Vinyltetrazoles and their derivatives are promising substrates in the synthesis of various tetrazole-containing polymers with valuable properties utilized in medicine and engineering [1]. Synthesis of some derivatives of vinyltetrazoles, in particular, of styryltetrazoles, is poorly understood.

In a series of publications [2, 3] the synthesis of styryltetrazoles, containing substituents with strong electron-acceptor properties (F, NO₂, CN, CO₂H) in the aryl fragment based on cross-coupling of C-, N-vinyltetrazole with halobenzenes by Heck reaction is described. However no information exists on the synthesis of similar compounds containing electron-donor substituents. The electronic effect of the substituent in the aromatic fragment may significantly affect the efficiency of this reaction. The nature of the halogen present in the haloarene and the composition of the catalytic system are also of fundamental importance [4–7].

In this study we synthesized styryltetrazoles 3a–3d, containing in the para-position of the aromatic fragment donor (Me, t-Bu, MeO) and weakly acceptor (Cl) substituents. In the reaction with 2-methyl-5-vinyl-2H-tetrazole iodoarenes 2a–2d were used applying as a catalyst Pd(OAc)₂. The reaction was carried out in the presence of K₂CO₃ in DMF at heating.

In all cases the reaction proceeded with high yields (73–80%). The cross-coupling occurs stereoselectively affording exclusively E-2-methyl-5-styryltetrazoles 3a–3d, as show the large values of the spin-spin coupling constants (J 16.5 Hz).

Hence, 2-methyl-5-vinyl-2H-tetrazole enters in Heck reaction with iodoarenes containing not only electron-acceptor (as has been shown in [2, 3]), but also electron-donor substituents at the use as a catalytic system Pd(OAc)₂ in the presence of K₂CO₃ in DMF.

2-Methyl-5-styryl-2H-tetrazoles (3a–3d). General procedure. Pd(OAc)₂ (4 mol %) was added to a solution of 45 mmol of iodoarene 2a–2d in 5 mL of DMF under an argon atmosphere. The reaction mixture
was heated at 50°C while stirring for 20 min, then 9 mmol of 2-methyl-5-vinyl-2H-tetrazole 1 and 18 mmol of K₂CO₃ was added. The obtained slurry was heated at 120°C for 3 h under stirring. On cooling the reaction mixture was poured in water, the product was extracted with ethyl acetate (3 × 50 mL), combined extracts were dried with Na₂SO₄. The solvent was distilled off in a vacuum, the residue was chromatographed on silica gel (Merck, Silica gel 60), eluent petroleum ether–ethyl ether.

(E)-2-Methyl-5-[2-(4-methylphenyl)ethenyl]-2H-tetrazole (3a). Yield 75%. Colorless crystals, mp 125–126°C. ¹H NMR spectrum, δ, ppm: 2.38 s (3H, CH₃), 4.35 s (3H, NCH₃), 7.08 d (1H, CH=CHPh, ³J 16.5 Hz), 7.19 d (2HAr, ³J 8.5 Hz), 7.45 (2HAr, ³J 8.5 Hz), 7.69 d (1H, CH=CHPh, ³J 16.5 Hz). ¹³C NMR spectrum, δ, ppm: 21.27, 39.23, 112.32, 127.01, 129.48, 132.90, 136.15, 152.39, 164.57. Found m/z 217.1084 [M + H]⁺. C₁₁H₁₂N₄. Calculated M + H 217.1089.

(E)-5-[2-(4-tert-Butylphenyl)ethenyl]-2-methyl-2H-tetrazole (3b). Yield 77%. Colorless crystals, mp 81–82°C. ¹H NMR spectrum, δ, ppm: 1.34 s [9H, C (CH₃)₃], 4.35 s (3H, NCH₃), 7.11 d (1H, CH=CHPh, ³J 16.5 Hz), 7.42 d (2HAr, ³J 8.3 Hz), 7.50 d (2HAr, ³J 8.3 Hz), 7.71 d (1H, CH=CHPh, ³J 16.5 Hz). ¹³C NMR spectrum, δ, ppm: 31.20, 34.74, 39.28, 112.57, 125.76, 128.50, 128.55, 135.88, 160.40, 164.69. Found m/z 243.1604 [M + H]⁺. C₁₄H₁₆N₄. Calculated M + H 243.1610.

(E)-2-Methyl-5-[2-(4-chlorophenyl)ethenyl]-2H-tetrazole (3c). Yield 64%. Colorless crystals, mp 130–131°C. ¹H NMR spectrum, δ, ppm: 3.84 s (3H, OCH₃), 7.10 d (1H, CH=CHPh, ³J 16.5 Hz), 7.36 d (2HAr, ³J 8.5 Hz), 7.48 d (2HAr, ³J 8.5 Hz), 7.67 d (1H, CH=CHPh, ³J 16.5 Hz). ¹³C NMR spectrum, δ, ppm: 39.31, 55.35, 111.12, 114.29, 128.50, 128.55, 135.88, 160.40, 164.69. Found m/z 201.1139 [M + H]⁺. C₁₁H₁₂ClN₄. Calculated M + H 201.1135.

(E)-2-Methyl-5-[2-(4-methoxyphenyl)ethenyl]-2H-tetrazole (3d). Yield 80%. Colorless crystals, mp 110–111°C. ¹H NMR spectrum, δ, ppm: 3.43 s (3H, OCH₃), 6.92 d (2HAr, ³J 8.7 Hz), 7.0 d (1H, CH=CHPh, ³J 16.4 Hz), 7.50 d (2HAr, ³J 8.7 Hz), 7.67 d (1H, CH=CHPh, ³J 16.4 Hz). ¹³C NMR spectrum, δ, ppm: 39.31, 55.35, 111.12, 114.29, 128.50, 128.55, 135.88, 160.40, 164.69. Found m/z 201.1139 [M + H]⁺. C₁₁H₁₂ClN₄. Calculated M + H 201.1135.

¹H and ¹³C NMR spectra were registered on a spectrometer Bruker AM-500 (operating frequencies 500 and 125.76 MHz respectively) in CDCl₃ at 20°C. The solvent signals served as internal references (δH 7.26, δC 77.0 ppm). High resolution mass spectra were measured on an instrument Bruker MicroTOF (ESI) in the resource center «Methods of analysis of substances composition» of the Saint-Petersburg State University.

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