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## SHORT COMMUNICATIONS

Dedicated to the memory of Professor G.I. Koldobskii

# First Example of a Reaction of *C*- and *N*-Styryltetrazoles with Benzene in Superacid $CF_3SO_3H$

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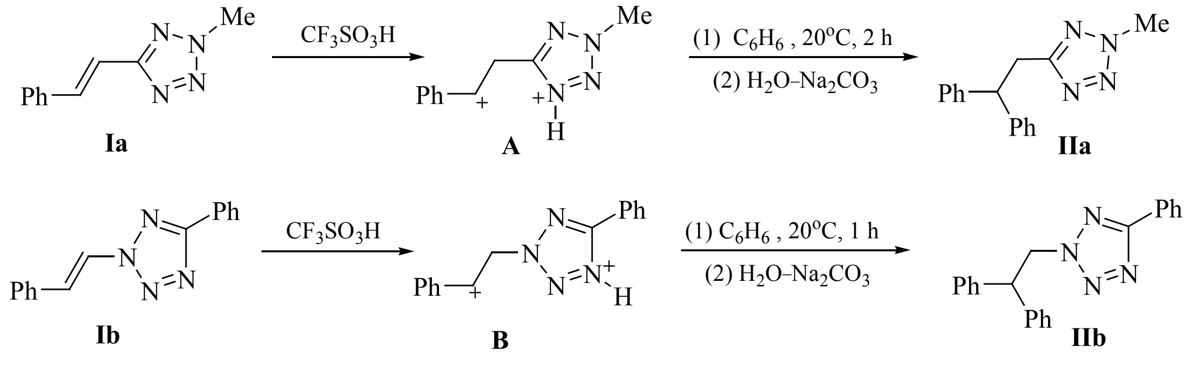
Tetrazole derivatives are utilized in versatile spheres of human action [1]. Among the most promising compounds for the organic synthesis are *C*- and *N*-styryltetrazoles [2], yet they are the least studied. These compounds possessing a heteroaromatic system conjugated with a double carbon-carbon bond can be involved into chemical reactions at both these structural moieties. The reactions of *C*- and *N*-styryltetrazoles in superacids are especially interesting. These reactions are able to result in new, previously unavailable tetrazole derivatives of unusual structure and practically useful properties. However no information was published on the action of superacids on the styryltetrazoles.

We report here on the investigation of the reactions between 2-methyl-5-[(*E*)-2-phenylethenyl]- and 5-phenyl-2-[(*E*)-2-phenylethenyl]-2*H*-tetrazoles (**Ia, Ib**) and benzene in the superacid of Brønsted type $CF_3SO_3H$ applied to the superelectrophilic activation of organic compounds [3].

The protonation in $CF_3SO_3H$ of compounds **Ia, Ib** at the atom $N^4$ of the tetrazole ring [4] and at the carbon atom of the C=C bond of the phenylvinyl substituent provides reactive dications **A** and **B**. These species are involved in the reaction of the electrophilic aromatic substitution with benzene at 20°C for 1–2 h and then are subjected to the treatment with aqueous alkali to destroy the superacid which leads to the formation of tetrazoles **IIa, IIb** in 70 and 67% yields respectively.

We have demonstrated for the first time that the conversion of both *C*- and *N*-styryltetrazoles in superacid proceeds chemoselectively exclusively at the C=C bond and does not affect the tetrazole ring.

Ethenyltetrazoles **Ia, Ib** were prepared and character-



ized before [5].

**Reaction of tetrazoles Ia, Ib with benzene in $CF_3SO_3H$**. To a mixture of 0.5 ml of anhydrous benzne and 1 ml of $CF_3SO_3H$ at 20°C while vigorously stirring was gradually added within 5 min 0.27 mmol of styryltetrazole **Ia, Ib**. The reaction mixture was stirred additionally for 1–2 h, then it was poured into 15 ml of $H_2O$, the saturated water solution of $Na_2CO_3$ was added to pH 8–9, and the product was extracted into chloroform (3 × 30 ml). The combined extract was dried with $Na_2SO_4$, evaporated in a vacuum, the residue was recrystallized from 2-propanol.

**5-(2,2-Diphenylethyl)-2-methyl-*2H*-tetrazole (IIa)**. Yield 70%, mp 113–114°C. $^1H$ NMR spectrum, δ, ppm: 3.58 d (2H, $CH_2$, *J* 8.1 Hz), 4.21 s (3H, Me), 4.59 t (1H, CH, *J* 8.1 Hz), 7.14 t ($2H_{arom}$, *J* 7.2 Hz), 7.24 t ($4H_{arom}$, *J* 7.2 Hz), 7.30 d ($4H_{arom}$, *J* 7.2 Hz). $^{13}C$ NMR spectrum, δ, ppm: 30.36, 39.25, 49.10, 126.27, 127.55, 128.36, 143.57, 164.56. Mass spectrum, *m/z*: 264.9852 $[M]^+$, 302.9377 $[M + K]^+$. $C_{16}H_{16}N_4$. Calculated: *M* 264.1375, [*M* + K] 303.1012.

**2-(2,2-Diphenylethyl)-5-phenyl-*2H*-tetrazole (IIb)**. Yield 67%, mp 104–105°C. $^1H$ NMR spectrum, δ, ppm: 4.91 t (1H, CH, *J* 8.4 Hz), 5.51 d (2H, $CH_2$, *J* 8.4 Hz), 7.17–7.20 m ($2H_{arom}$), 7.26–7.30 m ($4H_{arom}$), 7.45–7.54 m ($7H_{arom}$), 7.97–7.99 m ($2H_{arom}$). $^{13}C$ NMR spectrum, δ, ppm: 50.12, 56.43, 126.22, 126.91, 127.75, 128.52, 129.20, 130.62, 141.17, 164.01. Mss-spectrum, *m/z*: 326.9507 $[M]^+$, 364.9091 $[M + K]^+$. $C_{21}H_{18}N_4$. Calculated: *M* 326.1531, [*M* + K] 365.1169.

$^1H$ and $^{13}C$ NMR spectra were registered on a spectrometer Bruker Avance 400 (operating frequencies 400.13 and 100.62 MHz respectively) in DMSO-$d_6$ at 20°C. As internal references served the solvent signal, that of residual protons at δ 2.50 ppm ($^1H$) and of carbon atom at δ 39.5 ppm ($^{13}C$). Mass spectrum of high resolution was obtained on an instrument Waters LCT Premier, (ESI, TOF).

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