Letters to the Editor

Synthesis of first spiropyrans and spirooxazines based on thieno[3,2-*b*]pyrroles

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The most part of photochromic spiro compounds are indole derivatives.[1] It seemed of interest to synthesize close analogs of these substances containing thieno[3,2-*b*]pyrrole fragments instead of indole ones. Such a replacement of the benzene ring by the thiophene cycle in photochromic systems might induce new useful properties and cause the subsequent chemical modification of the products.

The scheme of the synthesis includes the hydrolysis and decarboxylation of thienopyrrole **1**, which has been described previously,[2] methylation of compound **2** to form tetramethyl derivative **3**, and alkylation of the latter affording salts **4a,b** (Scheme 1). The reaction of salt **4a** with 2-hydroxy-5-nitrobenzaldehyde yielded compound **5**, and the reactions of salts **4a** and **4b** with 1-nitroso-2-naphthol afforded spirooxazine **6a,b**. The alkylation of compound **3** and syntheses of target spiropyran **5** and spirooxazines **6**, whose photochromic properties will be discussed elsewhere, were carried out *in situ*.

The structures of the synthesized compounds were proved by ^{1}H and ^{13}C NMR spectroscopy and mass spectrometry and confirmed by elemental analysis. The ^{1}H NMR spectra of spiro compounds **5** and **6b** contain signals from protons of the CH_2 group of the *N*-ethyl fragment at 3.06—3.19 ppm (J_{AB} = 12.5, $J_{AX} = J_{BX}$ = 7.2 Hz). These signals are characteristic of the ABX_3 system. In addition, in the ^{1}H NMR spectrum of compound **5**, signals from protons of the pyran ring are presented by the AB-quartet with δ_A = 5.89 and δ_B = 6.83 (J_{AB} = 10.0 Hz). The spin-spin coupling constants correspond to the published data[3,4] for spiropyrans and spirooxazines of the indole series and indirectly confirm the structures of the spiro compounds, which we synthesized from thieno[3,2-*b*]pyrroles. The structure of spirooxazine **6b** was also studied by X-ray diffraction analysis (the X-ray diffraction data were deposited with the Cambridge Structural Database).

2,5,6-Trimethyl-4*H*-thieno[3,2-*b*]pyrrole (2), m.p. 44—46 °C. Found (%): C, 65.89; H, 6.83; S, 18.93. $C_9H_{11}NS$. Calculated (%): C, 65.41; H, 6.71; S, 19.40. ^{1}H NMR (250 MHz, $CDCl_3$), δ: 2.18 (s, 3 H, C(6)H_3); 2.30 (s, 3 H, C(5)H_3); 2.60 (s, 3 H, C(2)H_3); 6.57 (s, 1 H, CH_{thioph}); 7.58 (br.s, 1 H, NH). MS, *m/z*: 165 $[M]^+$.

2,5,6,6-Tetramethyl-6*H*-thieno[3,2-*b*]pyrrole (3), viscous oil. Found (%): C, 66.57; H, 6.92; S, 17.40. $C_{10}H_{13}NS$. Calculated (%): C, 66.99; H, 7.31; S, 17.88. ^{1}H NMR (200 MHz, $CDCl_3$), δ: 1.32 (s, 6 H, CMe_2); 2.22 (s, 3 H, C(5)H_3); 2.51 (s, 3 H, C(2)H_3); 6.80 (s, 1 H, CH_{thioph}). MS, *m/z*: 179 $[M]^+$.

4′-Ethyl-2′,6′,6′-trimethyl-6-nitrospiro[2*H*-1-benzopyran-2,5′-thieno[3,2-*b*]pyrroline] (5), m.p. 110—112 °C. Found (%):

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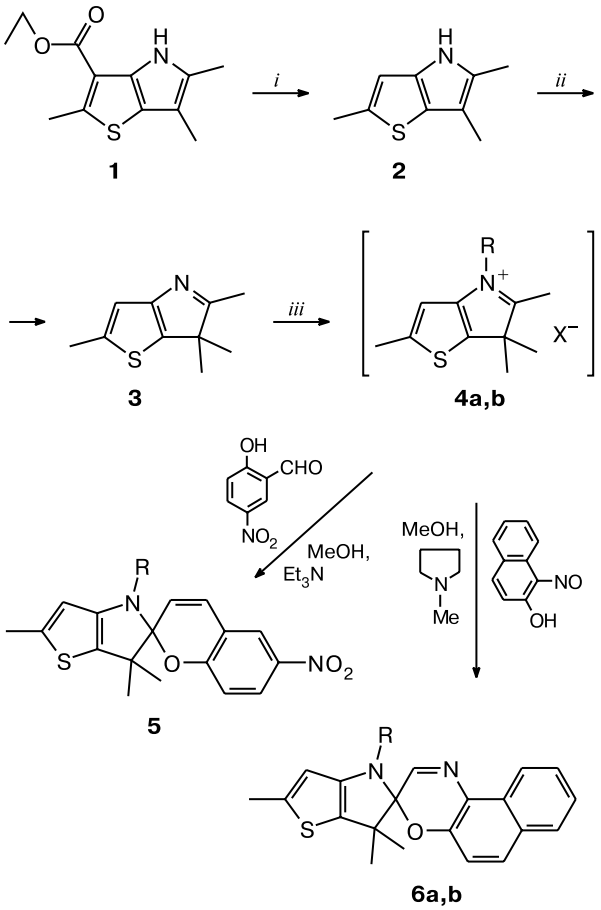
Scheme 1



Reagents and conditions: *i*. 1) KOH, MeOH, 2) Cu, quinoline; *ii*. THF, –75 °C, BuLi, MeI; *iii*. MeCN, RX.

N, 7.33. $C_{19}H_{20}N_2O_3S$. Calculated (%): N, 7.87. ^{1}H NMR (250 MHz, $CDCl_3$), δ: 1.20 (t, 3 H, $C\underline{H}_3CH_2$, J = 7.2 Hz); 1.25, 1.30 (both s, 3 H each, $C(CH_3)_2$); 2.50 (s, 3 H, Me); 3.04 (dq, 1 H, ABX_3, $C\underline{H}_2CH_3$, part A, J_{AX} = 7.2 Hz, J_{AB} = 12.5 Hz); 3.11 (dq, 1 H, ABX_3, $C\underline{H}_2CH_3$, part B, J_{BX} = 7.2 Hz, J_{AB} = 12.5 Hz); 5.89 (d, 1 H, C<u>H</u>=CH—Ph, J = 10.5 Hz); 6.33 (s, 1 H, CH_{thioph}); 6.81 (d, 1 H, CH=C<u>H</u>—Ph, J = 10.5 Hz); 6.86 (d, 1 H, CH_{benz}, J = 9.19 Hz); 7.97 (s, 1 H, CH_{benz}); 8.06 (d, 1 H, CH_{benz}, J = 9.19 Hz). MS, m/z: 356 $[M]^+$.

2,4,6,6-Tetramethylspiro(thieno[3,2-*b*]pyrroline-5,3´-[3*H*]naphtho[2,1-*b*][1,4]oxazine) (6a), m.p. 138—140 °C. Found (%): C, 72.07; H, 5.96; N, 7.99. $C_{21}H_{20}N_2OS$. Calculated (%): C, 72.38; H, 5.79; N, 8.04. ^{1}H NMR (250 MHz, $CDCl_3$), δ: 1.35, 1.40 (both s, 3 H each, $C(C\underline{H}_3)_2$); 2.51 (s, 3 H, Me); 2.72 (s, 3 H, N—Me); 6.32 (s, 1 H, CH_{thioph}); 7.11 (d, 1 H, CH_{naphth}, J = 9.1 Hz); 7.37—7.79 (m, 5 H, CH_{naphth}); 7.78 (s, 1 H, CH=N); 8.58 (d, 1 H, CH_{naphth}, J = 8.9 Hz). MS, m/z: 348 $[M]^+$.

4-Ethyl-2,6,6-trimethylspiro(thieno[3,2-*b*]pyrroline-5,3´-[3*H*]naphtho[2,1-*b*][1,4]oxazine) (6b), m.p. 110—112 °C. ^{1}H NMR (250 MHz, $CDCl_3$), δ: 1.23 (t, 3 H, $C\underline{H}_3CH_2$, J = 7.2 Hz); 1.31, 1.39 (both s, 3 H each, $C(C\underline{H}_3)_2$); 2.50 (s, 3 H, Me); 3.11 (dq, 1 H, ABX_3, $C\underline{H}_2CH_3$, part A, J_{AX} = 7.2 Hz, J_{AB} = 12.5 Hz); 3.19 (dq, 1 H, ABX_3, $C\underline{H}_2CH_3$, part B, J_{BX} = 7.2 Hz, J_{AB} = 12.5 Hz); 6.38 (s, 1 H, CH_{thioph}); 7.11 (d, 1 H, CH_{naphth}, J = 9.2 Hz); 7.39—7.78 (m, 4 H, CH_{naphth}); 7.80 (s, 1 H, CH=N); 8.57 (d, 1 H, CH_{naphth}, J = 9.0 Hz). ^{13}C NMR (62.9 MHz, $CDCl_3$), δ: 15.25 ($\underline{C}H_3CH_2$); 29.78 (2 $C(\underline{C}H_3)_2$); 40.53 ($CH_3\underline{C}H_2$); 53.67 ($\underline{C}(CH_3)_2$); 102.51 (NCO); 111.35, 117.00, 121.60, 121.88, 124.19, 127.13, 127.84, 129.37, 130.21, 130.98, 140.61, 142.09, 144.03, 149.10 (C arom.); 151.49 (<u>C</u>H=N). MS, m/z: 362 $[M]^+$.

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