(46%) with mp 138°C (from ethanol). PMR spectrum ($CDCl_3$): 1.24 (3H, s, CH_3); 2.00 (3H, s, CH_3); 3.20 (3H, s, OCH_3); 7.0-7.5 (5H, m, H_{arom}); 9.75 ppm (1H, s, NH). ^{13}C NMR spectrum ($CDCl_3$): 18.0 (CH_3); 25.1 (CH_3–C_5); 51.1 (CH_3O); 84.0 (C_5); 128.2-138.5 (6 signals, C_{arom}); 145.2 (C_6); 174.7 ppm (C=S). ^{15}N NMR spectrum ($CDCl_3$): 140.1 (s, N_4); 170.2 (d, J = 109.2 Hz, HN_2); 308.4 ppm (s, N_1).

TRICHLOROMETHYLATION OF BENZOXAZOLINE-2-THIONE AND BENZOTHIAZOLINE-2-THIONE BY CARBON TETRACHLORIDE IN THE PRESENCE OF ALUMINUM CHLORIDE

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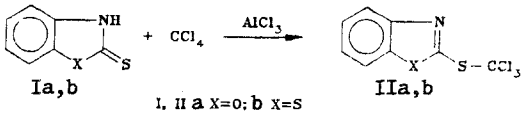
The reaction of benzoxazoline-2-thione (Ia) or benzothiazoline-2-thione (Ib) with carbon tetrachloride in the presence of aluminum chloride leads to high yields of 2-(trichloromethylthio)benzoxazole (IIa) or 2-(trichloromethylthio)benzothiazole (IIb) instead of the expected products of reaction of Ia,b in the benzene ring (as occurs with their oxygen analogs) [1].



Ia,b — I, II a X=O; b X=S — IIa,b

The products IIa,b were obtained by the addition of a threefold excess of $AlCl_3$ to a suspension of the corresponding thione in CCl_4, heating the reaction mixture at 80-90°C for 2 h, decomposition of the reaction mass with a mixture of ice and HCl, and fractionation of the organic layer in vacuo.

The mass spectra of IIa,b show characteristic peaks with m/z 118 $(M-SCCl_3)^+$ (IIa) and 134$(M - SCCl_3)^+$ (IIb). The UV spectra show absorption maxima near 280, 288 nm (IIa) and 280, 290, 300 nm (IIb)identifying them as S-alkylation products. By contrast, N-alkylbenzoxazoline-2-thiones [2] show absorption maxima near 308 nm and N-alkylbenzothiazoline-2-thiones [3] near 328 nm.

2-(Trichloromethylthio)benzoxazole (IIa). Yield 85%, bp 128-130°C (1 mm Hg). Mass spectrum, m/z: 267, 269, 271, 273 (M^+); 232, 234, 236 $(M - Cl)^+$; 150 $(M - CCl_3)^+$; 118 $(M - SCCl_3)^+$. UV spectrum λ_{max} (log ε): 280 (4.19), 288 nm (4.27).

2-Trichloromethylthio)benzothiazole (IIb). Yield 81 %. mp 93-95°C (from heptane). Mass spectrum, m/z: 283, 285, 287, 289 (M^+); 248, 250, 252, $(M - Cl)^+$; 166 $(M - CCl_3)^+$; 134 $(M - SCCl_3)^+$; UV spectrum, λ_{max} (log ε): 280 (4.07), 290 (4.00), 300 nm (3.90).

Elemental analytical data agreed with that calculated.

LITERATURE CITED

1. N. S. Mukhamedov, R. G. Aflyatunova, and N. A. Aliev, International Conference on Organic Synthesis, Summary Report, Moscow (1986), p. 432.
2. K. Giyasov and N. A. Aliev, Uzb. Khim. Zh., No. 6, 39 (1987).
3. N. K. Rozhkova, K. Sabirov, and K. L. Seitanidi, Khim. Geterotsikl. Soedin., No. 11, 1479 (1983).

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