1 H, OCH=); 4.31 and 4.05 (both dd, each 1 H, CH_2=, J_{cis} = 6.6 Hz, J_{trans} = 14.1 Hz, J_{gem} = 1.66 Hz); 4.09 (m, 1 H, C(3)H); 3.72 (m, 2 H, $C(1)H_2$); 2.61 (br.s, 1 H, OH); 1.64—1.84 (m, 2 H, $C(2)H_2$); 1.24 (d, 3 H, CH_3, $J_{4,3}$ = 6.2 Hz).

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Synthesis of 2-(furazanyl)indolizines

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Heating of *N*-[2-(4-methylfurazan-3-yl)-2-oxoethyl]-2-methylpyridinium bromides in *N,N*-dimethylaniline affords indolizine derivatives, whereas in aniline a mixture of indole and indolizine derivatives is formed.

Key words: furazans, indoles, indolizine.

Previously,[1] we showed that pyridinium salts obtained from 3-(2-bromoacetyl)furazan[2] give 3-(R-indol-2-yl)furazan derivatives upon refluxing in 4-R-anilines. The pyridine moiety functioned as a leaving group, while aniline served as a building block for constructing the indole moiety of the molecule that formed.

Under similar conditions, 2-methylpyridinium salts (**1**) react according to both pathway *a* and pathway *b* (Scheme 1) leading to indolizine derivatives **3**, in which the pyridine ring is a structural fragment, and aniline acts as a catalyst.

When the reaction is carried out in *N,N*-dimethylaniline (boiling, 2—3 h), only 2-(furazanyl)indolizines **3** are formed (yield 67—75%).

Experimental

Melting points were determined on a Kofler stage. ^1H and ^{13}C NMR spectra were recorded on Bruker AM-300 (300 and 75 MHz, respectively) and Bruker AM-200 instruments (200 and 50 MHz, respectively). ^{13}C signals were assigned with the use of double heteronuclear resonance and selective polarization transfer from H nuclei.

Mass spectra were obtained with Varian MAT CH-6 and Varian MAT CH-111 instruments (70 eV). IR spectra were recorded on a Specord IR-75 spectrometer (KBr).

The course of the reaction was monitored and the purity of reaction products was checked by TLC on Silufol UV-254 plates. Silica gel was used for preparative chromatography.

The starting pyridinium salts **1a—c** were obtained according to the known procedure.[1]

2-(4-Methylfurazan-3-yl)indolizine (3a). *A.* A mixture of *N*-[2-(4-methylfurazan-3-yl)-2-oxoethyl]-2-methylpyridinium bromide (**1a**) (2.84 g, 0.01 mol) and aniline (10 mL) was refluxed in an atmosphere of argon for 3.5 h. The reaction mixture was cooled to 20 °C, poured into 5% HCl, and stirred for 0.5 h. Products were extracted with CH_2Cl_2. The extract was dried with $MgSO_4$ and concentrated. The residue was chromatographed on a column with SiO_2 (pentane—CH_2Cl_2 as the eluent). Eluted first was compound **3a**, yield 35%, m.p. 123—124 °C (from hexane). Found (%): C, 66.43; H, 4.59;

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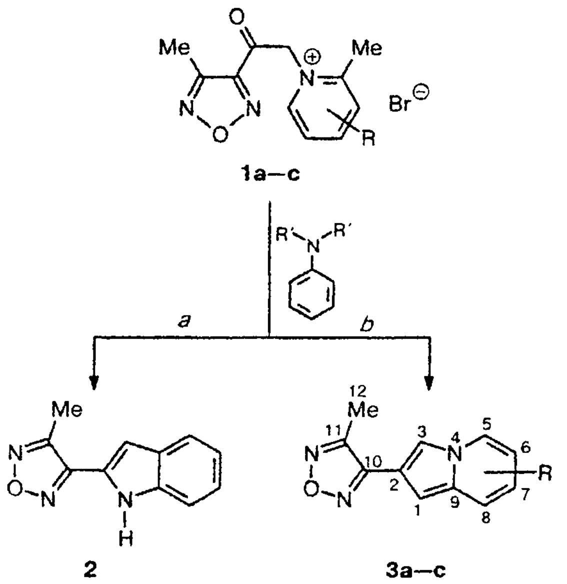
Scheme 1



R = H (**a**), 3-Me (**1b**), 8-Me (**3b**), 5-Et (**1c**), 6-Et (**3c**)
R' = H, Me

N, 21.00. $C_{11}H_9N_3O$. Calculated (%): C, 66.33; H, 4.52; N, 21.10. ^{1}H NMR (300 MHz, $CDCl_3$), δ: 2.6 (s, 3 H, Me); 6.5 (dd, 1 H, H(6), J = 7.0 Hz, J = 9.0 Hz); 6.7 (dd, 1 H, H(7), J = 7.0 Hz, J = 9.0 Hz); 6.75 (s, 1 H, H(1)); 7.35 (d, 1 H, H(8), J = 9.0 Hz); 7.65 (s, 1 H, H(3)); 7.9 (d, 1 H, H(5), J = 7.0 Hz). ^{13}C NMR ($CDCl_3$), δ: 9.3 (C(12)); 98.0 (C(1)); 111.6 (C(3), C(6)); 113.2 (C(2)); 118.3 (C(7)); 119.2 (C(8)); 125.0 (C(5)); 133.3 (C(9)); 149.5 (C(11)); 149.7 (C10)). MS, m/z (I_{rel} (%)): 199 [M]$^+$ (87). Eluted second was **3-(indol-2-yl)-4-methylfurazan (2)**, yield 17%, m.p. 184—185 °C; its spectral characteristics correspond to the literature data.[1]

B. Indolizine **3a** was obtained under similar conditions by refluxing salt **1a** (2.84 g, 0.01 mol) in 5 mL of *N,N*-dimethylaniline with subsequent acidification of the reaction mixture and recrystallization of the precipitate that formed (without chromatography), yield 75%.

Indolizines **3b** and **3c** were synthesized in a similar way.

8-Methyl-2-(4-methylfurazan-3-yl)indolizine (3b). Yield 71%, m.p. 111—112 °C (from hexane). Found (%): C, 67.68; H, 5.22; N, 19.63. $C_{12}H_{11}N_3O$. Calculated (%): C, 67.61; H, 5.16; N, 19.72. ^{1}H NMR (200 MHz, $CDCl_3$), δ: 2.4 (s, 3 H, 8-Me); 2.6 (s, 3 H, Me); 6.5 (m, 2 H, H(6), H(7)); 6.75 (s, 1 H, H(1)); 7.65 (s, 1 H, H(3)); 7.85 (d, 1 H, H(5)). ^{13}C NMR ($CDCl_3$), δ: 9.6 (C(12)); 17.7 (8-Me); 96.7 (C(1)); 111.9 (C(3), C(6)); 112.8 (C(2)); 117.5 (C(7)); 123.0 (C(5)); 128.4 (C(8)); 134.5 (C(9)); 149.5 (C(11)); 149.9 (C(10)). MS, m/z (I_{rel} (%)): 213 [M]$^+$ (71).

6-Ethyl-2-(4-methylfurazan-3-yl)indolizine (3c). Yield 67%, m.p. 80—81 °C (from hexane). Found (%): C, 68.81; H, 5.79; N, 18.41. $C_{13}H_{13}N_3O$. Calculated (%): C, 68.72; H, 5.73; N, 18.50. IR, ν/cm^{-1}: 3120, 2980, 2935, 1590, 1536, 1345, 1215, 1030, 890. ^{1}H NMR (200 MHz, DMSO-d_6), δ: 1.2 (t, 3 H, $\underline{CH_3}CH_2$); 2.5 (q, 2 H, $CH_3\underline{CH_2}$); 2.6 (s, 3 H, Me); 6.7 (d, 1 H, H(7), J = 9.6 Hz); 6.8 (s, 1 H, H(1)); 7.4 (d, 1 H, H(8), J = 9.6 Hz); 8.05 (s, 1 H, H(3)); 8.1 (s, 1 H, H(5)). ^{13}C NMR (DMSO-d_6), δ: 9.2 (C(12)); 14.6 ($\underline{CH_3}CH_2$); 25.1 ($CH_3\underline{CH_2}$); 97.6 (C(1)); 111.9 (C(2)); 112.5 (C(3)); 118.6 (C(8)); 121.0 (C(7)); 122.4 (C(5)); 125.8 (C(6)); 131.9 (C(9)); 150.0 (C(11)); 150.2 (C(10)). MS, m/z (I_{rel} (%)): 227 [M]$^+$ (58).

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