ISSN 1070-4280, Russian Journal of Organic Chemistry, 2013, Vol. 49, No. 1, pp. 130–137. © Pleiades Publishing, Ltd., 2013.
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Dedicated to Full Member of the Russian Academy of Sciences
G.A. Tolstikov on his 80th anniversary

Synthesis of Polynuclear Azoles Linked by Ether Tethers

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Received April 24, 2012

Abstract—Alkylation of NH-triazoles and tetrazoles and cycloaddition of organic and inorganic azides to propargyl ethers bearing a cyano group gave a number of polynuclear heterocyclic systems bridged by ether tethers.

DOI: 10.1134/S1070428013010223

We previously [1–4] synthesized non-fused polynuclear triazole- and tetrazole-containing systems bridged by methylene, carbamate, and urea fragments. In continuation of studies in this field, in the present work we examined a synthetic approach to polynuclear blocks in which azole rings are linked through ether tethers. For this purpose, we used 1,3-dipolar cycloaddition of organic and inorganic azides to ethers containing cyano groups and in some cases triple carbon–carbon bond.

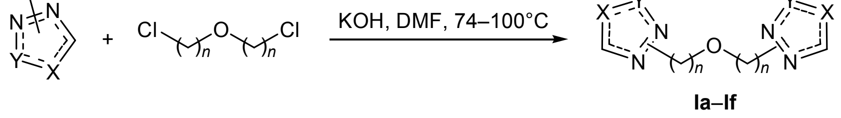
A classical version of synthesis of bis-azolyl ethers is based on reaction of potassium triazolate or tetrazolate with dihaloalkanes. The alkylation of triazoles and tetrazole with bis(chloromethyl) and bis(2-chloroethyl) ethers resulted in the formation of mixtures of regioisomeric bis-triazoles and bis-tetrazoles **Ia**–**If**, which were difficult to separate (Scheme 1). By column chromatography we succeeded in isolating N^1- and N^2-substituted isomers, the major products (~85%) being those alkylated at N^1.

In the ^1H NMR spectra of **Ia**, **Ic**, and **If** we observed signals from protons in the azole rings at δ 7.8–8.4, 7.6–8.2, and 8.6–9.2 ppm, respectively. The spectra of azoles **Ib**, **Id**, and **Ie** derived from bis(2-chloroethyl) ether contained signals at δ 7.9–8.1, 7.3–7.6, and 8.4–8.7 ppm. Signals from the bridging methylene groups were located at δ 5.5–6.4 (NCH_2O), 4.1–4.6 ($NC\mathbf{H}_2CH_2O$), and 3.7–4.2 ppm ($NCH_2C\mathbf{H}_2O$). N^1-Substituted isomers of the triazole series were identified on the basis of the ^1H NMR data. The presence of two different signals from the CH protons in the triazole rings of **Ia**–**Id** indicated formation of just N^1-substituted structures; the CH protons in N^2- and N^4-substituted isomers are equivalent due to symmetric structure of the azole ring. Tetrazoles **Ie** and **If** were assigned the structure of N^1-isomers on the basis of published data [5].

The above approach to bis-azolyl ethers is not free from disadvantages. In particular, the yields did not exceed 54%, and only N-substituted derivatives can be obtained in such a way. However, the most interesting are compounds possessing unsubstituted NH group which ensures their subsequent modifications and determines some specificity of their physical properties.

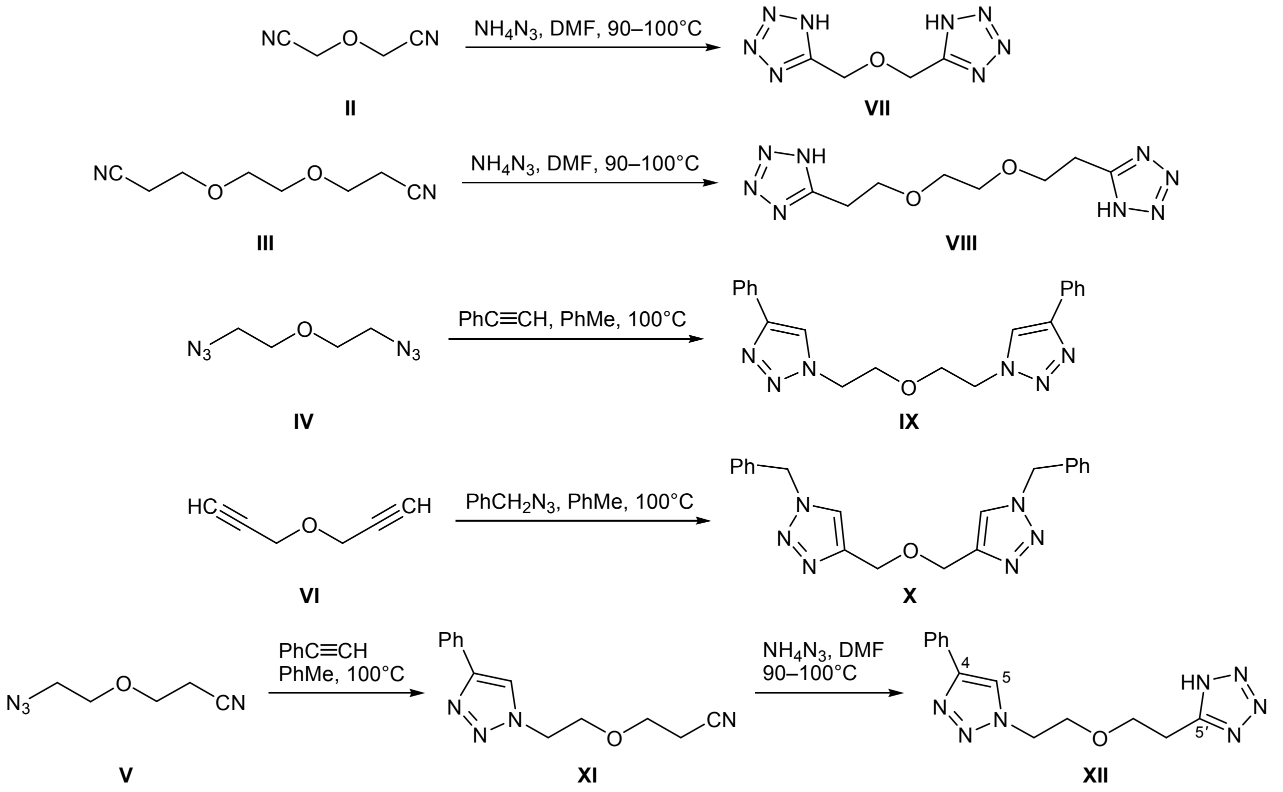
Therefore, we tried another approach to polynuclear azoles. It is based on the transformation of terminal functional groups in initial ethers into heterocyclic structures. Appropriate initial compounds are nitriles **II**

Scheme 1.



X = N, Y = CH, *n* = 1 (**a**), 2 (**b**); X = CH, Y = N, *n* = 1 (**c**), 2 (**d**); X = Y = N, *n* = 2 (**e**), 1 (**f**).

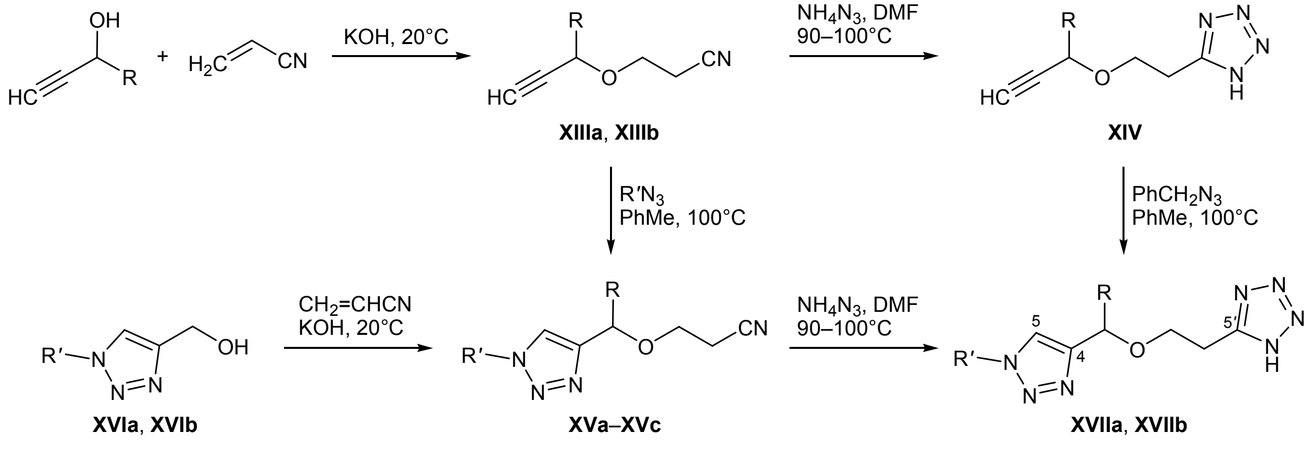
Scheme 2.



and **III**, bis-azide **IV**, azido nitrile **V**, and dipropargyl ether (**VI**) (Scheme 2). Dinitriles **II** and **III** were heated with ammonium azide to obtain tetrazolyl-substituted ethers **VII** and **VIII**, respectively. Bis(2-azidoethyl) ether (**IV**) reacted with phenylacetylene to give bis[2-(4-phenyl-1*H*-1,2,3-triazol-1-yl)ethyl] ether (**IX**). Addition of two benzyl azide molecules to bis(prop-2-yn-1-yl) ether (**VI**) afforded bis[2-(1-benzyl-1*H*-1,2,3-triazol-4-yl)ethyl] ether (**X**). 3-(2-Azidoethoxy)propanenitrile (**V**) reacted with phenylacetylene at the azido group, yielding 3-[2-(4-phenyl-1*H*-1,2,3-triazol-1-yl)ethoxy]propanenitrile (**XI**), and heating of the latter with ammonium azide led to the formation of ether **XII** containing both triazole and tetrazole rings.

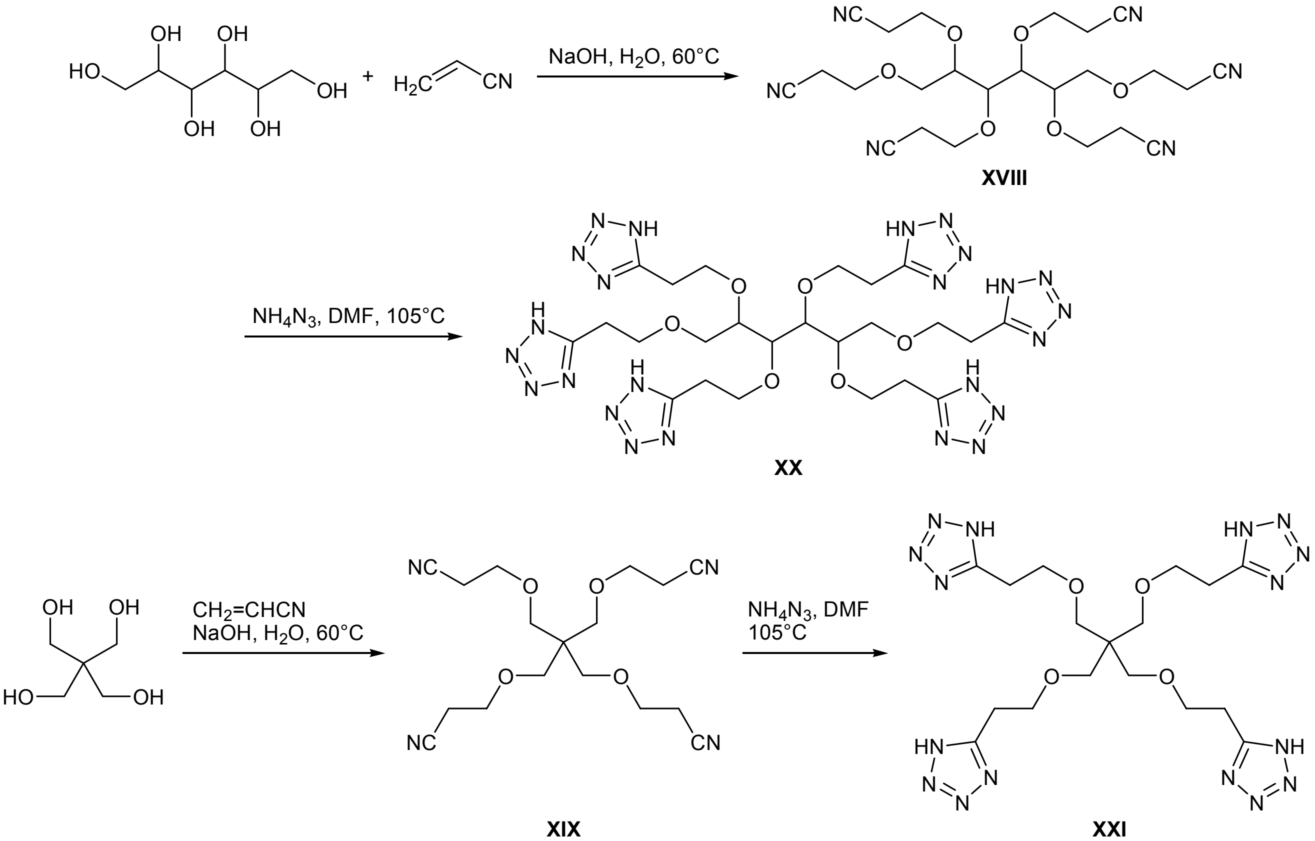
Acetylenic cyanoethyl ethers **XIIIa** and **XIIIb** occupy a specific place in the series of dipolarophiles.

Scheme 3.



XIII, R = H (**a**), Ph (**b**); **XV**, R = H, R′ = PhCH$_2$ (**a**), 1,2,4-triazol-3-yl (**b**); R = Ph, R′ = 1,2,4-triazol-3-yl (**c**);
XVI, **XVII**: R′ = PhCH$_2$ (**a**), 1,2,4-triazol-3-yl (**b**).

Scheme 4.



They were used as starting compounds to obtain bis-azoles with different heterocycles via the known cyanoethylation of acetylenic alcohols [6]. The presence of an ether moiety, triple carbon–carbon bond, and cyano group in a single molecule makes it possible to synthesize polynuclear structures with various combinations of triazole and tetrazole rings and extends their synthetic potential.

Prop-2-yn-1-ol and 1-phenylprop-2-yn-1-ol reacted with acrylonitrile under solvent-free conditions (Scheme 3). It is advisable to add acrylonitrile to a mixture of acetylenic alcohol and alkali. The reverse order of addition of the reactants favors formation of a considerable amount of acrylonitrile polymerization products. We examined two versions of synthesis of non-fused polycyclic azole systems. The first of these included cycloaddition of organic azides, namely benzyl azide and 3-azido-1,2,4-triazole, to the triple C≡C bond of cyanoethyl ethers **XIIIa** and **XIIIb** with formation of 1,2,3-triazole derivatives **XVa**–**XVc**. Compounds **XVa** and **XVb** were also synthesized independently by cyanoethylation of triazolylmethanols **XVIa** and **XVIb**. The subsequent reaction of triazole-containing cyanoethyl ethers **XVa**–**XVc** with ammonium azide at the cyano group gave bis-azoles **XVIIa** and **XVIIb**.

Following the second version, cyanoethyl ether **XIIIa** reacted with ammonium azide to give tetrazole derivative **XIV**, and reaction of the latter at the acetylenic bond with benzyl azide produced tetrazole–triazole system **XVII**. However, the initial reaction with ammonium azide to obtain compound **XIV** is impractical, for the acetylenic ether fragment in **XIIIa** decomposes under fairly severe conditions, and the yield of **XIV** does not exceed 20%.

We also used as dipolarophiles poly(cyanoethyl) ethers prepared by cyanoethylation of sorbitol and pentaerythritol (Scheme 4). These polyols are soluble in water, and they readily reacted with acrylonitrile to produce the corresponding poly(cyanoethyl) ethers **XVIII** and **XIX**. Compounds **XVIII** and **XIX** were isolated as powders, and their reaction with ammonium azide in dimethylformamide at 100–105°C afforded polytetrazolyl-substituted branched ethers **XX** and **XXI**. The products were colorless powders soluble in aqueous alkali, highly donor solvents, aqueous–organic mixtures (acetone, acetonitrile–water), and aqueous solutions of strong mineral acids and some inorganic salts (thiocyanates, iodides, perchlorates). The structure of the isolated compounds was proved by their NMR and IR spectra and elemental analyses.

EXPERIMENTAL

The IR spectra were obtained on an Infralum FT-801 spectrometer from samples dispersed in mineral oil or pelleted with KBr. The ^{1}H and ^{13}C NMR spectra were recorded on a Varian VXR-500s spectrometer from solutions in acetone-d_6 (^{1}H, 500 MHz) or DMSO-d_6 (^{13}C, 126 MHz) using the residual proton and carbon signals of the solvent as reference (δ 2.1, 2.6 ppm; δ_C 29.5, 39.5 ppm); the ^{13}C NMR spectra were recorded without decoupling from protons. The elemental compositions were determined on a FLASH EA 1112 Series CHN analyzer. The progress of reactions was monitored by TLC on Silufol UV-254 plates using ethyl acetate–hexane (3:2) as eluent; spots were visualized by treatment with iodine vapor.

The N^1-substituted isomers of **Ia**–**If** were isolated by column chromatography on Al_2O_3 of activity grade II; eluent diethyl ether–petroleum ether, 1:1.

Bis(2-azidoethyl) ether (**IV**) [6], 2-azidoethanol [7], bis(prop-2-yn-1-yl) ether (**VI**) [8], 3-azido-1,2,4-triazole [9], (1-benzyl-1,2,3-triazol-4-yl)- and [1-(1,2,4-triazol-3-yl)-1,2,3-triazol-4-yl]methanols **XVIa** and **XVIb** [10], 2,2′-oxydiacetonitrile (**II**) [11], and 3,3′-[ethane-1,2-diylbis(oxy)]dipropanenitrile (**III**) [12] were synthesized by known methods; their properties were consistent with published data.

1,1′-[Oxybis(methylene)]di(1*H*-1,2,4-triazole) (Ia). Potassium carbonate, 4.9 g (36 mmol), was dispersed in 25 ml of DMF, 5 g (73 mmol) of 1,2,4-triazole was added under stirring, the mixture was stirred for 15–20 min, and 4.1 g (36 mmol) of bis(chloromethyl) ether in 10 ml of DMF was added. The mixture was heated for 1.5 h at 70°C and for 4 h at 100°C. It was then cooled and filtered, the filtrate was evaporated under reduced pressure, the residue was treated with ethyl acetate and neutralized with an aqueous solution of sodium hydrogen carbonate, the organic layer was separated and dried over calcined magnesium sulfate, the solvent was removed by purging with warm air, and the residue was recrystallized from alcohol. Yield 3.5 g (54%), mp 74.5–75°C. IR spectrum, ν, cm^{-1}: 3090 (C–H, Ht), 1155–1100 (C–O–C). ^{1}H NMR spectrum, δ, ppm: 5.5 s (2H, CH_2), 7.5 d (1H, 3-H, J = 1.6 Hz), 8.4 d (1H, 5-H, J = 1.6 Hz). Found, %: C 39.87; H 4.53; N 46.21. $C_6H_8N_6O$. Calculated, %: C 40.00; H 4.48; N 46.65.

1,1′-[Oxybis(ethane-2,1-diyl)]di(1*H*-1,2,4-triazole) (Ib) was synthesized in a similar way from 4.0 g (58 mmol) of 1,2,4-triazole and 4.1 g (29 mmol) of bis(2-chloroethyl) ether. Yield 4.6 g (38%), mp 74.5–75°C. IR spectrum, ν, cm^{-1}: 3100 (C–H, Ht), 1100–1155 (C–O–C). ^{1}H NMR spectrum, δ, ppm: 3.9 t (2H, CH_2O, J = 13 Hz), 4.5 t (2H, CH_2, J = 14 Hz), 7.68 d (1H, 3-H, J = 1.6 Hz), 7.91 d (1H, 5-H, J = 1.6 Hz). Found, %: C 46.32; H 6.15; N 40.03. $C_8H_{12}N_6O$. Calculated, %: C 46.15; H 5.81; N 40.36.

1,1′-[Oxybis(methylene)]di(1*H*-1,2,3-triazole) (Ic). Powdered 85% potassium hydroxide, 16.8 g (0.3 mol), was dispersed in 75 ml of DMF, 20.7 g (0.3 mol) of 1,2,3-triazole was added dropwise at 35–40°C, the mixture was stirred until it became homogeneous, 5 g of anhydrous magnesium sulfate was added, and 11.5 g (0.1 mol) of bis(chloromethyl) ether was added dropwise, maintaining the temperature below 40°C. When the exothermic reaction was over, the mixture was heated for 5–7 h at 95–100°C, cooled, and filtered, the filtrate was evaporated under reduced pressure, and the residue was recrystallized from alcohol. Yield 7.4 g (41%), mp 46–47°C. IR spectrum, ν, cm^{-1}: 3135 (C–H, Ht), 1070–1075 (C–O–C). ^{1}H NMR spectrum, δ, ppm: 5.5 s (2H, CH_2), 7.7 d (1H, 5-H, J = 1.0 Hz), 8.1 d (1H, 4-H, J = 1.0 Hz). Found, %: C 39.70; H 4.41; N 46.21. $C_6H_8N_6O$. Calculated, %: C 40.00; H 4.48; N 46.65.

Compounds **Id**–**If** were synthesized in a similar way.

1,1′-[Oxybis(ethane-2,1-diyl)]di(1*H*-1,2,3-triazole) (Id) was synthesized from 10.35 g (0.15 mol) of 1,2,3-triazole and 7 g (0.05 mol) of bis(2-chloroethyl) ether. Yield 2.4 g (23%); distillation of the product was accompanied by decomposition. IR spectrum, ν, cm^{-1}: 3140 (C–H, Ht), 1070–1075 (C–O–C). ^{1}H NMR spectrum, δ, ppm: 3.9 t (2H, CH_2O, J = 13 Hz), 4.5 t (2H, CH_2, J = 14 Hz), 7.3 d (1H, 5-H, J = 1.0 Hz), 7.5 d (1H, 4-H, J = 1.0 Hz). Found, %: C 46.83; H 5.82; N 39.90. $C_8H_{12}N_6O$. Calculated, %: C 46.15; H 5.81; N 40.36.

1,1′-[Oxybis(ethane-2,1-diyl)]di(1*H*-tetrazole) (Ie) was synthesized from 2.1 g (0.03 mol) of tetrazole and 2.1 g (0.014 mol) of bis(2-chloroethyl) ether. Yield 1.2 g (40%), mp 106°C. IR spectrum, ν, cm^{-1}: 3145 (C–H, Ht), 1100–1075 (C–O–C). ^{1}H NMR spectrum, δ, ppm: 4.0 t (2H, CH_2O, J = 13 Hz), 4.6 t (2H, CH_2, J = 14 Hz), 8.4 s (1H, 5-H). Found, %: C 34.51; H 5.00; N 53.82. $C_6H_{10}N_8O$. Calculated, %: C 34.28; H 4.80; N 53.31.

1,1′-[Oxybis(methylene)]di(1*H*-tetrazole) (If) was synthesized from 2.1 g (0.03 mol) of tetrazole and 1.7 g (0.015 mol) of bis(chloromethyl) ether. Yield 1.1 g (40%), mp 97.5°C. IR spectrum, ν, cm^{-1}: 3090 (C–H, Ht), 1050–1100 (C–O–C). ^1H NMR spectrum, δ, ppm: 6.1 s (2H, CH_2), 9.2 s (1H, 5-H). Found, %: C 26.61; H 3.65; N 61.24. $C_4H_6N_8O$. Calculated, %: C 26.38; H 3.32; N 61.52.

3-(2-Azidoethoxy)propanenitrile (V). Acrylonitrile, 5.8 g (0.11 mol), was added dropwise under vigorous stirring to a mixture of 10 g (0.14 mol) of 2-azidoethanol and 2 g of 45% aqueous KOH, maintaining the temperature below 35°C. The mixture was then stirred for 4 h at room temperature and left overnight. It was neutralized with aqueous HCl, dried over $CaCl_2$, and filtered, and the filtrate was distilled under reduced pressure. Yield 11 g (71%), bp 140°C (2 mm). IR spectrum, ν, cm^{-1}: 2210 (C≡N), 2100 (N_3), 1210 (C–O–C). Found, %: C 42.31; H 5.85; N 39.75. $C_5H_8N_4O$. Calculated, %: C 42.85; H 5.75; N 39.98.

5,5′-[Oxybis(methylene)]di(1*H*-tetrazole) (VII). A solution of 23 g (0.2 mol) of bis(chloromethyl) ether and 16.6 g (0.1 mol) of potassium iodide in 80 ml of ethanol was added dropwise to a solution of 29.4 g (0.6 mol) of sodium cyanide in 30 ml of water. The mixture was stirred for 48 h at 80°C and treated with 100 ml of ethyl acetate, the precipitate was filtered off. the filtrate was dried over calcined $MgSO_4$, the solvent was distilled off, and 50 ml of DMF, 13 g (0.2 mol) of NaN_3, and 10.7 g (0.2 mol) of NH_4Cl were added to the residue under stirring. The mixture was stirred for 10 h at 90–100°C and evaporated under reduced pressure, the residue was treated with ethyl acetate, the aqueous phase was separated, acidified with concentrated hydrochloric acid to pH 2, and extracted with ethyl acetate (4×15 ml), the extracts were dried over $MgSO_4$, and the solvent was removed by purging with warm air. Yield 4.2 g (12%), mp 106°C (from ethanol). IR spectrum, ν, cm^{-1}: 1590 (Ht), 1210 (C–O–C). Found, %: C 26.98; H 3.35; N 60.58. $C_4H_6N_8O$. Calculated, %: C 26.38; H 3.32; N 61.52.

5,5′-[Ethane-1,2-diylbis(oxyethane-2,1-diyl)]di-(1*H*-tetrazole) (VIII). A mixture of 8 g (0.047 mol) of compound **III**, 7.7 g (0.12 mol) of NaN_3, and 6.4 g (0.12 mol) of NH_4Cl in 50 ml of DMF was stirred for 10 h at 90–100°C. The mixture was then evaporated under reduced pressure, the residue was treated with water, acidified with concentrated hydrochloric acid to pH 2, and extracted with ethyl acetate (5×15 ml), the extracts were dried over $MgSO_4$, and the solvent was removed by purging with warm air. Yield 1.8 g (15%), mp 200–205°C (from ethanol). ^{13}C NMR spectrum, δ_C, ppm: 24.7 t (5-CH_2, J_{CH} = 144 Hz), 67.6 t (OCH_2, J_{CH} = 147 Hz), 68.0 t (CH_2CH_2, J_{CH} = 142 Hz), 161.2 s (C^5). Found, %: C 37.87; H 6.09; N 44.57. $C_8H_{14}N_8O_2$. Calculated, %: C 37.79; H 5.55; N 44.07.

1,1′-[Oxybis(ethane-2,1-diyl)]bis(4-phenyl-1*H*-1,2,3-triazole) (IX). A solution of 4.2 g (27 mmol) of diazide **IV** and 5 g (49 mmol) of phenylacetylene in 25 ml of toluene was stirred for 5 h at 100°C. The mixture was evaporated, and the viscous oily residue was crystallized from ethanol. Yield 7 g (72%), mp 171–172°C. ^{13}C NMR spectrum δ_C, ppm: 49.1 t (2C, 1-CH_2, J_{CH} = 143 Hz), 69.3 t (2C, CH_2O, J_{CH} = 140 Hz), 119.3 d (2C, C^5, J_{CH} = 196 Hz), 129.0 s (C^i); 125.7, 128.4, 128.7 d (5C, C^o, C^m, C^p, J_{CH} = 162 Hz), 144.8 s (2C, C^4). Found, %: C 65.91; H 5.85; N 23.97. $C_{20}H_{20}N_6O$. Calculated, %: C 66.65; H 5.59; N 23.32.

Compounds **X** and **XI** were synthesized in a similar way.

4,4′-[Oxybis(methylene)]bis(1-benzyl-1*H*-1,2,3-triazole) (X) was synthesized from 1.88 g (0.02 mol) of dipropargyl ether (**VI**) in 15 ml of toluene and 4.76 g (0.04 mol) of benzyl azide. When the reaction was complete (TLC), the mixture was evaporated, the residue was dissolved in diethyl ether, and the solution was passed through a column charged with aluminum oxide. Yield 7 g (98%), mp 119–120°C. IR spectrum, ν, cm^{-1}: 1600 (Ph), 1580 (Ht), 1200–1100 (C–O–C). ^1H NMR spectrum, δ, ppm: 5.54 t (2H, CH_2), 7.30 (5H, H_{arom}), 8.01 (5-H). Found, %: C 67.00; H 5.85; N 23.08. $C_{20}H_{20}N_6O$. Calculated, %: C 66.65; H 5.59; N 23.32.

3-[2-(4-Phenyl-1,2,3-triazol-1-yl)ethoxy]propanenitrile (XI) was synthesized from 2.8 g (0.02 mol) of azide **V** and 2.55 g (0.025 mol) of phenylacetylene in 15 ml of toluene. Yield 3.3 g (70%), mp 77°C. IR spectrum, ν, cm^{-1}: 2210 (C≡N), 1600 (Ph), 1210 (C–O–C). ^{13}C NMR spectrum, δ_C, ppm: 18.4 t (1C, CH_2CN, J_{CH} = 138 Hz), 49.4 t (1C, 1-CH_2, J_{CH} = 148 Hz), 63.8 t (1C, OCH_2, J_{CH} = 149 Hz), 68.6 t (1C, OCH_2, J_{CH} = 145 Hz), 119.1 s (1C, C≡N), 117.1 d (1C, C^5, J_{CH} = 196 Hz), 129.1 s (1C, C^i); 124.9, 127.8, 128.3 d (5C, C^o, C^m, C^p, J_{CH} = 162 Hz), 144.8 s (1C, C^4). Found, %: C 64.37; H 5.85; N 23.75. $C_{13}H_{14}N_4O$. Calculated, %: C 64.45; H 5.82; N 23.13.

5-{2-[2-(4-Phenyl-1*H*-1,2,3-triazol-1-yl)ethoxy]-ethyl}-1*H*-tetrazole (XII) was synthesized as described above for compound **VIII** from 1 g

(0.015 mol) of NaN_3 and 0.8 g (0.015 mol) NH_4Cl in 15 ml of DMF and 2.5 g (0.01 mol) of **XI**. Yield 1.1 g (39%), mp 172–175°C. IR spectrum, ν, cm^{-1}: 1590 (Ph), 1450–1440 (Ht), 1210–1170 (C–O–C). ^{13}C NMR spectrum, δ_C, ppm: 24.9 t (1C, 5′-CH_2, J_{CH} = 139 Hz), 48.5 t (1C, 1-CH_2, J_{CH} = 141 Hz), 68.1 t (1C, OCH_2, J_{CH} = 145 Hz), 69.1 t (1C, CH_2O, J_{CH} = 149 Hz), 119.1 d (1C, C^5, J_{CH} = 190 Hz), 129.1 s (1C, C^i); 125.8, 128.4, 128.6 d (5C, C^o, C^m, C^p, J_{CH} = 161 Hz), 144.8 s (C^4), 161.3 s ($C^{5'}$). Found, %: C 53.98; H 5.56; N 34.81. $C_{13}H_{15}N_7O$. Calculated, %: C 54.73; H 5.30; N 34.37.

3-[(1-Phenylprop-2-yn-1-yl)oxy]propanenitrile (XIIIa) was synthesized as described above for compound **V** from 14.3 g (0.25 mol) of propargyl alcohol and 13.2 g (0.25 mol) of acrylonitrile. Yield 20 g (73%), bp 130°C (20 mm). ^{13}C NMR spectrum, δ_C, ppm: 17.2 t ($\mathbf{C}H_2CN$, J_{CH} = 136 Hz), 56.7 t (CH_2, J_{CH} = 148 Hz), 63.2 t (OCH_2, J_{CH} = 147 Hz), 75.7 d (H**C**≡C, J_{CH} = 252 Hz), 78.5 d (HC≡**C**, J_{CH} = 46 Hz), 117.9 s (CN). Found, %: C 66.53; H 6.25; N 13.03. C_6H_7NO. Calculated, %: C 66.04; H 6.47; N 12.84.

3-[(1-Phenylprop-2-yn-1-yl)oxy]propanenitrile (XIIIb) was synthesized as described above for compound **V** from 4.5 g (34 mmol) of 1-phenylprop-2-yn-1-ol and 1.8 g (34 mmol) of acrylonitrile using 1 g of 40% aqueous KOH. Yield 2.1 g (33%), bp 175–177°C (2 mm). ^{13}C NMR spectrum, δ_C, ppm: 16.7 t ($\mathbf{C}H_2CN$, J_{CH} = 137 Hz), 61.3 t (OCH_2, J_{CH} = 147 Hz), 69.2 d (CHO, J_{CH} = 144 Hz), 77.0 d (H**C**≡C, J_{CH} = 252 Hz), 79.8 d (HC≡**C**, J_{CH} = 47 Hz), 117.6 s (CN); 125.8, 127.0, 127.7 (CH_{arom}, J_{CH} = 163 Hz); 136.3 s (1C, C_{arom}).

5-[2-(Prop-2-yn-1-yloxy)ethyl]-1*H*-tetrazole (XIV) was synthesized from 1.95 g (0.03 mol) of NaN_3, 1.6 g (0.03 mol) of NH_4Cl, and 3 g (0.027 mol) of compound **XIIIa** in 15 ml of DMF. Yield 0.8 g (20%), mp 91–92°C. IR spectrum, ν, cm^{-1}: 1464–1440 (Ht), 1210–1150 (C–O–C). ^{13}C NMR spectrum, δ_C, ppm: 25.4 t (5-CH_2, J_{CH} = 137 Hz), 58.1 t (≡$\mathbf{C}CH_2O$, J_{CH} = 144 Hz), 68.4 t (OCH_2, J_{CH} = 147 Hz), 75.5 d (H**C**≡, J_{CH} = 252 Hz), 81.5 d (HC≡**C**, J_{CH} = 47 Hz), 158.7 s (C^5). Found, %: C 48.78; H 5.65; N 37.21. $C_6H_8N_4O$. Calculated, %: C 47.36; H 5.30; N 36.82.

3-[(1-Benzyl-1,2,3-triazol-4-yl)methoxy]propanenitrile (XVa). *a*. A mixture of 5 g (0.045 mol) of ether **XIIIa** and 6.6 g (0.05 mol) of benzyl azide in 15 ml of toluene was stirred for 6 h at 105°C until the initial azide disappeared (TLC). The precipitate was filtered off, recrystallized from water, and dried in air. Yield 9.2 g (83%), mp 101–102°C. IR spectrum, ν, cm^{-1}: 1600 (Ph), 1580 (Ht), 1200–1100 (C–O–C). Found, %: C 64.73; H 5.45; N 24.91. $C_{13}H_{14}N_4O$. Calculated, %: C 64.45; H 5.82; N 23.12.

b. Compound **XVa** was synthesized as described above for **XIIIa** from 2 g (0.01 mol) of **XVIa** and 0.79 g (0.015 mol) of acrylonitrile using 0.5 g of 40% aqueous KOH in 5 ml of dioxane. Yield 0.9 g (36%), mp 100–102°C. The product showed no depression of the melting point on mixing with a sample prepared as described in *a*.

3-{[(1,2,4-Triazol-3-yl)-1,2,3-triazol-4-yl]methoxy}propanenitrile (XVb). *a*. The procedure was analogous to the synthesis of **XVa** (*a*); from 1.5 g (0.013 mol) of 3-azido-1,2,4-triazole and 1.5 g (0.013 mol) of ether **XIIIa** in 10 ml of toluene we obtained 1.7 g (60%) of **XVb** with mp 162°C. ^{13}C NMR spectrum, δ_C, ppm: 16.7 t ($\mathbf{C}H_2CN$, J_{CH} = 139 Hz), 61.8 t (CH_2O, J_{CH} = 149 Hz), 64.0 t (OCH_2, J_{CH} = 145 Hz), 118.9 s (CN), 122.7 d (C^5, J_{CH} = 196 Hz), 143.6 s ($C^{3''}$), 145.8 d ($C^{5''}$, J_{CH} = 217 Hz), 153.5 s (C^4). Found, %: C 44.03; H 4.22; N 44.56. $C_8H_9N_7O$. Calculated, %: C 43.83; H 4.14; N 44.73.

b. As described above for compound **V**, from 1.5 g (0.009 mol) of **XVIb** and 0.47 g (0.009 mol) of acrylonitrile using 0.3 g of 40% aqueous KOH in 5 ml of dioxane we obtained 0.8 g (42%) of **XVb** with mp 160–162°C. The product showed no depression of the melting point on mixing with a sample prepared as described in *a*.

3-{Phenyl[1-(1,2,4-triazol-3-yl)-1,2,3-triazol-4-yl]methoxy}propanenitrile (XVc) was synthesized as described above for compound **IX** from 1.5 g (8.1 mmol) of **XIIIb** and 1.03 g (9.4 mmol) of 3-azido-1,2,4-triazole in 10 ml of toluene. Yield 0.8 g (31%), mp 168–170°C. ^{13}C NMR spectrum, δ_C, ppm: 118.2 s (CN), 17.2 t ($\mathbf{C}H_2CN$, J_{CH} = 136 Hz), 62.4 t (OCH_2, J_{CH} = 147 Hz), 74.3 d (**C**HPhO, J_{CH} = 145 Hz), 153.5 s (C^4), 120.9 d (C^5, J_{CH} = 201 Hz), 147.3 s ($C^{3''}$), 144.2 d ($C^{5''}$, J_{CH} = 214 Hz), 138.5 s (Ph); 126.0, 127.5, 127.1 (CH, Ph, J_{CH} = 164 Hz).

5-{2-[(1-Benzyl-1*H*-1,2,3-triazol-4-yl)methoxy]-ethyl}-1*H*-tetrazole (XVIIa). *a*. A solution of 4 g (0.026 mol) of compound **XIV** and 4 g (0.03 mol) of benzyl azide in 20 ml of toluene was heated for 15 h at 100–105°C until the initial acetylenic compound disappeared (TLC). The solvent was distilled off under reduced pressure. Yield 5 g (67%), mp 143°C (from ethanol). IR spectrum, ν, cm^{-1}: 1465–1440 (Ht), 1250–1120 (C–O–C). ^{13}C NMR spectrum, δ_C, ppm: 24.9 t

(1C, 5′-CH_2, J_{CH} = 137 Hz), 55.2 t (1C, **C**H_2Ph, J_{CH} = 140 Hz), 63.2 t (1C, 4-CH_2, J_{CH} = 139 Hz), 65.0 t (1C, OCH_2, J_{CH} = 145 Hz), 69.1 t (1C, CH_2O, J_{CH} = 149 Hz), 126.5 d (1C, C^5, J_{CH} = 192 Hz), 133.8 s (1C, C^i); 128.4, 129.3, 129.1 d (5C, C^o, C^m, C^p, J_{CH} = 160 Hz), 145.9 s (1C, C^4), 161.1 s (1C, $C^{5'}$). Found, %: C 54.21; H 5.92; N 34.47. $C_{13}H_{15}N_7O$. Calculated, %: C 54.73; H 5.30; N 34.37.

b. As described above for compound **VIII**, from 3.4 g (0.052 mol) of NaN_3, 2.6 g (0.05 mol) of NH_4Cl, and 9.6 g (0.04 mol) of **XVa** in 25 ml of DMF we obtained 4.6 g (41%) of **XVIIa** with mp 143°C. The product showed no depression of the melting point on mixing with a sample prepared as described in *a*.

5-(2-{[1-(1*H*-1,2,4-triazol-3-yl)-1*H*-1,2,3-triazol-4-yl]methoxy}ethyl)-1*H*-tetrazole (XVIIb) was synthesized as described above for compound **VIII** from 2.5 g (0.011 mol) of **XVb**, 1.4 g (0.022 mol) of NaN_3, and 1.2 g (0.022 mol) of NH_4Cl in 15 ml of DMF. Yield 2.4 g (84%), mp 158–158°C. IR spectrum, ν, cm^{-1}: 1465–1440 (Ht), 1245–1110 (C–O–C). ^{13}C NMR spectrum, δ_C, ppm: 24.7 t (5′-CH_2, J_{CH} = 139 Hz), 63.0 t (4-CH_2, J_{CH} = 135 Hz), 65.1 t (OCH_2, J_{CH} = 147 Hz), 126.8 d (C^5, J_{CH} = 191 Hz), 143.0 s (C^4), 148.1 d ($C^{5''}$, J_{CH} = 220 Hz), 149.7 s ($C^{3''}$), 161.3 s ($C^{5'}$). Found, %: C 36.89; H 3.48; N 53.95. $C_8H_{10}N_{10}O$. Calculated, %: C 36.64; H 3.84; N 53.41.

1,2,3,4,5,6-Hexakis(2-cyanoethoxy)hexane (XVIII). A solution of 0.3 g of sodium hydroxide in 1 ml of water was added under stirring over a period of 10 min to a solution of 5 g (0.027 mol) of sorbitol and 10 g (0.18 mol) of acrylonitrile in 5 ml of water, and the mixture was stirred for 5 h at 60°C. The mixture was cooled to room temperature, poured into 25 ml of water under stirring, and neutralized with 0.1 N aqueous HCl. The solvent was distilled off under reduced pressure, the residue was extracted with ethyl acetate (4×20 ml), the extracts were combined and dried over calcined $MgSO_4$, the solvent was removed on a rotary evaporator, and the viscous oily residue was dried under reduced pressure. Yield 8.5 g (90%). ^{13}C NMR spectrum, δ_C, ppm: 21.0 t (4C, **C**H_2CN, J_{CH} = 137 Hz), 21.9 t (2C, **C**H_2CN, J_{CH} = 137 Hz), 61.8 t (4C, OCH_2, J_{CH} = 148 Hz), 62.6 t (2C, OCH_2, J_{CH} = 148 Hz), 68.8 t (2C, CH_2, J_{CH} = 148 Hz), 76.6–77.9 (overlapping signals, 4C, CH), 119.1 br.s (6C, **C**≡N). Found, %: C 57.88; H 7.31; N 16.10. $C_{24}H_{32}N_6O_6$. Calculated, %: C 57.59; H 6.44; N 16.79.

1,3-Bis[(2-cyanoethoxy)methyl]-2,2-bis[(2-cyanoethoxy)methyl]propane (XIX) was synthesized in a similar way from 5.7 g (0.043 mol) of pentaerythritol and 10 g (0.18 mol) of acrylonitrile. Yield 27.4 g (84%), mp 43°C. ^{13}C NMR spectrum, δ_C, ppm: 20.7 t (4C, **C**H_2CN, J_{CH} = 143 Hz), 48.8 s [**C**$(CH_2)_4$], 61.3 t (4C, CH_2O, J_{CH} = 146 Hz), 71.9 t (4C, CH_2O, J_{CH} = 144 Hz), 118.1 s (4C, C≡N). Found, %: C 59.40; H 6.81; N 15.88. $C_{17}H_{24}N_4O_4$. Calculated, %: C 58.61; H 6.94; N 16.08.

1,2,3,4,5,6-Hexakis[2-(1*H*-tetrazol-5-yl)ethoxy]-hexane (XX). A suspension of 7.5 g (0.12 mol) of NaN_3 and 5 g (0.09 mol) of NH_4Cl in 30 ml of DMF was added at room temperature to a solution of 5 g (0.001 mol) of compound **XVIII** in 25 ml of DMF, and the mixture was stirred for 24 h at 105°C. The mixture was cooled to 20–25°C, the solvent was distilled off under reduced pressure, and 50 ml of 0.1 N aqueous HCl was added to the residue until pH 2. The precipitate was filtered off, repeatedly washed with water until neutral washings, and dried in air. Yield 7.2 g (97%), mp 150°C. ^{13}C NMR spectrum, δ_C, ppm: 21.9 t (4C, 5-CH_2, J_{CH} = 137 Hz), 22.3 t (2C, 5-CH_2, J_{CH} = 137 Hz), 63.8 t (4C, OCH_2, J_{CH} = 147 Hz), 64.7 t (2C, OCH_2, J_{CH} = 147 Hz), 68.7 t (2C, CH_2), 76.5–77.8 (overlapping signals, 4C, CH), 152.5–152.8 br.s (C^5). Found, %: C 38.10; H 5.01; N 43.38. $C_{24}H_{38}N_{24}O_6$. Calculated, %: C 37.99; N 5.05; N 44.31.

1,3-Bis[2-(1*H*-tetrazol-5-yl)ethoxymethyl]-2,2-bis[2-(1*H*-tetrazol-5-yl)ethoxymethyl]propane (XXI) was synthesized in a similar way from 5 g of (0.014 mol) tetranitrile **XIX**, 7.5 g (0.12 mol) of NaN_3, and 5 g (0.09 mol) of NH_4Cl in 25 ml of DMF. Yield 6.1 g (84%), mp 143°C. ^{13}C NMR spectrum, δ_C, ppm: 20.7 (5-CH_2, J_{CH} = 135 Hz), 48.5 s [**C**$(CH_2)_4$], 63.1 t (OCH_2, J_{CH} = 144 Hz), 71.6 t (OCH_2, J_{CH} = 143 Hz), 152.5 s (C^5). Found, %: C 38.10; H 5.01; N 42.51. $C_{17}H_{28}N_{16}O_4$. Calculated, %: C 39.23; N 5.42; N 43.06.

This study was performed under financial support by the Ministry of Education and Science of the Russian Federation.

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