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Cyanoacetylene and Its Derivatives: XXXIV.* Nucleophilic Addition of Tetrazole to Cyanoacetylenes

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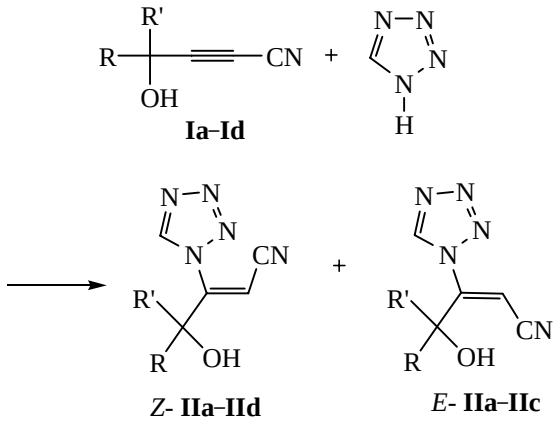
Abstract—Nucleophilic addition of tetrazole to 4-hydroxy-4-alkyl-2-alkynonitriles and to 3-phenyl-2-propynonitrile occurred regiospecifically and afforded *E*-, *Z*-4-hydroxy-4-methyl-3-tetrazolyl-2-alkenonitriles and 3-tetrazolyl-3-phenyl-2-propenonitrile [20–40°C, 13–50 h, 4–15 wt% MOH (M = Na, K), THF (or DMSO)] in up to 69% yield. The attempt to perform cyclization of the hydroxy-containing adducts into iminodihydrofurans (KOH, ethanol, 23–25°C) resulted in vinyl nucleophilic substitution of the tetrazole moiety by an ethoxy group.

The nucleophilic addition of a number of azoles (imidazole, 2-methylimidazole, benzimidazole, 2-ethyl-benzimidazole, pyrazole, 3,5-dimethylpyrazole, 1,2,4-triazole, 5-methyl-3-chloro-1,2,4-triazole) to cyanoacetylene alcohols and to 3-phenyl-2-propynonitrile occurs regio- and stereoselectively and furnishes the corresponding alkenes of a *Z*-configuration, 3-azolyl-2-alkenonitriles, in a quantitative yield [2–5]. The reaction of 3-phenyl-2-propynonitrile with pyrrole, 2-phenylpyrrole, and 4,5,6,7-tetrahydroindole (KOH, 20°C, 3 h, DMSO) gave rise to a mixture of *E*- and *Z*-isomers of N-adducts in a 43–88% yield [6].

No published data exist on nucleophilic addition of tetrazole to cyanoacetylenes. The tetrazole is only known to react with activated acetylenes, in particular, with α-acetylene ketones and with propiolic acid in the presence of triethylamine (ethanol, boiling, 3–4 h) affording both mono- and diadducts [7].

This study deals with reactions of tetrazole with 4-hydroxy-4-alkyl-2-alkynonitriles **Ia–Id** and 3-phenyl-2-propynonitrile aiming at preparation of alkenonitrile tetrazole derivatives, promising building blocks for the synthesis of heterocyclic compounds and energy-rich substances [8, 9], pharmaceuticals, and their precursors [9, 10]. The tetrazole derivatives are known to find application in medicine [10], biochemistry [11], agriculture [12], and also in photography [13] and analytical chemistry [14].

The reaction of 4-hydroxy-2-alkynonitriles **Ia–Id** with tetrazole occurs regiospecifically in a solution (in THF or DMSO) in the presence of alkali metal hydroxides (4–15 wt% NaOH, KOH) giving *E*-, *Z*-4-hydroxy-4-methyl-3-(tetrazol-1-yl)-2-alkenonitriles **IIa–IId** in 6–69% yield.



R = R' = Me (**a**); R = Me, R' = Et (**b**), *t*-Bu (**c**); R, R' = $(CH_2)_5$ (**d**).

The yield and the ratio of compounds **IIa–IId** synthesized are essentially affected by the structure of the initial cyanoacetylenes and by the nature of the alkali metal hydroxide. For instance, in reaction of cyanoacetylene **Ia** and tetrazole in the presence of 7 wt% of NaOH in THF (35–40°C, 28 h) a mixture of *E*- and *Z*-isomers of 4-hydroxy-4-methyl-3-(tetrazol-1-yl)-2-pentenonitrile (**IIa**) was obtained in yield not exceeding 9%. At the same time in the presence of KOH, all the other conditions being the same, the yield of alkenonitrile **IIa** reached 69%. The use in the reaction of DMSO instead of THF permit-

* For communication XXXIII, see [1].

ted decreasing the temperature (20–25°C) and reducing the reaction time from 28 to 13 h, but the yield of the product under these conditions diminished to 34%. In all cases the ratio of *E*- and *Z*-isomers was ~ 1:1 (according to NMR data).

The reaction of cyanoacetylene **Ib** with tetrazole (7 wt% KOH, 35–40°C, 28 h, THF) also gave rise to a mixture (1:1) of *E*- and *Z*-4-hydroxy-4-methyl-3-(tetrazol-1-yl)-2-hexenonitrile (**IIb**) in a 40% yield.

The presence in the molecule of cyanoacetylene **Ic** of a *tert*-butyl group resulted in a sharp decrease in the yield (to 6%) of alkenonitrile **IIc** in THF despite the increasing of the reaction time to 50 h and of the amount of KOH to 15 wt%. The reaction afforded the mixture of *E*- and *Z*-isomers of alkenonitrile **IIc** in a ratio 2:1.

Unlike cyanoacetylenes **Ia–Ic**, 3-(1-hydroxycyclohexyl)-2-propynonitrile (**Id**) reacted with the tetrazole (7 wt% KOH, 35–40°C, 28 h, THF) stereospecifically providing *E*-1-(hydroxycyclohexyl)-3-(tetrazol-1-yl)-2-propenonitrile (**IId**) in a 45% yield.

Alkenonitriles **IIa–IIc** are oily fluids, and compound **IId** is a crystalline substance. These products are soluble in most organic solvents.

The structure of synthesized compounds **IIa–IId** is confirmed by the data of IR, ^{1}H and ^{13}C NMR spectroscopy, and the composition is proved by elemental analysis.

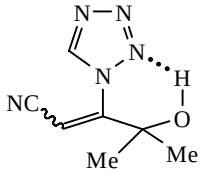
^{1}H NMR spectra of compounds **IIa–IIc** contain singlets of olefin protons in the region δ 6.04–6.20 ppm for *E*-isomers and 6.32–6.45 ppm for *Z*-isomers. The assignment of signals to *E*- and *Z*-isomers was performed with the use of two-dimensional experiment NOESY, for in the 2D-spectrum of the *Z*-isomer where the substituent R and the olefin protons were located in the *cis*-position with respect to each other cross-peaks appeared due to the dipole interaction between the nuclei of these groups. The double set of all other signals in the ^{1}H and ^{13}C NMR spectra also proved the presence of two isomers.

In the ^{1}H NMR spectrum of compound **IId** a single peak of olefin proton is present at δ 6.10 ppm belonging apparently to the *E*-isomer. Presumably the *Z*-isomer of compound **IId** arising at first undergoes isomerization in condition of the reaction into the thermodynamically more stable compound **IId** of *E*-configuration.

In the IR spectra of compounds **IIa–IId** (thin film, KBr) appear absorption bands in the region 3080–3065, 1650–1630 cm^{-1} (C=C), the cyano group gives rise to a band at 2234–2200 cm^{-1}, hydroxy group at 3370–3500 cm^{-1}.

IR spectra of alkenonitrile **IIa** were studied in detail in solutions in $CHCl_3$ and CCl_4 at concentrations (*c* 2×10^{-2}–2×10^{-3} mol l^{-1}, *d* 5–100 mm) totally excluding formation of intermolecular hydrogen bonds. Therewith three absorption bands appear in the IR spectrum: 3618, 3593, 3535 cm^{-1}. The first band belongs to nonassociated OH group at the tertiary carbon in the *Z*-isomer, and the second band corresponds to the OH group involved into a hydrogen bond with the π-electrons of the C≡N group or the double bond of the *E*-isomer [15]. The band at 3535 cm^{-1} reveals the formation of an intramolecular hydrogen bond with a nitrogen atom of tetrazole.

The absorption band at 2230 cm^{-1} corresponding to



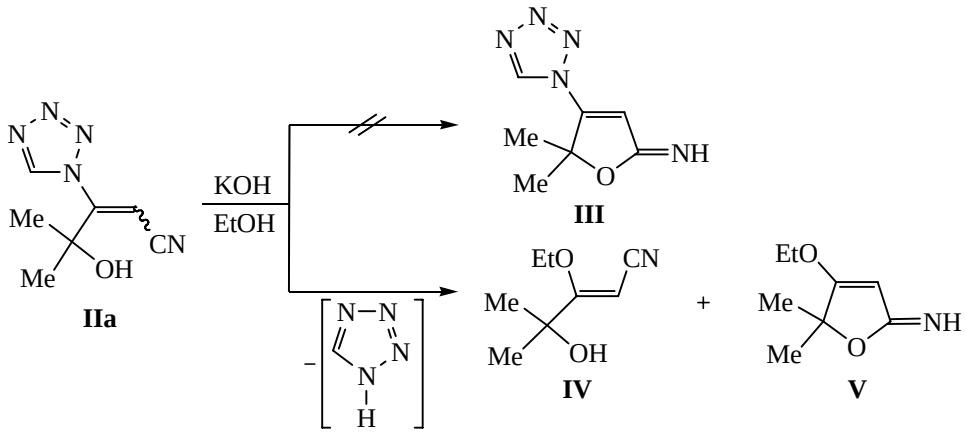
cyano group in the diluted solution of compound **IIa** splits in two bands at 2222 and 2202 cm^{-1} belonging presumably to *E*- and *Z*-configurations respectively [4].

Thus tetrazole in contrast to imidazole, 2-methyl-imidazole, pyrazole, and 3,5-dimethylpyrazole added to cyanoacetylenes **Ia–Id** under more stringent conditions apparently due to the low basicity of tetrazole (pK_a 2.8) and, consequently, to the low nucleophilicity of its anion [16].

As reported before among the azole 2-alkenonitrile analogs of compounds **IIa–IId** only 3-imidazolyl-2- [4] and 3-pyrazolyl-2-alkenonitriles [5] underwent intramolecular cyclization into 2-iminodihydrofurans [5–10% MOH (M = Na, K), dioxane], and at the attempt to carry out cyclization of 3-benzimidazolyl-2-alkenonitriles (triethylamine, 78°C, ethanol) the elimination of benzimidazole was observed [3].

The study of intramolecular cyclization of alkenonitrile **IIa** revealed that under mild conditions (23–25°C, 10% KOH, ethanol, 3.5 h) it did not form the expected iminodihydrofuran **III** but exchanged the tetrazole substituent for an ethoxy group affording 4-hydroxy-4-methyl-3-ethoxy-2-pentenonitrile (**IV**) and its cyclization product, 5,5-dimethyl-4-ethoxy-2,5-dihydro-2-iminofuran (**V**).

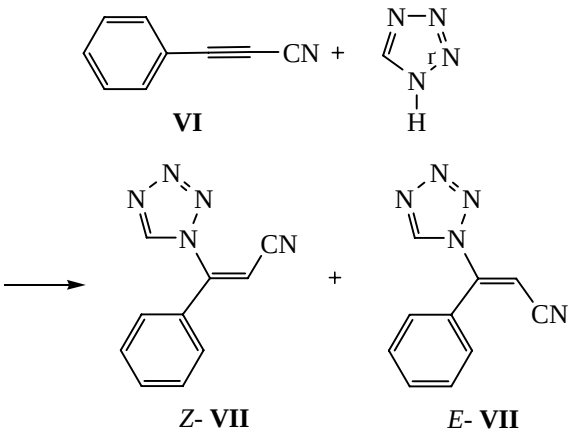
In the ^{1}H NMR spectrum of the reaction mixture after removing the main amount of tetrazole singlets of olefin protons are observed in the region δ 6.37, 5.05, and 4.99 ppm belonging respectively to *Z*-alkenonitriles



IIa and **IV** [17], and to iminodihydrofuran **V** (52, 40, and 8%respectively). Methylene protons of the ethoxy groups of compounds **IV** and **V** appear as quartets at δ 4.56 and 4.05 ppm respectively.

The IR spectrum of the reaction mixture in CCl_4 solution (c 1×10^{-1}–6×10^{-3} mol l–1) contained absorption bands at 3618, 3603, 3544, 3480, 3308, 3155, and 3081 cm^{-1}, where two first bands corresponded to nonassociated OH group in alkenonitriles **IIa** and **IV**, and the third one to the intramolecular hydrogen bond with a nitrogen atom (see above). The rest of the bands belonged to the NH and HC= bonds of iminodihydrofuran **V** and tetrazole.

In the IR spectrum of solutions in $CHCl_3$ at the same concentration appeared absorption bands of OH group at 3535, 3475 cm^{-1}, and also bands at 3300 and 3076 cm^{-1} belonging to =NH group and HC= bond of iminodihydrofuran **V** respectrively. The band of cyano group at the frequency 2213 cm^{-1} (KBr) in $CHCl_3$ and CCl_4 is split in two bands at 2215 and 2229 cm^{-1} in conformity to the presence of two alkenonitriles **IIa** and **IV** [17].



Hence under conditions applied we observed an uncommon nucleophilic substitution of tetrazole moiety in alkenonitrile **IIa** by ethoxy group and partial cyclization of the arising alkenonitrile **IV** into iminodihydrofuran **V**.

Performing the cyclization in conditions described in [5] (50°C, 8 h, 10% KOH, dioxane) for 4-hydroxy-4-methyl-3-(pyrazol-1-yl)-2-pentenonitrile we obtained a complex mixture of compounds that we failed to separate by column chromatography.

The attempts to carry out the intramolecular cyclization of alkenonitrile **IIa** by treating with gaseous hydrogen chloride as it happened with 3-imidazolyl-2-alkenonitriles [4] were also unsuccessful.

3-Phenyl-2-propynonitrile (**VI**) reacted with the tetrazole regiospecifically both in THF (50–55°C, 14 h) and DMSO (20–25°C, 3 h) in the presence of 6–13 wt% of KOH affording a mixture of *E*- and *Z*-isomers of 3-tetrazolyl-3-phenyl-2-propenonitrile **VII** in a 67–69% yield.

The yield of 3-tetrazolyl-3-phenyl-2-propenonitrile **VII** is sensitive to the solvent and reaction conditions: At 20–25°C in THF (25 h) it was 40% (on reacted 3-phenyl-2-propynonitrile at conversion 9%) whereas in DMSO the reaction at this temperature was complete in 3 h with 67% yield.

The presence in the ^1H NMR spectrum of compound **VII** of two signals both from the olefin protons (5.97 and 5.93 ppm in 1:1 ratio) and from the CH of the tetrazole ring (δ 9.00 and 8.78 ppm), and also a double set of all carbon signals in the ^{13}C NMR spectrum indicated the formation of two isomers.

In the IR spectrum (KBr) of compound **VII** appear two bands from the stretching vibrations of the C=C bond in the region 1620 and 1640 cm^{-1} whereas the ab-

sorption of the cyano group is observed as a single band at 2220 cm^{-1}.

By reprecipitation of the isomer mixture of compound **VII** from ethyl ether into hexane we succeeded to isolate the product of *Z*-configuration as shown by the presence of cross-peaks between the signal of the olefin proton (δ 5.93 ppm) and the *ortho*-proton of the phenyl ring [data of the two-dimensional ^1H NMR spectroscopy (NOESY)]. In the IR spectrum (KBr) of the *Z*-isomer of compound **VII** there is a single absorption band of the stretching vibrations of the C=C bond at 1621 cm^{-1}.

Isomeric composition of compound **VII** at storage for a month at room temperature changed: The product of *Z*-configuration transformed completely into the *E*-isomer.

In such a way by the reaction of nucleophilic addition of tetrazole to 4-hydroxy-4-alkyl-2-alkynonitriles and 3-phenyl-2-propynonitrile a series of new functional tetrazole derivatives was prepared which can find application to the synthesis of energy-rich and biologically active substances.

EXPERIMENTAL

IR spectra were recorded on a spectrophotometer Specord 75IR from KBr pellets, thin film, and solutions in $CHCl_3$ and CCl_4 (*c* 1×10^{-1}–6×10^{-3} mol l^{-1}, *d* 5, 20, 50, 100 mm). ^1H (400.13 MHz) and ^{13}C (100.69 MHz) NMR spectra were registered on spectrometer Bruker DPX-400 in $CDCl_3$, internal reference HMDS. The reaction progress was monitored by TLC on Al_2O_3 and Silufol plates (eluent chloroform–benzene–ethanol, 20:4:1).

The initial acetylenes **Ia–Id** were prepared along procedure described in [18].

4-Hydroxy-4-methyl-3-tetrazolyl-2-pentenonitrile (IIa). *a*. To a mixture containing 0.18 g (2.5 mmol) of tetrazole and 0.02 g of KOH in 5 ml of THF was added 0.27 g (2.5 mmol) of cyanoacetylene **Ia** in 1 ml of THF in the course of 20 min. The mixture was stirred at 35–40°C for 28 h, then it was passed through a bed (5 cm) of Al_2O_3. The solvent was removed at reduced pressure, the residue was reprecipitated from ethyl ether into hexane to obtain 0.31 g (69%) of alkenonitrile **IIa**. Oily substance. IR spectrum (KBr), ν, cm^{-1}: 582, 637, 670, 696, 715, 831, 851, 880, 955, 984, 1018, 1084, 1144, 1193, 1220, 1283, 1370, 1394, 1463, 1645, 2232, 2882, 2939, 2986, 3081, 3403. ^1H NMR spectrum (*E*-isomer), δ, ppm: 1.46 s (6H, $2CH_3$), 6.20 s (1H, =CH), 9.25 s (1H, tetrazole). ^1H NMR spectrum (*Z*-isomer), δ, ppm: 1.54 s (6H, $2CH_3$), 6.40 s (1H, =CH), 8.78 s (1H, tetrazole). Ratio of *E*:*Z*-isomers 1:1. ^{13}C NMR spectrum $C^{6,7}H_3)_2C^5(OH)C^3(C^4HN_4)=C^2HC^1N]$, δ, ppm: 157.61, 159.53 (C^3), 152.83, 143.50 (C^4), 113.10, 113.70 (C^1), 95.92, 97.77 (C^2), 71.97, 72.66 (C^5), 27.58, 28.10 ($C^{6,7}$), for *E*-, *Z*-isomers respectively. Found, %: C 46.56; H 5.40; N 38.72. $C_7H_9N_5O$. Calculated, %: C 46.92; H 5.06; N 39.09.

b. Likewise from 0.18 g (2.5 mmol) of tetrazole, 0.27 g (2.5 mmol) of cyanoacetylene **Ia**, and 0.03 g of NaOH in 6 ml of THF we obtained 0.04 g (9%) of alkenonitrile **IIa**.

c. To a solution of 0.36 g (5 mmol) of tetrazole and 0.02 g of KOH in 6 ml of DMSO was added at stirring 0.54 g (5 mmol) of cyanoacetylene **Ia** in 4 ml of DMSO within 20 min. The mixture was stirred at 20–25°C for 13 h, diluted with 10 ml of H_2O, extracted with ethyl ether, and the extract was dried on $MgSO_4$. The solvent was removed at reduced pressure to give 0.31 g (34%) of alkenonitrile **IIa** (a mixture of *Z*- and *E*-isomers in a ratio 1:1 according to ^1H NMR data).

4-Hydroxy-4-methyl-3-tetrazolyl-2-hexenonitrile (IIb). Likewise by procedure *a* from 0.18 g (2.5 mmol) of tetrazole, 0.31 g (2.5 mmol) of cyanoacetylene **Ib**, and 0.03 g of KOH in 5 ml of THF we obtained 0.19 g (40%) of alkenonitrile **IIb**, oily substance. IR spectrum (KBr), ν, cm^{-1}: 560, 685, 745, 810, 840, 915, 980, 1025, 1075, 1170, 1270, 1340, 1365, 1445, 1560, 1630, 1650, 2200, 2225, 2875, 2930, 2970, 3065, 3350. ^1H NMR spectrum (*E*-isomer), δ, ppm: 0.92 t (2H, CH_2), 1.50 s (3H, CH_3), 1.88 s (3H, CH_3), 6.18 s (1H, =CH), 9.17 s (1H, tetrazole). ^1H NMR spectrum (*Z*-isomer), δ, ppm: 0.92 t (2H, CH_2), 1.53 s (3H, CH_3), 1.69 s (3H, CH_3), 6.32 s (1H, =CH), 8.71 s (1H, tetrazole). Ratio of *E*:*Z*-isomer 1:1. Found, %: C 49.36; H 5.32; N 35.83. $C_8H_{11}N_5O$. Calculated, %: C 49.73; H 5.74; N 36.25.

4-Hydroxy-4,5,5-trimethyl-3-tetrazolyl-2-hexenonitrile (IIc). To a mixture containing 0.36 g (5 mmol) of tetrazole and 0.04 g of KOH in 10 ml of THF was slowly added 0.76 g (5 mmol) of cyanoacetylene **Ic** in 2 ml of THF, and the reaction mixture was stirred at 35–40°C for 50 h. The fraction insoluble in THF was filtered off and washed with ethyl ether to obtain 0.15 g of tetrazole. The solvents from the filtrate were removed at reduced pressure to isolate 0.95 g of a substance that was treated with dry ethyl ether to separate additional 0.11 g of tetrazole (in total unreacted tetrazole amounted to 0.26 g). On removing ethyl ether from the filtrate we obtained 0.83 g of oily fluid that was subjected to column chromatography on SiO_2, eluent chloroform–benzene–ethanol, 20:4:1. Thus was isolated 0.67 g of acetylene **Ic**

(conversion 9%) and 0.07 g (54%) of alkenonitrile **IIc**, oily substance. IR spectrum (KBr), ν, cm^{-1}: 495, 620, 695, 765, 845, 910, 980, 1000, 1080, 1105, 1165, 1220, 1370, 1390, 1455, 1465, 1480, 1550, 1630, 2230, 2875, 2910, 2965, 3080, 3470. ^{1}H NMR spectrum (*E*-isomer), δ, ppm: 0.81 s (9H, $3CH_3$), 1.73 s (3H, CH_3), 6.04 s (1H, =CH), 9.13 s (1H, tetrazole). ^{1}H NMR spectrum (*Z*-isomer), δ, ppm: 0.77 s (9H, $3CH_3$), 1.66 s (3H, CH_3), 6.45 s (1H, =CH), 8.72 s (1H, tetrazole). Ratio of *E*:*Z*-isomer 2:1. Found, %: C 54.08; H 6.97; N 32.00. $C_{10}H_{15}N_5O$. Calculated, %: C 54.28; H 6.83; N 31.65.

3-(1-Hydroxycyclohexyl)-3-tetrazolyl-2-propenonitrile (IId). To a solution of 0.36 g (5 mmol) of tetrazole and 0.04 g of KOH in 10 ml of THF was slowly added 0.75 g (5 mmol) of cyanoacetylene **Id** in 4 ml of THF. The mixture was stirred at 35–40°C for 28 h, passed through a bed (5 cm) of Al_2O_3, the solvent was removed at reduced pressure. The residue was subjected to column chromatography on SiO_2, eluent chloroform–benzene–ethanol, 20:4:1. Thus was isolated 0.49 g (45%) of alkenonitrile **IId**, mp 56–60°C (from ethyl ether). IR spectrum (KBr), ν, cm^{-1}: 504, 634, 648, 692, 759, 810, 841, 855, 913, 927, 967, 993, 1043, 1061, 1082, 1140, 1152, 1168, 1202, 1248, 1263, 1272, 1317, 1342, 1387, 1415, 1454, 1476, 1552, 1641, 2234, 2857, 2935, 3082, 3289. ^{1}H NMR spectrum, δ, ppm: 1.64 m (10H, $5CH_2$), 6.10 s (1H, =CH), 9.09 s (1H, tetrazole). Found, %: C 54.32; H 6.19; N 31.50. $C_{10}H_{13}N_5O$. Calculated, %: C 54.78; H 5.98; N 31.94.

3-Tetrazolyl-3-phenyl-2-propenonitrile (VII). *a*. To a solution of 0.18 g (2.5 mmol) of tetrazole and 0.04 g of KOH in 6 ml of DMSO was added at stirring 0.32 g (2.5 mmol) of cyanoacetylene **VI** in 2 ml of DMSO within 20 min. The mixture was stirred at 20–25°C for 3 h, diluted with 10 ml of H_2O, and extracted with ethyl ether. The extract was dried on $MgSO_4$, and the solvent was removed in a vacuum to obtain 0.33 g (67%) of alkenonitrile **VII** (a mixture of *E*- and *Z*-isomers in a ratio 1:1). IR spectrum (KBr), ν, cm^{-1}: 515, 600, 620, 645, 690, 765, 810, 885, 925, 980, 995, 1015, 1080, 1105, 1140, 1185, 1210, 1245, 1280, 1340, 1400, 1440, 1460, 1576, 1620, 1640, 2220, 2910, 3050, 3130.

The isomer mixture obtained converted into *E*-isomer on standing at room temperature for a month. White crystals, mp 107–109°C. ^{1}H NMR spectrum, δ, ppm: 5.97 s (1H, =CH), 7.63–7.26 m (5H, Ar), 8.97 s (1H, tetrazole). ^{13}C NMR spectrum [*E*-$C_6^{5,6,7,8,9,10}H_5C^3(C^4HN_4)=C^2HC^1N$], δ, ppm: 148.85 ($C^3$), 143.16 ($C^4$), 133.28, 131.36, 129.79, 127.63 ($C^{5,6,7,8,9,10}$), 113.70 (C^1), 93.52 (C^2).

At reprecipitation of the isomer mixture from ethyl ether into hexane we isolated *Z*-3-tetrazolyl-3-phenyl-2-propenonitrile (**VII**). White crystals, mp 72–74°C. IR spectrum (KBr), ν, cm^{-1}: 627, 650, 693, 762, 816, 889, 914, 928, 980, 1016, 1084, 1111, 1145, 1190, 1217, 1236, 1284, 1399, 1450, 1576, 1621, 2222, 2851, 2920, 3051, 3160. ^{1}H NMR spectrum, δ, ppm: 5.93 s (1H, =CH), 7.61–7.25 m (5H, Ar), 8.79 s (1H, tetrazole). ^{13}C NMR spectrum [*Z*-$C_6^{5,6,7,8,9,10}H_5C^3(C^4HN_4)=C^2HC^1N$], δ, ppm: 153.44 ($C^3$), 143.16 ($C^4$), 132.71, 131.30, 129.34, 128.19 ($C^{5,6,7,8,9,10}$), 113.85 (C^1), 93.53 (C^2). Found, %: C 61.16; H 3.80; N 34.98. $C_{10}H_7N_5$. Calculated, %: C 60.91; H 3.58; N 35.51.

b. From 0.18 g (2.5 mmol) of tetrazole, 0.32 g (2.5 mmol) of cyanoacetylene **VI**, and 0.02 g KOH in 5 ml of THF at 50–55°C in 14 h was obtained 0.15 g of acetylene **VI** (conversion 53%) and 0.18 g (69%) of alkenonitrile **VII** (Ratio of *Z*:*E*-isomer 1:1, ^{1}H NMR data).

c. Likewise from 0.18 g (2.5 mmol) of tetrazole, 0.32 g (2.5 mmol) of cyanoacetylene **VI** and 0.02 g of KOH in 5 ml THF at 20–25°C in 25 h we obtained 0.02 g (40%) of alkenonitrile **VII** and 0.29 g of acetylene **VI** (conversion 9%).

Cyclization of 4-hydroxy-4-methyl-3-tetrazolyl-2-pentenonitrile (IIa). A mixture of 0.18 g (1 mmol) of alkenonitrile **IIa** and 0.02 g of KOH in 8 ml of ethanol was stirred at 24–25°C for 3.5 h. The solvent was removed in a vacuum, the residue was treated with dry ethyl ether. The most part of the solvent was removed at a reduced pressure, the separated precipitate was filtered off, and dried to obtain 0.04 g of tetrazole. The filtrate was kept in a vacuum to get 0.14 g of oily substance that was subjected to column chromatography on SiO_2, eluent chloroform–benzene–ethanol, 20:4:1. Thus a mixture was obtained containing 0.07 g of alkenonitrile **IIa** (*Z*-isomer according to ^{1}H NMR data, conversion 59%), 0.06 g (67%) of 4-hydroxy-4-methyl-3-ethoxy-2-pentenonitrile (**IV**), and 0.01 g (11%) of 5,5-dimethyl-4-ethoxy-2,5-dihydro-2-iminofuran (**V**). ^{1}H NMR spectrum, δ, ppm: 8.78 s (1H, tetrazole), 6.36 s [1H, =CH, *Z*-(**IIa**)], 5.05 s (1H, =CH, alkenonitrile **IV**), 4.99 s (1H, =CH, iminodihydrofuran **V**), 4.56 q (2H, $O\underline{CH_2}CH_3$, alkenonitrile **IV**), 4.05 q (2H, $O\underline{CH_2}CH_3$, iminodihydrofuran **V**), 1.54 s (6H, $2CH_3$), 1.35 m (9H, $3CH_3$, alkenonitrile **IV**), 1.37 s (6H, $2CH_3$, iminodihydrofuran **V**), 1.29 t (3H, CH_3, $OCH_2\underline{CH_3}$, iminodihydrofuran **V**).

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