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## SHORT COMMUNICATIONS

# Synthesis of New Sulfur-Containing Vinyl Monomers Derived from Tetrazole-5-thiols

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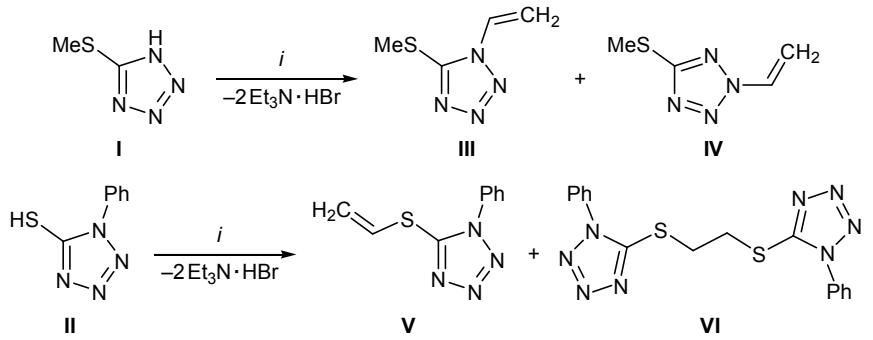
Polyvinyltetrazoles are high-molecular compounds which were used to prepare nitrogen-rich composite materials [1–3]. Monomers for the synthesis of polyvinyltetrazoles are *C*- and *N*-vinyltetrazoles, including those containing various aliphatic, aromatic, or other substituents on the heteroring [2–3]. There are no published data on vinyltetrazoles having a sulfur-containing substituent. On the other hand, it is known that sulfur-containing monomers are quite promising from the viewpoint of preparation of polymeric materials widely used in modern technologies and medicine [4]. Therefore, synthesis and further study of monomers containing a nitrogen-rich tetrazole ring, sulfur atom, and vinylic double bond constitute an important problem.

We were the first to synthesize vinyl-substituted derivatives of 5-methylsulfanyl-1*H*-tetrazole (**I**) and 1-phenyl-1*H*-tetrazole-5-thiol (**II**) (Scheme 1). Vinyltetrazoles **III**–**VI** were obtained according to [5] by alkylation of tetrazoles **I** and **II** with 1,2-dibromoethane in the presence of triethylamine in acetonitrile, followed by elimination of triethylamine hydrobromide. According to the $^1$H NMR data, the ratio of 1- and 2-vinyl derivatives **III** and **IV** in the reaction mixture was 70:30. Vinylation of 1-phenyl-1*H*-tetrazole-5-thiol (**II**) gave 1-phenyl-5-vinylsulfanyl-1*H*-tetrazole (**V**) and 1,2-bis(1-phenyl-1*H*-tetrazol-5-ylsulfanyl)ethane (**VI**) at a ratio of 75:25. By Heck arylation [6] of tetrazole **IV** we synthesized 5-methylsulfanyl-2-[(*E*)-2-phenylethenyl]-2*H*-tetrazole (**VII**) (Scheme 2).

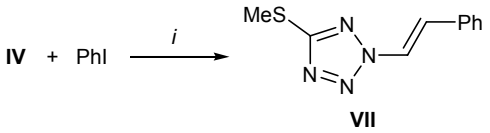
**Tetrazoles III–VI (***general procedure***).** A solution of 58.8 mmol of 1,2-dibromoethane in 10 ml of acetonitrile was heated to the boiling point, a solution of 29.4 mmol of tetrazole **I** or **II** and 115 mmol of triethylamine in 30 ml of acetonitrile was added under vigorous stirring over a period of 2 h, and the mixture was heated for 5 h under reflux. The resulting suspension was cooled to 5°C, the precipitate of triethylamine hydrobromide was filtered off, the filtrate was evaporated to dryness under reduced pressure, and 30 ml of chloroform was added to the residue. The solution was washed with water (28 ml) and dried over anhydrous $Na_2SO_4$, and the solvent was removed under reduced

**Scheme 1.**




*i*: $Br(CH_2)_2Br$, $Et_3N$, MeCN, Δ.

**Scheme 2.**




**VII**

*i*: $Pd(OAc)_2$, $PPh_3$, CuI, $Cs_2CO_3$, DMF, 100°C.

pressure. The product ratio in the residue was determined by $^1$H NMR. Regioisomeric vinyltetrazoles **III** and **IV** were isolated and purified by column chromatography on silica gel using hexane–chloroform–ethyl acetate (8 : 1 : 1) as eluent. A mixture of tetrazoles **V** and **VI** was treated with 60 ml of boiling 70% aqueous ethanol, the mixture was heated for 10 min under reflux and filtered, and the precipitate (tetrazole **VI**) was recrystallized from 40 ml of carbon tetrachloride. The filtrate was cooled, and the precipitate (tetrazole **V**) was filtered off and dried in a stream of air over a period of 1 h.

**5-Methylsulfanyl-1-vinyl-1*H*-tetrazole (III).** Yield 1.1 g (25%), light yellow oily liquid, $R_f$ 0.3 (hexane–ethyl acetate, 7 : 3). $^1$H NMR spectrum (DMSO-$d_6$), δ, ppm: 2.79 s (3H, $CH_3$), 5.52 d.d (1H, =$CH_2$, $J$ = 1.5, 8.8 Hz), 5.90 d.d (1H, =$CH_2$, $J$ = 1.5, 15.4 Hz), 7.32 d.d (1H, CH=, $J$ = 8.8, 15.4 Hz). $^{13}$C NMR spectrum, $\delta_C$, ppm: 15.50 ($CH_3$), 110.90 (=$CH_2$), 126.76 (CH=), 154.59 ($C^5$). Mass spectrum: $m/z$ 143.21 $[M + H]^+$. $M$ 142.18.

**5-Methylsulfanyl-2-vinyl-2*H*-tetrazole (IV).** Yield 2.7 g (65%), colorless crystals, mp 40–41°C, $R_f$ 0.7 (hexane–ethyl acetate, 7 : 3). $^1$H NMR spectrum (DMSO-$d_6$), δ, ppm: 2.68 s (3H, $CH_3$), 5.48 d.d (1H, =$CH_2$, $J$ = 1.4, 8.7 Hz), 6.06 d.d (1H, =$CH_2$, $J$ = 1.5, 15.5 Hz), 7.79 d.d (1H, CH=, $J$ = 8.7, 15.5 Hz). $^{13}$C NMR spectrum, $\delta_C$, ppm: 14.37 ($CH_3$), 109.51 (=$CH_2$), 130.40 (CH=), 165.41 ($C^5$). Mass spectrum: $m/z$ 143.20 $[M + H]^+$. $M$ 142.18.

**1-Phenyl-5-vinylsulfanyl-1*H*-tetrazole (V).** Yield 4.1 g (70%), colorless crystals, mp 56–57°C, $R_f$ 0.8 (hexane–ethyl acetate, 7 : 3). $^1$H NMR spectrum (DMSO-$d_6$), δ, ppm: 5.69 d (1H, =$CH_2$, $J$ = 1.2 Hz), 5.72 d.d (1H, =$CH_2$, $J$ = 1.2, 9.8 Hz), 6.92 m (1H, CH=, $J$ = 1.3, 9.8, 16.7 Hz), 7.66 s (5H, Ph). $^{13}$C NMR spectrum, $\delta_C$, ppm: 120.85 (=$CH_2$), 124.61 (CH=); 125.25, 129.76, 130.42, 130.61, 131.27, 132.94 (Ph); 152.27 ($C^5$). Mass spectrum: $m/z$ 205.15 $[M + H]^+$. $M$ 204.25.

**1,2-Bis(1-phenyl-1*H*-tetrazol-5-ylsulfanyl)ethane (VI).** Yield 1.9 g (18%), colorless crystals, mp 143–144°C, $R_f$ 0.2 (hexane–ethyl acetate, 7 : 3). $^1$H NMR spectrum (DMSO-$d_6$), δ, ppm: 3.79 s (4H, $CH_2$), 7.60–7.66 m (10H, Ph). $^{13}$C NMR spectrum, $\delta_C$, ppm: 32.32 ($CH_2$); 124.57, 129.96, 130.64, 132.97 (Ph); 153.71 ($C^5$). Mass spectrum: $m/z$ 383.51 $[M + H]^+$. $M$ 382.47.

**5-Methysulfanyl-2-[(*E*)-2-phenylethenyl]-2*H*-tetrazole (VII).** A suspension of 0.2 g (1.4 mmol) of tetrazole **IV**, 0.28 g (1.4 mmol) of CuI, 0.7 g (2.2 mmol) of $Cs_2CO_3$, 0.013 g (0.056 mmol) of $Pd(OAc)_2$, 0.044 g (0.17 mmol) of $PPh_3$, and 1.5 g (7 mmol) of iodobenzene in 2 ml of DMF was heated to 100°C and was kept for 6 h at that temperature under argon. The mixture was cooled to 25°C and poured into 10 ml of water, and the resulting suspension was filtered through celite. The filtrate was extracted with ethyl acetate (3×15 ml), the combined extracts were dried over anhydrous $Na_2SO_4$ and evaporated under reduced pressure, the residue was dispersed in 20 ml of hexane, and the precipitate was filtered off. Yield 0.3 g (85%), colorless crystals, mp 60–61°C, $R_f$ 0.2 (hexan–ethyl acetate, 9 : 1). $^1$H NMR spectrum (DMSO-$d_6$), δ, ppm: 2.72 s (3H, $CH_3$), 7.37–7.42 m (3H, Ph), 7.58 d (1H, C**H**Ph, $J$ = 14.4 Hz), 7.74–7.76 m (2H, Ph), 8.48 d (1H, 2-CH, $J$ = 14.4 Hz). $^{13}$C NMR spectrum, $\delta_C$, ppm: 14.44 ($CH_3$), 123.39 (**C**HPh); 124.96, 128.07, 129.37 (Ph); 129.74 (2-CH), 133.36 (Ph), 165.21 ($C^5$). Mass spectrum: $m/z$ 219.31 $[M + H]^+$. $M$ 218.28.

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 solvent as reference (DMSO-$d_5$, δ 2.50 ppm; DMSO-$d_6$, $\delta_C$ 39.52 ppm). The mass spectra were obtained on a Thermo Scientific TSQ Quantum Access MAX LC/MS instrument. The melting points were determined on a PTP melting point apparatus; samples were heated at a rate of 1 deg/min near the melting point. The purity of the isolated compounds was checked by TLC on Kieselgel $60F_{254}$ plates (Merck); spots were detected under UV light (λ 254 nm). The properties of initial tetrazoles **I** and **II** were consistent with published data [7].

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