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Brief Communications

Mononuclear rearrangement of difurazanyltriazenes

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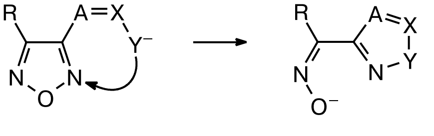
Base-catalyzed rearrangement in one of the heterocycles of difurazanyltriazenes gave the corresponding 2-furazanyltetrazoles bearing functional groups capable of further transformations.

Key words: furazans, 1,2,5-oxadiazoles, triazenes, tetrazoles, 2-furazanyltetrazoles, rearrangement.

Mononuclear rearrangements of heterocycles are very common and attract the attention of researchers by their easy occurrence and the possibility of obtaining reactive functionalized derivatives of other classes of heterocyclic compounds.[1,2] In the series of 1,2,5-oxadiazoles, such rearrangements are being extensively investigated. Oximes, hydrazones, formamidines, and thioureas of the furazan series are known to be capable of undergoing base-catalyzed mononuclear rearrangements at sufficiently high temperatures (Scheme 1).[3]

Scheme 1



We found that difurazanyltriazenes **1a,b** can also be involved in an analogous rearrangement (Scheme 2).

The reaction occurs under comparatively mild conditions (90—95 °C) in aqueous KOH to give earlier unknown 2-furazanyltetrazoles **2a,b** containing functional groups convenient for construction of various polyheterocyclic systems. The structures of tetrazoles **2a,b** were proved by ^{1}H and ^{13}C NMR spectroscopy (Table 1). For instance, the ^{1}H NMR spectrum of compound **2a**, in contrast to **1a**, shows, apart from the signal of the proton of the hydroxyimino group at δ 12.33, two signals at δ 2.33 and 2.70 corresponding to two nonequivalent Me groups. The ^{13}C NMR spectra agree completely with the structures assigned. Comparison of the ^{13}C NMR spectra of compounds **2a,b**, as well as a survey of the literature data,[4] allow their unambiguous interpretation. The ^{13}C NMR spectra of furazans **2a,b** contain two most general and characteristic signals (see Table 1): the signal for the C(3) atom of the tetrazole ring appears at δ 158—163 and the signal for the tetrazole-bonded C(2) atom of the furazan ring is shifted upfield (δ 150—151). The chemical shifts for the other C atom of the furazan ring (C(1)) and the

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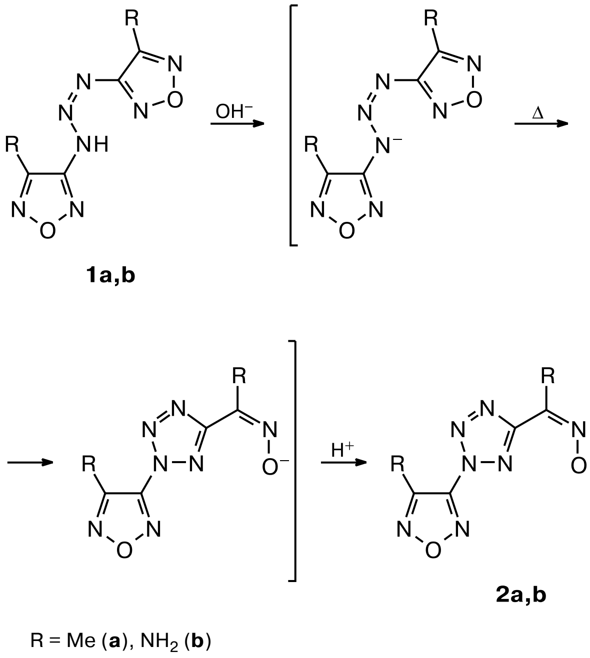
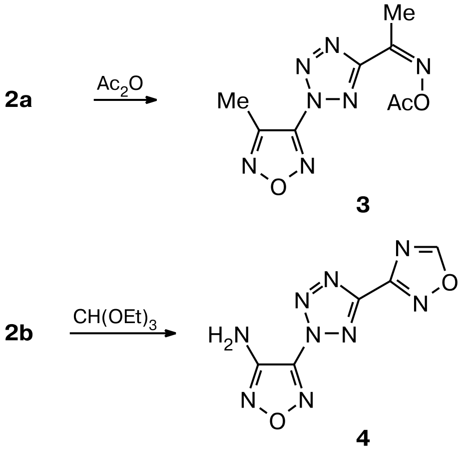
Scheme 2



C atom of the hydroxyimino group depend on the electronic properties of the substituent.

Some of the chemical properties of 2-furazanyltetrazoles **2a,b** were studied (Scheme 3). The reaction of hydroxyimino compound **2a** with Ac_2O afforded the corresponding acetyl derivative **3**. The condensation of amide oxime **2b** with $CH(OEt)_3$ yielded 1,2,4-oxadiazole **4**.

Scheme 3



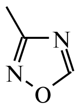
Experimental

^1H and ^{13}C NMR spectra were recorded on a Bruker AM-500 spectrometer in DMSO-d_6 with reference to the signals of the solvent (δ 2.50 and 39.5, respectively). Compounds **1a,b** were prepared according to a known procedure.[5]

Synthesis of compounds 2a,b (general procedure). Triazene **1a,b** (4.8 mmol) was added to a solution of KOH (0.81 g, 14.4 mmol) in 20 mL of water. The suspension was slowly heated to homogenization and allowed to cool to ~20 °C. Then the reaction mixture was neutralized with 5% HCl to pH 7. The precipitate that formed was filtered off, washed with water, and dried.

5-(1-Hydroxyiminoethyl)-2-(4-methylfurazan-3-yl)tetrazole (2a). Yield 86%, m.p. 125—126 °C (decomp., from MeOH).

Table 1. ^1H and ^{13}C NMR spectra of 2-furazanyltetrazoles **2**—**4** in DMSO-d_6 (R^1 and R^2 refer to the substituents in the furazan and tetrazole rings, respectively)

Compound	R^1	R^2	NMR, δ				
			^1H	^{13}C			
				C(1)	C(2)	C(3)	Other C atoms
2a	Me	C(=NOH)Me	2.33, 2.70 (both s, 3 H each, Me); 12.33 (s, 1 H, NOH)	147.34	150.27	163.28	9.31 (Me); 11.74 (C(=NOH)<u>Me</u>); 143.70 (<u>C</u>(=NOH)Me)
2b	NH_2	C(=NOH)NH_2	6.40, 6.93 (both s, 2 H each, NH_2); 10.44 (s, 1 H, NOH)	142.28	150.53	159.96	141.42 (C(=NOH)NH_2)
3	Me	C(=NOAc)Me	2.30, 2.57, 2.72 (all s, 3 H each, Me)	147.46	150.31	161.53	9.24 (Me); 14.05 (C(=NOAc)<u>Me</u>); 19.17 (CO<u>Me</u>); 152.70 (<u>C</u>(=NOAc)Me); 167.34 (<u>C</u>OMe)
4	NH_2		6.81 (s, 2 H, NH_2); 10.04 (s, 1 H, CH)	142.72	151.14	158.34	155.42 (N—C=N); 168.91 (O—C—N)

Found (%): C, 34.45; H, 3.37; N, 46.87. $C_6H_7N_7O_2$. Calculated (%): C, 34.51; H, 3.43; N, 46.81.

2-(4-Aminofurazan-3-yl)tetrazole-5-carbamide oxime (2b). Yield 74%, m.p. 176—177 °C (decomp., from water). Found (%): C, 22.75; H, 2.39; N, 59.70. $C_4H_5N_9O_2$. Calculated (%): C, 22.69; H, 2.44; N, 59.67.

5-(1-Acetoxyiminoethyl)-2-(4-methylfurazan-3-yl)tetrazole (3). A mixture of furazan **2a** (0.79 g, 3.8 mmol) and Ac_2O (10 mL) was heated to 70—80 °C and a catalytic amount of AcONa was added. The reaction mixture was stirred at this temperature for 10 min, cooled, and diluted with water (50 mL). The product was filtered off, washed with water, and dried. The yield of compound **3** was 0.78 g (82%), m.p. 120—121 °C (decomp., from hexane—$CHCl_3$ (3 : 1)). Found (%): C, 38.25; H, 3.61; N, 39.03. $C_8H_9N_7O_3$. Calculated (%): C, 38.28; H, 3.62; N, 39.12.

2-(4-Aminofurazan-3-yl)-5-(1,2,4-oxadiazol-3-yl)tetrazole (4). A mixture of furazan **2b** (0.25 g, 1.2 mmol) and $CH(OEt)_3$ (5 mL) was heated to 70—80 °C and one drop of $BF_3 \cdot Et_2O$ was added. The reaction mixture was stirred at this temperature for 10 min, cooled, and concentrated in air. The product was washed with water and dried. The yield of compound **4** was 0.24 g (91%), m.p. 157—158 °C (decomp., from water). Found (%): C, 27.16; H, 1.37; N, 57.01. $C_5H_3N_9O_2$. Calculated (%): C, 27.23; H, 1.32; N, 57.10.

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