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Vinyltetrazoles: II.* Synthesis of 5-Substituted 1(2)-Vinyltetrazoles

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Abstract—5-R-Substituted 1(2)-vinyltetrazoles (R = Ar, Alk, CH_2=CH, NH_2, H) were synthesized by alkylation of 5-R-tetrazoles with 1,2-dibromoethane in the presence of triethylamine in acetonitrile, followed by elimination of triethylamine hydrobromide. Vinylation of dinuclear substrates, such as bis(1*H*-tetrazol-5-yl)-methane and 1,3-bis(1*H*-tetrazol-5-yl)benzene, under analogous conditions gave the corresponding N^1,$N^{2'}$- and N^2,$N^{2'}$-divinyl derivatives.

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C,N-Vinyl-substituted tetrazole derivatives are promising as monomers; products of their polymerization are base components of binding energetic materials, super desiccants, and components of filter materials and polymeric membranes [2–6].

In addition, C,N-vinyltetrazoles attract interest as reagents for the synthesis of new tetrazole derivatives. Functionalization of vinyltetrazoles generally implies addition of electrophilic or nucleophilic reagents at the CH=CH_2 bond [7]. In recent years, extensive studies have been performed on the development of alternative methods for functionalization of vinyltetrazoles with conservation of the double bond. We previously reported on the first examples of metal-catalyzed arylation of C-vinyl- and C-ethynyltetrazoles according to Heck and Sonogashira, respectively; as a result, the corresponding C-styryl- and C-arylethynyltetrazoles were obtained [8]. The application of analogous functionalization methodology to *N*-vinyltetrazoles is complicated because of their limited accessibility. Obviously, development of an afficient procedure for the synthesis of regioisomeric *N*-vinyl-5-R-tetrazoles is an important problem.

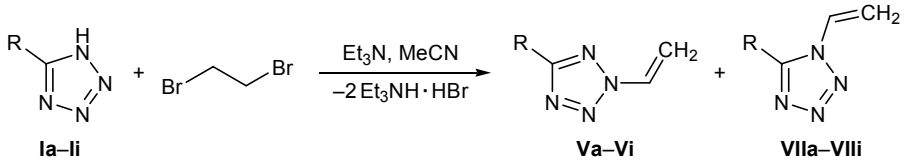
Let us consider known synthetic approaches to *N*-vinyltetrazoles. One of these implies formation of double bond via elimination of exocyclic substituents from the side chain attached to the nitrogen atom of 5-substituted tetrazoles, in particular halide ion [2, 7] or *p*-toluenesulfonate group [9]. Another method is based on direct introduction of a vinyl group into 5-R-tetrazole molecule by metal-catalyzed alkylation with electrophilic reagents containing a CH=CH_2 group. Vinyl acetate and butyl vinyl ether [10–12] are commonly used as such reagents, and the alkylation process is generally catalyzed by mercury(II) acetate with addition of acetic, trifluoroacetic, or sulfuric acid, as well as of boron trifluoride–diethyl ether complex [6]. The main disadvantages of the above procedures are large number of steps, low yields of intermediate and target products, necessity of using toxic reagents, and unsatisfactory reproducibility.

One of the most promising methods for the synthesis of vinylazoles is their metal-catalyzed vinylation according to Ullmann. Vinylation of various imidazoles, pyrazoles, and triazoles with vinyl halides in the presence of copper(I) iodide was performed in [13, 14], and the corresponding *N*-vinyl derivatives were obtained. However, according to [13], tetrazoles failed to react under analogous conditions.

The synthesis of *N*-vinyl-5-R-tetrazoles by alkylation of 5-R-tetrazoles with 1,2-dibromoethane in the presence of triethylamine in different solvents, followed by elimination (*in situ*) of triethylammonium bromide, was recently described in [15–17]. It should be noted that the yields of vinyltetrazoles in [15, 16] were fairly poor (8–16%), whereas Roh et al. [17] succeeded in obtaining 2-vinyl-5-R-tetrazoles in up to 88% yield. The procedure proposed in [17] may now

* For communication I, see [1].

Scheme 1.



Ia–Ii **Va–Vi** **VIIa–VIIi**

R = Ph (**a**), *p*-MeC_6H_4 (**b**), *p*-$F_3CC_6H_4$ (**c**), *o*-NCC_6H_4 (**d**), Me (**e**), Et (**f**), CH_2=CH (**g**), H_2N (**h**), H (**i**).

be regarded as the most efficient for the synthesis of *N*-vinyltetrazoles; it ensures high yields of target compounds and does not require the use of difficultly accessible and toxic reagents. According to [17], vinylation of 5-aryl and 5-alkyltetrazoles gives only one regioisomer, 2-vinyl-5-R-tetrazole. However, the results of studying the kinetics, selectivity, and mechanism of alkylation of salts derived from NH-5-R-tetrazoles with various electrophiles indicated the possibility for formation of isomeric N-substituted 5-R-tetrazoles even if R = Ar [18, 19]. Obviously, the procedure described in [17] requires further study.

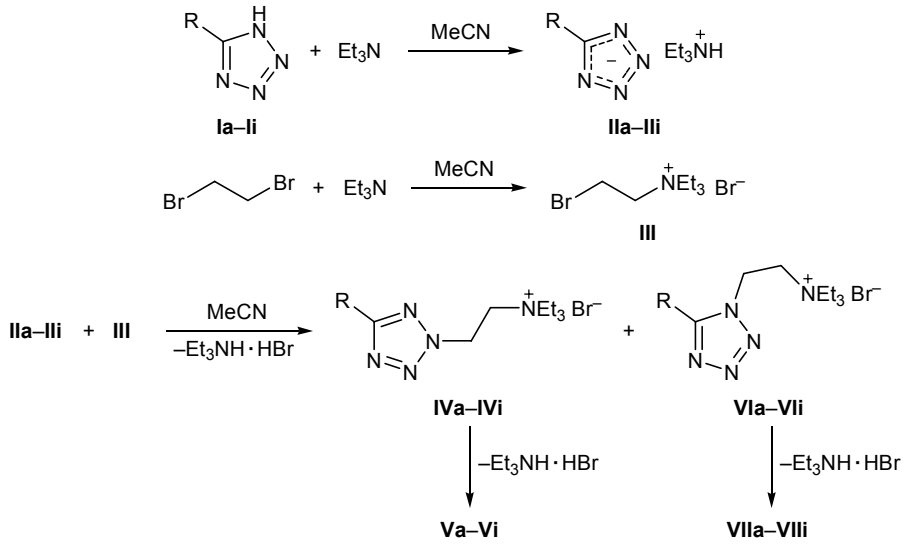
For this purpose, we reproduced the conditions reported in [17] for the vinylation of 5-substituted tetrazoles with 1,2-dibromoethane. As model substrates we selected tetrazoles **Ia**–**Ii**. The conversion of initial compounds **Ia**–**Ii** and accumulation of final products **Va**–**Vi** and **VIIa**–**VIIi** were monitored by TLC and ^{1}H NMR spectroscopy (Scheme 1). The results showed that the alkylation of all 5-R-tetrazoles **Ia**–**Ii** with 1,2-dibromoethane (2 equiv) in the presence of Et_3N (4 equiv) in acetonitrile gives regioisomeric 1(2)-vinyl-5-R-tetrazoles **Va**–**Vi** and **VIIa**–**VIIi**.

The regioselectivity in the vinylation of 5-R-tetrazoles is determined at the stage of alkylation of salts **IIa**–**IIi** with 2-bromoethyl(triethyl)ammonium bromide (**III**), which leads to the formation of isomeric tetrazoles **IVa**–**IVi** and **VIa**–**VIi**. Elimination of triethylammonium bromide from compounds **IVa**–**IVi** and **VIa**–**VIi** yields vinyltetrazoles **Va**–**Vi** and **VIIa**–**VIIi** (Scheme 2).

In the vinylation of 5-aryltetrazoles, the ratio of 1- and 2-vinyl derivatives was 5:95 (according to the ^{1}H NMR data); if R is a relatively small group (R = Alk, CH-=CH, NH_2, H), the fraction of 1-vinyl-substituted isomer increases, and the ratio **V**:**VII** attains 40:60. Our results are consistent with the data obtained previously [18] by studying the kinetics, selectivity, and mechanism of alkylation of 5-aryltetrazole salts with ethyl bromoacetate in acetonitrile.

Roh et al. [17] detected dimeric products in the reaction mixtures obtained by vinylation of 5-R-tetrazoles. Such by-products can be formed due to the presence of two electrophilic centers in the alkylating agent. In the present work no by-products were detected in the reaction mixtures.

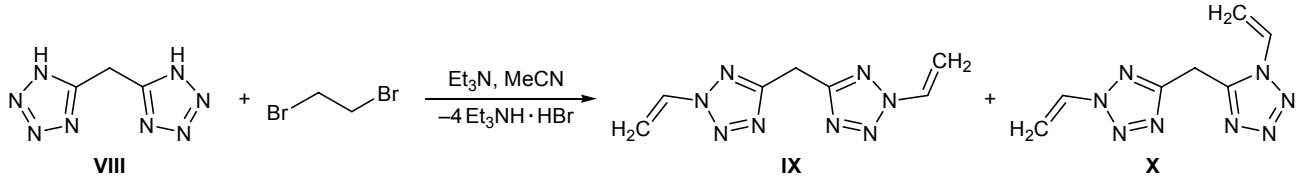
Scheme 2.



Ia–Ii **IIa–IIi** **III** **IVa–IVi** **VIa–VIi** **Va–Vi** **VIIa–VIIi**

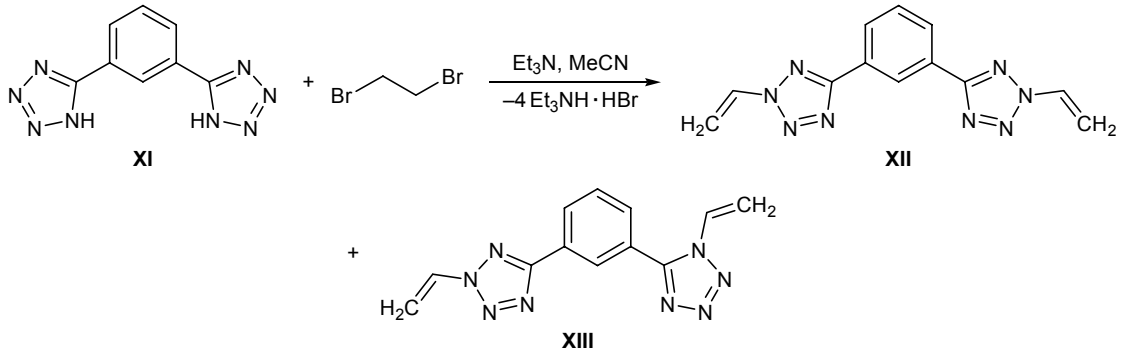
R = Ph (**a**), *p*-MeC_6H_4 (**b**), *p*-$F_3CC_6H_4$ (**c**), *o*-NCC_6H_4 (**d**), Me (**e**), Et (**f**), CH_2=CH (**g**), H_2N (**h**), H (**i**).

Scheme 3.



VIII IX X

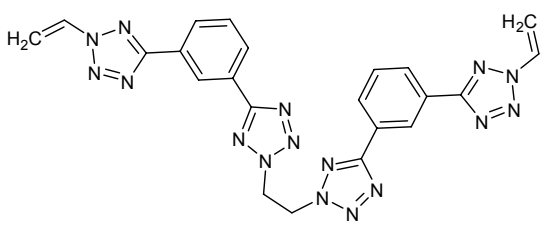
Scheme 4.



XI XII XIII

We then tried to extend the above procedure for the vinylation of mononuclear 5-R-tetrazoles to dinuclear substrates, bis(1*H*-tetrazol-5-yl)methane (**VIII**) and 1,3-bis(1*H*-tetrazol-5-yl)benzene (**XI**). Taking into account the presence of two tetrazole rings in molecules **VIII** and **XI**, the reactions were carried out using 4 equiv of 1,2-dibromoethane and 8 equiv of triethylamine, other conditions being equal. In both cases, mixtures of regioisomeric vinyltetrazoles **IX**/**X** and **XII**/**XIII** were formed, and the reactions involved positions *2*,*2*′ and *1*,*2*′ of the dinuclear substrate. No 1,1′-divinyl isomers were detected (Schemes 3, 4).

According to the ^{1}H NMR data, the ratio of *2*,*2*′ and *1*,*2*′ isomers was 63:37 (**IX**:**X**) or 70:30 (**XII**:**XIII**). The complete conversion of dinuclear tetrazoles **VIII** and **XI** required a longer time (up to 25 h) as compared to mononuclear derivatives **Ia**–**Ii**. Compounds **IX**, **X**, **XII**, and **XIII** were isolated and purified by column chromatography on silica gel. Their yields were not high, presumably due to their poor solubility in solvents used as eluents for column chromatography. In the vinylation of bis-tetrazole **XI** we isolated and identified dimeric product **XIV** (yield 2%).



XIV

Thus the described procedure is applicable to the synthesis of N-vinyl derivatives of dinuclear tetrazoles; it ensures preparation of regioisomeric 1,2′- and 2,2′-substituted compounds.

EXPERIMENTAL

The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DPX-300 spectrometer at 300.1 and 75.5 MHz, respectively, using the residual proton and carbon signals of deuterated solvents as reference (DMSO-d_6, δ 2.50, δ_C 39.52 ppm; $CDCl_3$, δ 7.26, δ_C 77.16 ppm). The mass spectrum was obtained on a Waters LCT Premier (ESI, TOF) LC–MS system. The elemental compositions were determined on a Hewlett–Packard 185 automatic analyzer. The melting points were measured on a PTP melting point apparatus; samples were heated at a rate of 1 deg/min in the vicinity of melting point. The purity of the products was checked by TLC on Kieselgel $60F_{245}$ plates (Merck). Column chromatography was performed on Silicagel 60 (0.063–0.200 mm, Merck). The ratio of regioisomeric 1- and 2-vinyltetrazoles in the reaction mixtures were determined by ^{1}H NMR spectroscopy.

The properties of compounds **Ia**–**Ii**, **VIII**, and **XI** were consistent with published data [20].

Vinylation of 5-R-tetrazoles (*general procedure***).** A solution of 46.4 mmol of 1,2-dibromoethane in 15 ml of acetonitrile was heated to the boiling point, and a solution of 23.2 mmol of tetrazole **Ia**–**Ii**, **VIII**, or **XI** and 50 mmol of triethylamine in 50 ml of aceto-

nitrile was added under stirring over a period of 3 h. The mixture was heated for 8 h under reflux, and the resulting suspension was cooled and filtered from triethylamine hydrobromide. The filtrate was evaporated to dryness under reduced pressure, the residue was dispersed in appropriate solvent system which was then used as eluent for column chromatography (indicated below for each compound), and the precipitate was filtered off. The filtrate was evaporated to dryness under reduced pressure, and the residue (a mixture of regioisomeric vinyltetrazoles) was separated by column chromatography on silica gel.

In the vinylation of tetrazoles **VIII** and **XI**, the residue obtained after first evaporation of the reaction mixture was extracted with chloroform under TLC monitoring. The combined extracts were dried over anhydrous sodium sulfate and evaporated to dryness under reduced pressure. The residue was separated by column chromatography on silica gel.

In the vinylation of 5-vinyltetrazole (**Ig**) 0.2 g of hydroquinone was added to the reaction mixture.

5-Phenyl-2-vinyl-2*H*-tetrazole (Va). Yield 3.4 g (85%), colorless crystals, mp 41°C, R_f 0.8 (hexane–ethyl acetate, 7:3). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 5.35 d (1H, CH_2=, J = 8.82 Hz), 6.22 d (1H, CH_2=, J = 16.18 Hz), 7.45 m (3H, C_6H_5), 7.51 d.d (1H, =CH, J = 8.82, 16.18 Hz), 8.14 t (2H, C_6H_5). ^{13}C NMR spectrum, δ_C, ppm: 108.52 (CH_2=); 127.02, 127.16, 129.02, 130.73 (C_6H_5); 129.87 (=CH); 164.97 (C^5). Found, %: C 62.09; H 5.90; N 32.01. $C_9H_8N_4$. Calculated, %: C 62.78; H 4.68; N 32.54.

5-Phenyl-1-vinyl-1*H*-tetrazole (VIIa). Yield 0.23 g (6%), colorless crystals, mp 105°C, R_f 0.1 (hexane–ethyl acetate, 7:3). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 5.43 d (1H, CH_2=, J = 8.71 Hz), 6.18 d (1H, CH_2=, J = 15.26 Hz), 7.07 d.d (1H, =CH, J = 8.71, 15.25 Hz), 7.55 m (3H, C_6H_5), 7.68 m (2H, C_6H_5). ^{13}C NMR spectrum, δ_C, ppm: 111.29 (CH_2=); 123.44, 129.33, 129.42, 131.71 (C_6H_5); 126.26 (=CH), 153.10 (C^5). Found, %: C 62.15; H 4.20; N 33.65. $C_9H_8N_4$. Calculated, %: C 62.78; H 4.68; N 32.54.

5-(4-Methylphenyl)-2-vinyl-2*H*-tetrazole (Vb). Yield 3.2 g (75%), colorless crystals, mp 40–41°C, R_f 0.7 (hexane–ethyl acetate, 7:3). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.38 s (3H, CH_3), 5.33 d (1H, CH_2=, J = 8.82 Hz), 6.23 d (1H, CH_2=, J = 16.92 Hz), 7.27 d (2H, C_6H_4), 7.51 d.d (1H, =CH, J = 8.82, 16.92 Hz), 8.04 d (2H, C_6H_4). ^{13}C NMR spectrum, δ_C, ppm: 21.59 (CH_3), 108.26 (CH_2=); 124.20, 129.70, 129.86, 140.93 (C_6H_4); 127.07 (=CH), 165.04 (C^5). Found, %: C 64.20; H 5.63; N 30.17. $C_{10}H_{10}N_4$. Calculated, %: C 64.50; H 5.41; N 30.09.

5-(4-Methylphenyl)-1-vinyl-1*H*-tetrazole (VIIb). Yield 0.04 g (1%), colorless crystals. R_f 0.2 (hexane–ethyl acetate, 7:3). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.42 s (1H, CH_3), 5.40 d (1H, CH_2=, J = 8.83 Hz), 6.15 d (1H, CH_2=, J = 15.44 Hz), 7.05 d.d (1H, =CH, J = 8.83, 15.44 Hz), 7.34 d and 7.56 d (2H each, C_6H_4).

5-[4-(Trifluoromethyl)phenyl]-2-vinyl-2*H*-tetrazole (Vc). Yield 4.6 g (83%), colorless crystals, mp 44°C, R_f 0.9 (hexane–ethyl acetate, 6:4). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 5.41–5.44 m (1H, CH_2=, J = 7.36 Hz), 6.26 d (1H, CH_2=, J = 14.71 Hz), 7.54 d.d (1H, =CH, J = 7.36, 14.71 Hz), 7.56 d and 8.29 d (2H each, C_6H_4). ^{13}C NMR spectrum, δ_C, ppm: 109.16 (CH_2=); 125.44 q (CF_3, J = 5.19 Hz); 125.97, 126.02, 127.46, 132.42 (C_6H_4); 129.84 (=CH), 163.78 (C^5). Found, %: C 50.21; H 3.10; N 23.00. $C_{10}H_7N_4F_3$. Calculated, %: C 50.01; H 2.94; N 23.33.

5-[4-(Trifluoromethyl)phenyl]-1-vinyl-1*H*-tetrazole (VIIc). Yield 0.1 g (2%), colorless crystals, mp 79–80°C, R_f 0.1 (hexane–ethyl acetate, 6:4). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 5.50 d (1H, CH_2=, J = 8.09 Hz), 6.19 d.d (1H, CH_2=, J = 1.47, 13.97 Hz), 7.05 d.d (1H, =CH, J = 8.09, 13.97 Hz), 7.84 m (4H, C_6H_4). ^{13}C NMR spectrum, δ_C, ppm: 112.45 (CH_2=); 124.40 q (CF_3, J = 5.18 Hz); 125.32, 125.94, 126.44, 133.42 (C_6H_4); 129.87 (=CH), 151.96 (C^5).

2-(2-Vinyl-2*H*-tetrazol-5-yl)benzonitrile (Vd). Yield 3.4 g (75%), colorless crystals, mp 95–96°C, R_f 0.8 (methylene chloride–methanol, 9:1). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 5.48 d (1H, CH_2=, J = 8.83 Hz), 6.38 d (1H, CH_2=, J = 15.45 Hz), 7.57–7.63 m (2H, =CH, H_{arom}), 7.67 d (1H, H_{arom}), 7.75 m (1H, H_{arom}), 8.32 d (1H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 110.41 (CH_2=), 117.37 (CN); 128.25, 130.27, 131.43, 133.87, 135.11 (C_6H_4); 129.43 (=CH), 161.71 (C^5). Found, %: C 60.50; H 4.60; N 34.90. $C_{10}H_7N_5$. Calculated, %: C 60.91; H 3.58; N 35.51.

2-(1-Vinyl-1*H*-tetrazol-5-yl)benzonitrile (VIId). Yield 0.05 g (1%), colorless crystals, R_f 0.1 (methylene chloride–methanol, 9:1). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 5.44 d.d (1H, CH_2=, J = 1.47, 7.36 Hz), 6.10 d (1H, CH_2=CH, J = 16.91 Hz), 6.93 d.d (1H, =CH, J = 7.36, 16.91 Hz), 7.67 d (1H, H_{arom}), 7.77 m (1H, H_{arom}), 7.82 m (1H, H_{arom}), 7.85 d (1H, H_{arom}).

5-Methyl-2-vinyl-2*H*-tetrazole (Ve). Yield 0.6 g (25%), light yellow oily liquid, R_f 0.8 (hexane–ethyl

acetate, 4:6). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.55 s (3H, CH_3), 5.29 d (1H, CH_2=, J = 8.83 Hz), 6.10 d (1H, CH_2=, J = 16.18 Hz), 7.44 d.d (1H, =CH, J = 8.83, 16.18 Hz). ^{13}C NMR spectrum, δ_C, ppm: 10.79 (CH_3), 107.83 (CH_2=), 129.66 (=CH), 162.87 (C^5). Found, %: C 43.50; H 6.10; N 50.40. $C_4H_6N_4$. Calculated, %: C 43.6; H 5.49; N 50.88.

5-Methyl-1-vinyl-1*H*-tetrazole (VIIe). Yield 0.8 g (30%), light yellow oily liquid, R_f 0.2 (hexane–ethyl acetate, 4:6). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.53 s (3H, CH_3), 5.34 d (1H, CH_2=, J = 8.83 Hz), 5.95 d (1H, CH_2=, J = 15.44 Hz), 6.97 d.d (1H, =CH, J = 8.83, 15.44 Hz). ^{13}C NMR spectrum, δ_C, ppm: 9.26 (CH_3), 110.36 (CH_2=), 125.43 (=CH), 150.47 (C^5). Found, %: C 43.80; H 5.16; N 51.04. $C_4H_6N_4$. Calculated, %: C 43.63; H 5.49; N 50.88.

5-Ethyl-2-vinyl-2*H*-tetrazole (Vf). Yield 1.2 g (40%), light yellow oily liquid, R_f 0.8 (hexane–ethyl acetate, 8:2). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.39 t (3H, $CH_2C\mathbf{H}_3$), 2.29 m (2H, $C\mathbf{H}_2CH_3$), 5.30 d (1H, CH_2=, J = 8.82 Hz), 6.14 d (1H, CH_2=, J = 15.44 Hz), 7.47 d.d (1H, =CH, J = 8.82, 15.44 Hz). ^{13}C NMR spectrum, δ_C, ppm: 12.36 ($CH_2\mathbf{C}H_3$), 19.15 ($\mathbf{C}H_2CH_3$), 108.01 (CH_2=), 129.88 (=CH), 168.00 (C^5). Found, %: C 48.20; H 6.22; N 45.58. $C_5H_8N_4$. Calculated, %: C 48.37; H 6.50; N 45.13.

5-Ethyl-1-vinyl-1*H*-tetrazole (VIIf). Yield 1.2 g (40%), light yellow oily liquid, R_f 0.1 (hexane–ethyl acetate, 8:2). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.41 t (3H, $CH_2C\mathbf{H}_3$), 2.90 m (2H, $C\mathbf{H}_2CH_3$), 5.37 d (1H, CH_2=, J = 8.83 Hz), 6.03 d (1H, CH_2=, J = 15.45 Hz), 6.99 d.d (1H, =CH, J = 8.83, 15.45 Hz). ^{13}C NMR spectrum, δ_C, ppm: 11.32 ($CH_2\mathbf{C}H_3$), 17.16 ($\mathbf{C}H_2CH_3$), 110.32 (CH_2=), 125.26 (=CH), 154.79 (C^5). Found, %: C 48.70; H 6.20; N 45.10. $C_5H_8N_4$. Calculated, %: C 48.37; H 6.50; N 45.13.

2,5-Divinyl-2*H*-tetrazole (Vg). Yield 1.7 g (60%), colorless crystals, mp 35–37°C, R_f 0.9 (hexane–methylene chloride–ethyl acetate, 4:4:2). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 5.47 d (1H, $C\mathbf{H}_2$=CHN, J = 8.86 Hz), 5.77 d (1H, $C\mathbf{H}_2$=CHC, J = 8.86 Hz), 6.10 d (1H, $C\mathbf{H}_2$=CHN, J = 15.75 Hz), 6.37 d (1H, $C\mathbf{H}_2$=CHC, J = 15.75 Hz), 6.84 d.d (1H, 5-CH, J = 8.86, 15.75 Hz), 7.75 d.d (1H, 2-CH, J = 8.86, 15.75 Hz). ^{13}C NMR spectrum, δ_C, ppm: 109.23 ($\mathbf{C}H_2$=CHN), 122.67 ($\mathbf{C}H_2$=CHC), 123.62 (5-CH), 130.22 (2-CH), 163.10 (C^5). Found, %: C 49.50; H 5.00; N 45.50. $C_5H_6N_4$. Calculated, %: C 49.17; H 4.95; N 45.88.

1,5-Divinyl-1*H*-tetrazole (VIIg). Yield 0.7 g (25%), light yellow oily liquid, R_f 0.6 (hexane–methylene chloride–ethyl acetate, 4:4:2). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 5.47 d (1H, $C\mathbf{H}_2$=CHN, J = 8.82 Hz), 5.99 m (2H, $C\mathbf{H}_2$=CHC, $C\mathbf{H}_2$=CHN), 6.47 d (1H, $C\mathbf{H}_2$=CHC, J = 11.03 Hz), 7.00 d.d (1H, 5-CH, J = 11.03, 15.45 Hz), 7.55 d.d (1H, 1-CH, J = 8.82, 15.44 Hz). ^{13}C NMR spectrum, δ_C, ppm: 111.00 ($\mathbf{C}H_2$=CHN), 122.60 ($\mathbf{C}H_2$=CHC), 123.80 (5-CH), 126.30 (1-CH), 151.09 (C^5). Found, %: C 49.30; H 5.07; N 45.63. $C_5H_6N_4$. Calculated, %: C 49.17; H 4.95; N 45.88.

2-Vinyl-2*H*-tetrazol--5-amine (Vh). Yield 1.3 g (53%), colorless crystals, mp 47–49°C, R_f 0.8 (hexane–ethyl acetate, 1:1). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 4.69 br.s (2H, NH_2), 5.18 d (1H, CH_2=, J = 8.83 Hz), 5.92 d (1H, CH_2=, J = 15.44 Hz), 7.32 d.d (1H, =CH, J = 8.83, 15.44 Hz). ^{13}C NMR spectrum δ_C, ppm: 106.35 (CH_2=), 129.63 (=CH), 166.09 (C^5). Found, %: C 32.22; H 4.21; N 63.57. $C_3H_5N_5$. Calculated, %: C 32.43; H 4.54; N 63.03.

1-Vinyl-1*H*-tetrazol-5-amine (VIIh). Yield 0.5 g (18%), light yellow crystals, mp 158°C, R_f 0.3 (hexane–ethyl acetate, 1:1). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 4.96 br.s (2H, NH_2), 5.34 d (1H, CH_2=, J = 8.09 Hz), 5.83 d (1H, CH_2=, J = 15.45 Hz), 6.92 d.d (1H, =CH, J = 8.09, 15.45 Hz). ^{13}C NMR spectrum, δ_C, ppm: 104.22 (CH_2=), 124.53 (=CH), 153.27 (C^5). Found, %: C 32.40; H 4.65; N 62.95. $C_3H_5N_5$. Calculated, %: C 32.43; H 4.54; N 63.03.

2-Vinyl-2*H*-tetrazole (Vi). Yield 0.6 g (30%), light yellow oily liquid, R_f 0.6 (hexane–ethyl acetate, 1:1). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 5.39 d (1H, CH_2=, J = 8.82 Hz), 6.23 d (1H, CH_2=, J = 15.44 Hz), 7.54 d.d (1H, =CH, J = 8.82, 15.44 Hz). ^{13}C NMR spectrum, δ_C, ppm: 109.15 (CH_2=), 129.06 (=CH), 153.41 (C^5). Found, %: C 35.70; H 4.47; N 59.83. $C_3H_4N_4$. Calculated, %: C 35.50; H 4.20; N 58.31.

1-Vinyl-1*H*-tetrazole (VIIi). Yield 1.0 g (45%), light yellow oily liquid, R_f 0.2 (hexane–ethyl acetate, 1:1). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 5.40 d (1H, CH_2=, J = 8.71 Hz), 5.98 d (1H, CH_2=, J = 15.25 Hz), 7.30 d.d (1H, =CH, J = 8.71, 15.25 Hz). ^{13}C NMR spectrum, δ_C, ppm: 109.66 (CH_2=), 127.20 (=CH), 141.98 (C^5). Found, %: C 35.55; H 4.35; N 60.1. $C_3H_4N_4$. Calculated, %: C 35.50; H 4.20; N 58.31.

5,5′-Methylenebis(2-vinyl-2*H*-tetrazole) (IX). Yield 1.4 g (30%), light yellow crystals, mp 53–54°C, R_f 0.6 (methylene chloride–hexane–ethyl acetate, 8:1:1). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 4.72 d

(2H, CH_2), 5.51 d (2H, CH_2=, J = 8.72 Hz), 6.10 d (2H, CH_2=, J = 15.99 Hz), 7.83 d.d (2H, =CH, J = 8.72, 15.99 Hz). ^{13}C NMR spectrum, δ_C, ppm: 22.04 (CH_2), 109.58 (CH_2=), 130.14 (=CH), 162.08 (C^5). Found, %: C 41.10; H 4.19; N 54.71. $C_7H_8N_8$. Calculated, %: C 41.17; H 3.95; N 54.88.

1-Vinyl-5-(2-vinyl-2*H*-tetrazol-5-ylmethyl)-1*H*-tetrazole (X). Yield 0.9 g (20%), light yellow crystals, mp 46–47°C, R_f 0.2 (methylene chloride–hexane–ethyl acetate, 8:1:1). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 4.91 s (2H, CH_2), 5.48–5.54 m and 6.01–6.12 m (2H each, 1-CH=C**H**$_2$, 2′-CH=C**H**$_2$), 7.48 d.d (1H, 1-CH, J = 8.02, 14.21 Hz), 7.84 d.d (1H, 2′-CH, J = 8.72, 15.99 Hz). ^{13}C NMR spectrum, δ_C, ppm: 20.01 (CH_2), 109.77 (2′-CH=**C**H_2), 110.31 (1-CH=**C**H_2), 126.52 (1-CH), 130.12 (2′-CH), 153.41 (C^5), 160.81 ($C^{5'}$). Found, %: C 41.60; H 3.90; N 54.50. $C_7H_8N_8$. Calculated, %: C 41.17; H 3.95; N 54.88.

5,5′-(Benzene-1,3-diyl)bis(2-vinyl-2*H*-tetrazole) (XII). Yield 3.6 g (59%), colorless crystals, mp 130–131°C, R_f 0.7 (methylene chloride–hexane–ethyl acetate, 8.5:1:0.5). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 5.58 d (2H, CH_2=, J = 8.72 Hz), 6.23 d (2H, CH_2=, J = 15.26 Hz), 7.75 m (1H, C_6H_4), 7.90 d.d (2H, =CH, J = 8.72, 15.26 Hz), 8.21 d (2H, C_6H_4), 8.71 s (1H, C_6H_4). ^{13}C NMR spectrum, δ_C, ppm: 109.82 (CH_2=); 124.33, 127.24, 130.24, 130.47 (C_6H_4); 128.76 (=CH); 163.28 (C^5). Found, %: C 54.27; H 3.45; N 42.28. $C_{12}H_{10}N_8$. Calculated, %: C 54.13; H 3.79; N 42.08.

1-Vinyl-5-[3-(2-vinyl-2*H*-tetrazol-5-yl)phenyl]-1*H*-tetrazole (XIII). Yield 0.9 g (15%), colorless crystals, mp 146–147°C, R_f 0.5 (methylene chloride–hexane–ethyl acetate, 8.5:1:0.5). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 5.60 d (2H, 2′-CH=C**H**$_2$, 1-CH=C**H**$_2$, J = 8.72 Hz), 6.08 d (1H, 1-CH=C**H**$_2$, J = 15.26 Hz), 6.27 d (1H, 2′-CH=C**H**$_2$, J = 16.71 Hz), 7.41 d.d (1H, 1-CH, J = 8.72, 15.26 Hz), 7.83–7.89 m (3H, 2′-CH, H_{arom}), 8.37 d (2H, H_{arom}), 8.48 s (1H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 110.03 (2′-CH=**C**H_2), 112.52 (1-CH=**C**H_2), 124.42 (1-CH), 129.40 (2′-CH); 127.28, 130.30, 130.47, 131.57 (C_6H_4); 152.21 (C^5), 163.16 ($C^{5'}$). Found, %: C 54.23; H 3.75; N 42.02. $C_{12}H_{10}N_8$. Calculated, %: C 54.13; H 3.79; N 42.08.

1,2-Bis{5-[3-(2-vinyl-2*H*-tetrazol-5-yl)phenyl]-2*H*-tetrazol-2-yl}ethane (XIV). Yield 0.1 g (2%), colorless crystals, mp 204–205°C, R_f 0.3 (methylene chloride–hexane–ethyl acetate, 8.5:1:0.5). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 5.48 s (4H, CH_2), 5.55 d (2H, CH_2=, J = 8.72 Hz), 6.18 d (2H, CH_2=, J = 15.26 Hz), 7.70 m (2H, H_{arom}), 7.87 d.d (2H, =CH, J = 8.72, 15.26 Hz), 8.12–8.19 m (4H, H_{arom}), 8.61 s (2H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 51.94 (CH_2), 109.75 (CH_2=), 128.44 (=CH); 124.13, 127.22, 127.51, 128.51, 130.18, 130.43 (C_{arom}); 163.25 (C^5), 163.64 ($C^{5'}$). Mass spectrum: m/z 507.48 $[M + H]^+$. M 506.49.

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