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SHORT COMMUNICATIONS

Dedicated to Full Member of the Russian Academy of Sciences N.S. Zefirov on his 80th anniversary

Hydroarylation of (*E*)-2-Methyl-5-(2-phenylethenyl)-2*H*-tetrazole under Superelectrophilic Activation

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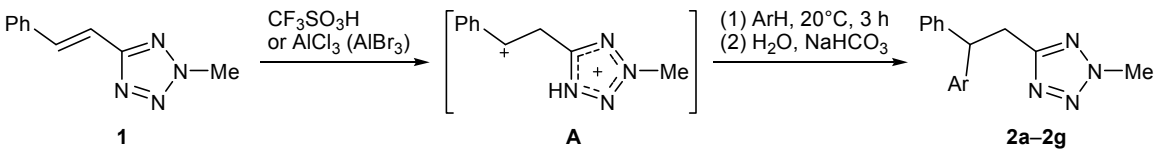
5-(2-Phenylethenyl)tetrazoles (5-styryltetrazoles) are promising monomers for the preparation of tetrazole-containing polymers [1–4]. Functionalized styryltetrazoles themselves exhibit antimicrobial [5], antidiabetic [6], and other kinds of biological activity. 5-Styryltetrazoles contain an exocyclic double C=C bond conjugated with the heterocyclic system and are capable of entering classical chemical transformations typical of that bond. Of particular interest are reactions of 5-styryltetrazoles occurring in Brønsted or Lewis acids. These reactions could give rise to various functional derivatives of 5-alkyltetrazoles. Up to now such chemical transformations remain almost unexplored. We previously reported on the reaction of 2- and 5-(2-phenylethenyl)-2*H*-tetrazoles with benzene in CF_3SO_3H (Brønsted superacid) [7].

Herein we describe the hydroarylation of (*E*)-2-methyl-5-(2-phenylethenyl)-2*H*-tetrazole (**1**) at the exocyclic double bond with benzene, *m*- and *p*-xylenes, anisole, and veratrole in trifluoromethanesulfonic acid or in the presence of strong Lewis acids ($AlCl_3$, $AlBr_3$), i.e., under conditions of superelectrophilic activation [8–10].

Obviously, tetrazole **1** in superacids can be protonated at both N^4 of the tetrazole ring [11] and double-bonded carbon atom to form reactive dication **A** [8] which then reacts as electrophile with arenes, yielding hydroarylation products at the C=C bond, compounds **2a**–**2g**. In the reactions with anisole and veratrole, regioisomer mixtures **2d**/**2e** and **2f**/**2g**, respectively, were obtained.

Thus, (*E*)-2-methyl-5-(2-phenylethenyl)-2*H*-tetrazole (**1**) effectively reacts with various arenes containing electron-donating substituents in the presence of Brønsted or Lewis superacids to give 5-(2-aryl-2-phenylethyl)-2-methyl-2*H*-tetrazoles **2a**–**2g**.

5-(2,2-Diphenylethyl)-2-methyl-2*H*-tetrazole (2a). Tetrazole **1**, 0.27 mmol, was slowly added to a mixture of 4 mL of anhydrous benzene and 1.34 mmol of $AlBr_3$ or $AlCl_3$ under vigorous stirring at 20°C. The mixture was stirred for 3 h, poured into 20 mL of water, treated with a saturated aqueous solution of $NaHCO_3$ until pH 8–9, and extracted with chloroform (3×30 mL). The combined extracts were dried over Na_2SO_4, and the solvent was removed under reduced pressure. Yield 90–95%, colorless crystals,



1 **A** **2a–2g**

Ar = Ph (**a**), 2,4-$Me_2C_6H_3$ (**b**), 2,5-$Me_2C_6H_3$ (**c**), 4-$MeOC_6H_4$ (**d**), 2-$MeOC_6H_4$ (**e**), 3,4-$(MeO)_2C_6H_3$ (**f**), 2,3-$(MeO)_2C_6H_3$ (**g**).

mp 115–116°C [7]. ^{1}H NMR spectrum, δ, ppm: 3.64 d (2H, CH_2, J = 8.2 Hz), 4.20 s (3H, CH_3), 4.70 t (1H, CH, J = 8.2 Hz), 6.78–6.80 m (3H, H_{arom}), 7.15–7.29 m (7H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 31.6, 39.1, 49.5, 126.5, 127.8, 128.5, 143.3, 165.2.

5-[2-(2,4-Dimethylphenyl)-2-phenylethyl]-2-methyl-2*H*-tetrazole (2b). Tetrazole **1**, 0.27 mmol, was slowly added to a solution of 0.32 mmol of the corresponding arene in 1 mL of CF_3SO_3H under vigorous stirring at 20°C. The mixture was stirred for 3 h, poured into 20 mL of water, and then treated as described above. Yield 73%, oily substance. ^{1}H NMR spectrum, δ, ppm: 2.25 s (6H, CH_3), 3.60 d (2H, CH_2, J = 8.2 Hz), 4.21 s (3H, CH_3), 4.61 t (1H, CH, J = 8.2 Hz), 7.00–7.27 m (8H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 21.3, 31.6, 39.2, 49.4, 125.6, 126.4, 126.5, 127.8, 128.2, 128.4, 128.5, 137.9, 143.3, 143.5, 165.3. Mass spectrum, m/z (I_{rel}, %): 292 (16) $[M]^+$, 195 (100), 180 (18), 165 (25). Found: m/z 293.1760 $[M + H]^+$. $C_{18}H_{20}N_4$. Calculated: M + H 293.1761.

Compounds **2c**–**2g** were synthesized in a similar way.

5-[2-(2,5-Dimethylphenyl)-2-phenylethyl]-2-methyl-2*H*-tetrazole (2c). Yield 80%, oily material. ^{1}H NMR spectrum, δ, ppm: 2.24–2.33 m (6H, CH_3), 3.60–3.64 m (2H, CH_2), 4.21 s (3H, CH_3), 4.60–4.71 m (1H, CH), 7.08–7.27 m (8H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 20.9, 31.5, 39.1, 49.5, 124.6, 126.4, 127.7, 128.4, 129.1, 129.8, 132.4, 134.0, 143.3, 165.1. Found: m/z 293.1764 $[M + H]^+$. $C_{18}H_{20}N_4$. Calculated: M + H 293.1761.

5-[2-(4-Methoxyphenyl)-2-phenylethyl]-2-methyl-2*H*-tetrazole (2d). Yield 62%, oily material. ^{1}H NMR spectrum, δ, ppm: 3.59 d (2H, CH_2, J = 8.2 Hz), 3.75 s (3H, OCH_3), 4.21 s (3H, CH_3), 4.64 t (1H, CH, J = 8.2 Hz), 6.79 d (2H, H_{arom}, J = 8.7 Hz), 7.14–7.18 m (4H, H_{arom}), 7.25 s (3H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 31.8, 39.2, 48.8, 55.2, 113.9, 126.4, 127.7, 128.5, 128.8, 135.5, 143.8, 158.1, 165.3. Mass spectrum, m/z (I_{rel}, %): 294 (5) $[M]^+$, 197 (100), 182 (4), 165 (10), 153 (11). Found: m/z 295.1558 $[M + H]^+$. $C_{17}H_{18}N_4O$. Calculated: M + H 295.1553.

5-[2-(2-Methoxyphenyl)-2-phenylethyl]-2-methyl-2*H*-tetrazole (2e). Yield 24%, oily material. ^{1}H NMR spectrum, δ, ppm: 3.49–3.55 m (2H, CH_2), 3.81 s (3H, OCH_3), 4.19 s (3H, CH_3), 4.50–4.56 m (1H, CH), 6.75–7.85 m (9H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 31.8, 39.1, 48.7, 55.5, 113.8, 115.4, 127.8, 128.7, 129.4, 135.4, 143.2, 158.1, 165.1. Found: m/z 295.1558 $[M + H]^+$. $C_{17}H_{18}N_4O$. Calculated: M + H 295.1553.

5-[2-(3,4-Dimethoxyphenyl)-2-phenylethyl]-2-methyl-2*H*-tetrazole (2f). Yield 66%, oily material. ^{1}H NMR spectrum, δ, ppm: 3.59 d.d (2H, CH_2, J = 8.3 Hz), 3.81 s (3H, OCH_3), 3.82 s (3H, OCH_3), 4.20 s (3H, CH_3), 4.64 t (1H, CH, J = 9 Hz), 6.72–7.27 m (8H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 31.9, 39.2, 49.1, 55.8, 55.8, 111.2, 111.5, 119.6, 126.5, 127.7, 128.5, 135.9, 143.6, 147.6, 148.8, 165.3. Found: m/z 325.1654 $[M + H]^+$. $C_{18}H_{20}N_4O_2$. Calculated: M + H 325.1659.

5-[2-(2,3-Dimethoxyphenyl)-2-phenylethyl]-2-methyl-2*H*-tetrazole (2g). Yield 10%, oily material. ^{1}H NMR spectrum, δ, ppm: 3.59 d (2H, CH_2, J = 8.3 Hz), 3.81 s (3H, OCH_3), 3.82 s (3H, OCH_3), 4.20 s (3H, CH_3), 4.59 t (1H, CH, J = 8.3 Hz), 6.72–7.27 m (8H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 31.7, 39.2, 49.0, 55.8, 111.2, 114.2, 119.1, 127.8, 126.4, 128.5, 135.9, 143.6, 147.6, 165.3. Found: m/z 325.1654 $[M + H]^+$. $C_{18}H_{20}N_4O_2$. Calculated: M + H 325.1659.

(*E*)-2-Methyl-5-(2-phenylethenyl)-2*H*-tetrazole (**1**) was reported previously [12].

The ^{1}H and ^{13}C NMR spectra were recorded at 25°C on Bruker AM-500 (500 and 125 MHz, respectively) and Bruker AM-400 spectrometers (400 and 100 MHz) from solutions in $CDCl_3$; the chemical shifts were measured relative to the residual proton and carbon signals of the solvent ($CHCl_3$, δ 7.26 ppm; $CDCl_3$, δ_C 77.0 ppm). GC/MS analyses were obtained on an Agilent Technologies G2570A/6850s instrument (HP-5MS capillary column, 3 m×0.25 mm, film thickness 0.25 μm). The high-resolution mass spectra were recorded on a Bruker MicroTOF spectrometer (electrospray ionization) at the Resource Center for Chemical Analysis and Materials Research (St. Petersburg State University).

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