods.

**4(5)-Nitro-1-(2-propynyl)-1,2,3-triazole (Ia).** Potassium hydroxide, 2.5 g (0.044 mol), was added to a solution of 5 g (0.044 mol) of triazole **IIa** in 20 ml of ethanol, the mixture was stirred until it became homogeneous, and 5.24 g (0.044 mol) of 2-propynyl bromide was added. The mixture was heated with stirring for 3 h under reflux and cooled, the precipitate of potassium bromide was filtered off, the solvent was distilled off from the filtrate under reduced pressure, and the residue was recrystallized. By fractional crystallization from ethanol we isolated two isomers in an overall yield of 4.2 g (63%). Light yellow crystals, isomer ratio 1:1. 4-Nitro isomer: mp 110–111°C (from EtOH); 5-nitro isomer: mp 51°C (from EtOH). $^1$H NMR spectrum, δ, ppm: 8.5 s (1H, CH, 4-nitro isomer), 9.1 s (1H, CH, 5-nitro isomer), 5.5 s (2H, $CH_2$), 3.3 s (1H, CH). IR spectrum, ν, cm$^{-1}$: 3260 (C–H); 2100 (C–C); 1560, 820 ($NO_2$). Found, %: C 40.12; H 2.50; N 36.75. $C_5H_4N_4O_2$. Calculated, %: C 39.5; H 2.63; N 36.8.

**5-Phenyl-1(2)-(2-propynyl)tetrazole (Ib).** A solution of 10.2 g (0.07 mol) of tetrazole **IIb** and 7.6 g (0.075 mol) of triethylamine in 20 ml of acetone was stirred for 30 min at room temperature, 8.9 g (0.075 mol) of 2-propynyl bromide in 7 ml of acetone was added, and the mixture was stirred for 5–7 h at 20–25°C. The precipitate was filtered off, the solvent was distilled off from the filtrate under reduced pressure, and the residue was distilled in a vacuum. A fraction with bp 135–140°C (1 mm) was collected, 9.8 g (76%). According to the $^1$H NMR data, it contained 53% of 5-phenyl-1-(2-propynyl)tetrazole and 47% of 5-phenyl-2-(2-propynyl)tetrazole. By column chromatography we isolated 2-(2-propynyl) isomer **Ib** with mp 45–47°C (from EtOH). $^1$H NMR spectrum, δ, ppm: 5.36 s (2H, $CH_2$), 2.67 s (1H, CH), 7.6–8.1 m (5H, $H_{arom}$). Found, %: C 65.13; H 4.24; N 30.40. $C_{10}H_8N_4$. Calculated, %: C 65.22; H 4.35; N 30.43.

Following an analogous procedure, oily 1-(2-propynyl)benzotriazole (**Ic**) was synthesized from 5.95 g (0.05 mol) of benzotriazole (**IIc**), 6.06 g (0.06 mol) of triethylamine, and 7.4 g (0.06 mol) of 2-propynyl bromide in 7 ml of benzene. Yield 4.8 g (61%). $^1$H NMR spectrum, δ, ppm: 2.7 s (1H, CH), 5.38 s (2H, $CH_2$), 6.2–7.4 m (4H, $H_{arom}$).

**1-Benzotriazolylacetonitrile (IVb).** A mixture of 21.42 g (0.18 mol) of benzotriazole (**IIc**) and 20.2 g (0.2 mol) of triethylamine in 10 ml of benzene was stirred for 30 min, 15.1 g (0.2 mol) of chloroacetonitrile in 3 ml of benzene was added, and the mixture was heated for 5–7 h under reflux with stirring. The mixture was cooled, the precipitate was filtered off, the solvent was distilled off from the filtrate under reduced pressure, and the residue was recrystallized. We thus obtained a mixture of benzotriazole **IVb** isomers at a ratio of 1:10, which were separated by column chromatography on aluminum oxide of activity grade II using ethyl acetate–hexane (2:3) as eluent. Yield of 1-benzotriazolylacetonitrile (**IVb**) 12.2 g (57%), mp 75–76°C (from EtOH). $^1$H NMR spectrum, δ, ppm: 6.09 s (2H, $CH_2$), 7.5–8.1 m (4H,

$H_{arom}$). Found, %: C 60.54; H 3.75; N 35.29. $C_8H_6N_4$. Calculated, %: C 60.76; H 3.8; N 35.44.

**5-Phenyl-2-tetrazolylacetonitrile (IVa)** was synthesized in a similar way using 7.3 g (0.05 mol) of tetrazole **IIb**, 5 g (0.05 mol) of triethylamine in 30 ml of acetone, and 3.8 g (0.05 mol) of chloroacetonitrile. Yield 5.3 g (57%), mp 75–77°C. $^1$H NMR spectrum, δ, ppm: 6.15 s (2H, $CH_2$), 7.6–8.15 m (5H, $H_{arom}$). $^{13}$C NMR spectrum, $\delta_C$, ppm: 166.54 (CH), 42.25 ($CH_2$). Found, %: C 58.02; H 3.69; N 37.48. $C_9H_7N_5$. Calculated, %: C 58.38; H 3.78; N 37.84.

**Azidoacetonitrile (VII).** Sodium azide, 9.7 g (0.15 mol), and benzyltriethylammonium chloride, 0.5 g, were slowly added with stirring at 20–25°C to a dispersion of 10 g (0.13 mol) of chloroacetonitrile in 20 ml of water. The mixture was heated to 45–50°C, stirred for 3 h, cooled, and extracted with ether (3 × 30 ml). The extract was dried over $CaCl_2$, the solvent was distilled off, and the residue was distilled in a vacuum. Yield 8.1 g (75%), bp 70°C (17 mm), $n_D^{25}$ = 1.4470.

**4-Nitro-1-(1-phenyl-1,2,3-triazol-4-ylmethyl)-1,2,3-triazole (IXa).** A solution of 0.3 g (3 mmol) of *N*-(2-propynyl)triazole **Ia** and 0.48 g (4 mol) of azidobenzene in 4 ml of toluene was heated for 5 h under reflux. The solvent was distilled under reduced pressure, and the residue was recrystallized. Yield 0.22 g (21%), mp 137–138°C (from EtOH). $^1$H NMR spectrum, δ, ppm: 8.8 s (1H, CH in phenyltriazole), 9.5 s (1H, CH in nitrotriazole), 6.0 s (2H, $CH_2$), 7.5–8 m (5H, $H_{arom}$). Found, %: C 49.03; H 3.46; N 35.8. $C_{11}H_9N_7O_2$. Calculated, %: C 48.7; H 3.32; N 36.2.

Compounds **IXb**–**IXe** and **VI** were synthesized in a similar way.

**1-(1-Benzyl-1,2,3-triazol-4-ylmethyl)-4-nitro-1,2,3-triazole (IXb)** was obtained from 1.0 g (7 mmol) of propynyltriazole **Ia** and 1.06 g (8 mmol) of benzyl azide in 5 ml of toluene. Yield 1.05 g (56%), mp 175°C (from EtOH). $^1$H NMR spectrum, δ, ppm: 8.99 s (1H, CH in nitrotriazole), 8.19 s (1H, CH in benzyltriazole), 5.9 s (2H, $CH_2N$), 5.65 s (2H, C**H**$_2$Ph), 7.3–7.4 m (5H, $H_{arom}$). Found, %: C 50.26; H 3.9; N 34.05. $C_{12}H_{11}N_7O_2$. Calculated, %: C 50.53; H 3.85; N 34.39.

**1-(1-Benzyl-1,2,3-triazol-4-ylmethyl)benzotriazole (IXc)** was obtained from 1.77 g (0.01 mol) of propynylbenzotriazole **Ic** and 1.6 g (0.012 mol) of benzyl azide in 15 ml of ethyl acetate. Yield 0.7 g (21%), mp 158–160°C (from EtOH). $^1$H NMR spectrum, δ, ppm: 5.6 s (2H, C**H**$_2$Ph), 6.2 s (2H, $CH_2N$), 7.2–7.4 m (5H, $C_6H_5$). Found, %: C 66.11; H 4.44; N 28.76. $C_{16}H_{14}N_6$. Calculated, %: C 66.21; H 4.83; N 28.97.

**4-(5-Phenyltetrazol-2-ylmethyl)-1,2,3-triazol-1-ylacetonitrile (IXd)** was synthesized from 3.0 g (0.016 mol) of tetrazole (**Ib**) and 1.5 g (0.018 mol) of azidoacetonitrile (**VII**) in 5 ml of ethanol. Yield 2.5 g (59%), mp 105°C (from butyl acetate–hexane, 1 : 1). $^1$H NMR spectrum, δ, ppm: 5.42 s (2H, $CH_2CN$), 5.84 s (2H, $CH_2N$), 7.5–8.34 m (5H, $H_{arom}$), 7.61 s (1H, CH in triazole). Found, %: C 54.12; H 3.70; N 42.15. $C_{12}H_{10}N_8$. Calculated, %: C 54.14; H 3.76; N 42.11.

**2-(1-Benzyl-1,2,3-triazol-4-ylmethyl)-5-phenyltetrazole (IXe)** was prepared from 3.0 g (0.016 mol) of tetrazole **Ib** and 2.4 g (0.018 mol) of benzyl azide in 5 ml of ethanol. Yield 2.7 g (53%), mp 132–133°C (from EtOH). $^1$H NMR spectrum, δ, ppm: 6.6 s (2H, $CH_2N$), 5.65 s (2H, C**H**$_2$Ph), 7.58–7.7 m (5H, $H_{arom}$, benzyl), 7.4–7.6 m (5H, $H_{arom}$), 8.2 s (1H, CH in triazole). Found, %: C 64.12; H 4.48; N 30.87. $C_{17}H_{15}N_7$. Calculated, %: C 64.35; H 4.73; N 30.91.

**4-Phenyl-1,2,3-triazol-1-ylacetonitrile (VI)** was synthesized from 2.0 g (0.0196 mol) of phenylacetylene and 1.6 g (0.0196 mol) of azidoacetonitrile (**VII**) in 10 ml of toluene. The $^1$H NMR spectrum of the product contained signals from two isomers at a ratio of 1 : 10. By fractional crystallization we succeeded in isolating 4-phenyl-1,2,3-triazol-1-ylacetonitrile. Yield 1.5 g (42%), mp 69–71°C. $^1$H NMR spectrum, δ, ppm: 5.71 s (2H, $CH_2$), 7.6–7.8 m (5H, $H_{arom}$), 7.87 s (1H, CH in triazole). Found, %: C 65.13; H 4.41; N 30.27. $C_{10}H_8N_4$. Calculated, %: C 65.22; H 4.35; N 30.43.

**1-(Tetrazol-5-ylmethyl)benzotriazole (Xb).** A suspension of 0.65 g (0.01 mol) of sodium azide in 10 ml of DMF was heated for 30 min at 100–105°C under stirring. It was then cooled to 40–50°C, 1.1 g (0.010 mol) of diethylamine hydrochloride was added, the mixture was stirred for 30 min, 1.26 g (8 mmol) of benzotriazole **IVb** was added, and the mixture was stirred for 4–5 h at 110–115°C, cooled, and poured into 50 ml of cold water. The aqueous solution was washed with ether and acidified to pH 2–3 with dilute hydrochloric acid. The precipitate was filtered off, washed with cold water, and recrystallized. Yield 1.4 g (87%), mp 196°C (from EtOH). $^1$H NMR spectrum, δ, ppm: 6.45 s (2H, $CH_2$), 7.5–7.6 m (4H, $H_{arom}$). Found, %: C 47.67; H 3.62; N 48.61. $C_8H_7N_7$. Calculated, %: C 47.76; H 3.48; N 48.76.

Compounds **III**, **Xa**, **Xc**, **XI** (method *a*), and **XIII** were synthesized in a similar way.

**5-(2-Phenyl-1,2,3-triazol-4-yl)tetrazole (III)** was obtained from 1.09 g (6 mmol) of triazole **VIII**, 0.78 g (0.012 mol) of sodium azide, and 0.64 g (0.012 mol) of ammonium chloride in 5 ml of DMF. Yield 1.1 g (83%), mp 214–215°C (from EtOH). $^1$H NMR spectrum, δ, ppm: 8.59 s (1H, CH in triazole), 7.5–8.1 m (5H, $H_{arom}$). Found, %: C 50.57; H 3.13; N 46.21. $C_9H_7N_7$. Calculated, %: C 50.70; H 3.29; N 46.01.

**4-(5-Phenyltetrazol-2-ylmethyl)-1-(tetrazol-5-yl)-1,2,3-triazole (XIII)** was synthesized from 0.27 g (4 mmol) of sodium azide, 0.46 g (4 mmol) of diethylamine hydrochloride, and 0.98 g (4 mmol) of compound **IXd** in 5 ml of DMF. Yield 0.91 g (79%), mp 164–166°C (from EtOH). $^1$H NMR spectrum, δ, ppm: 6.08 s (2H, $CH_2N_{triazole}$), 6.13 s (2H, $CH_2N_{tetrazole}$), 8.47 s (1H, CH in triazole), 7.6–8.1 m (5H, $H_{arom}$). Found, %: C 46.54; H 3.47; N 49.75. $C_{12}H_{11}N_{11}$. Calculated, %: C 46.60; H 3.56; N 49.84.

**5-Phenyl-2-[2-(tetrazol-5-yl)ethyl]tetrazole (Xc)** was synthesized from 5 g (0.025 mol) of tetrazole **IVc**, 2.44 g (0.038 mol) of sodium azide, and 4.2 g (0.038 mol) of diethylamine hydrochloride in 20 ml of DMF. Yield 3.2 g (49%), mp 143–144°C (from EtOH). $^1$H NMR spectrum, δ, ppm: 5.27 t (2H, $CH_2N$), 3.85 t (2H, $CH_2C$), 7.5–8.3 m (5H, $H_{arom}$). Found, %: C 49.67; H 4.02; N 46.12. $C_{10}H_{10}N_8$. Calculated, %: C 49.59; H 4.13; N 46.28.

**5-Phenyl-2-(tetrazol-5-ylmethyl)tetrazole (Xa)** was synthesized from 2.1 g (0.01 mol) of tetrazole **IVa**, 0.78 g (0.012 mol) of sodium azide, and 1.3 g (0.012 mol) of diethylamine hydrochloride in 10 ml of DMF. Yield 1.92 g (79% ), mp 178–179°C (from EtOH). $^1$H NMR spectrum, δ, ppm: 5.8 s (2H, $CH_2$), 7.5–8.3 m (5H, $H_{arom}$), 14 (1H, NH). Found, %: C 47.15; H 3.41; N 49.07. $C_9H_8N_8$. Calculated, %: C 47.37; H 3.51; N 49.12.

**4-Phenyl-1-(tetrazol-5-ylmethyl)-1,2,3-triazole (XI).** *a*. Compound **XI** was synthesized from 7.3 g (0.039 mol) of triazole **VI**, 3.0 g (0.045 mol) of sodium azide, and 5 g (0.045 mol) of diethylamine hydrochloride in 25 ml of DMF. Yield 7.84 g (87%), mp 173–174°C (from EtOH). $^1$H NMR spectrum, δ, ppm: 6.05 s (2H, $CH_2$), 7.8 s (1H, CH in triazole), 7.5–7.6 m (5H, $H_{arom}$). Found, %: C 52.69; H 4.03; N 43.11. $C_{10}H_9N_7$. Calculated, %: C 52.86; H 3.96; N 43.17.

*b*. A solution of 2.5 g (0.02 mol) of 5-azidomethyltetrazole (**XII**) and 6.12 g (0.06 mol) of phenylacetylene in 10 ml of ethanol was kept for 2 days at 80°C. The solvent was distilled off under reduced pressure, and the residue was recrystallized. Yield 2.3 g (50.6%), mp 173–174°C (from EtOH).

**5-(2-Phenyl-1,2,3-triazol-4-yl)-2-(tetrazol-5-ylmethyl)tetrazole (XIV).** Triethylamine, 0.56 g (5 mmol), was added with stirring to a solution of 1.07 g (5 mmol) of compound **III** in 6 ml of acetone; after 30 min, 0.4 g (5 mmol) of chloroacetonitrile in 2 ml of acetone was added. The mixture was heated for 2 days under reflux and cooled, the precipitate was filtered off, and the filtrate was evaporated under reduced pressure. A suspension of 0.195 g (3 mmol) of sodium azide and 0.19 g (3 mmol) of ammonium chloride in 5 ml of DMF was added to the residue (0.7 g), and the mixture was stirred for 5 h at 110°C, poured into 50 ml of cold water, washed with ether, and acidified to pH 2–3 with dilute hydrochloric acid. The precipitate was filtered off, washed with cold water, and recrystallized. Yield 0.59 g (72%), mp 182°C (from EtOH). $^1$H NMR spectrum, δ, ppm: 6.54 s (2H, $CH_2$), 8.5 s (1H, CH in triazole), 7.5–7.6 m (5H, $H_{arom}$). Found, %: C 44.68; H 3.11; N 52.25. $C_{11}H_9N_{11}$. Calculated, %: C 44.75; H 3.05; N 52.20.

**5-Azidomethyltetrazole (XII).** A solution of 1.96 g (0.024 mol) of azidoacetonitrile (**VII**) in 2 ml of DMF was added to a suspension of 1.95 g (0.03 mol) of sodium azide and 3.3 g (0.03 mol) of diethylamine hydrochloride in 10 ml of DMF, which was prepared as described avobe. The mixture was carefully heated (a sharp temperature rise with tarring is possible). For this purpose, the mixture was maintained at 50–55°C over a period of 30 min using a cold water bath. The cooling bath was removed, and the mixture sharply warmed up to 105–110°C. It was kept for 1 h at 100°C, cooled, washed with ether, and acidified to pH 2–3 with dilute hydrochloric acid. Yield 1.9 g (64%), mp 56°C (from EtOH). $^1$H NMR spectrum, δ, ppm: 4.91 s (2H, $CH_2$). $^{13}$C NMR spectrum, $\delta_C$, ppm: 44.9 ($CH_2$), 157.5 (NCN). Found, %: C 18.84; H 2.21; N 78.56. $C_2H_3N_7$. Calculated, %: C 19.2; H 2.4; N 78.4.

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