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SYNTHESIS OF S-(α-HYDROXYALKYL) ESTERS OF HETEROCYCLIC THIOSULFONIC ACIDS

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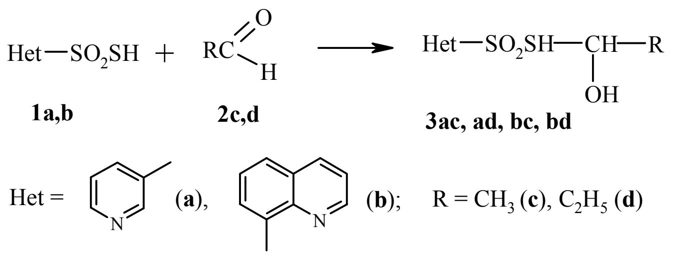
In most cases, thiosulfonic acids are unstable compounds which spontaneously decompose with liberation of elemental sulfur and formation of sulfonic acids; aminoarenethiosulfonic acids are distinguished by higher stability, owing to their structural features [1].

8-Quinolinethiosulfonic acid that we have obtained for the first time and the familiar 3-pyridinethiosulfonic acids **1a,b** are stable compounds, for which we have observed a capability for addition to carbonyl compounds, aliphatic aldehydes as an example, with formation of previously unknown α-hydroxyalkyl esters of thiosulfonic acids.



The structure of the addition products **3ac, ad, bc, bd** has been confirmed by elemental analysis results and the IR and ^{1}H NMR spectra.

Introducing functional groups onto the alkyl chain of the ester group of the thiosulfonic acids should have an effect on the biological activity of these compounds and their physical and chemical properties. The results obtained are of interest as a characteristic of previously unknown chemical properties of aldehydes and thiosulfonic acids, and may be used as a new method for obtaining esters of thiosulfonic acids containing functional groups in the α position.

S-(α-Hydroxyethyl)-3-pyridinethiosulfonate (3ac). Acetic anhydride (0.88 g, 20 mmol) at 20°C was added to a suspension of compound **1a** (3.5 g, 20 mmol) in chloroform; then boron trifluoride etherate was added dropwise to the reaction mass, cooled by ice. The reaction mixture was allowed to stand with cooling. After the solvent was driven off, the product was crystallized from aqueous alcohol. Yield 2.1 g (52%); mp 72-73°C. IR spectrum (KBr), ν, cm^{-1}: 3375 br (OH), 3075 (CH), 1605, 1575, 1478 (C=C$_{Ar}$), 1305, 1117

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(SO_2). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 7.16-7.78 m (4H, C_5H_4N); 4.52-4.66 d (OH); 5.62 (1H, CHOH); 1.92 d (3H, CH_3). Found, %: C 38.52; H 4.24; N 6.50; S 28.83. $C_7H_9NO_3S_2$. Calculated, %: C 38.34; H 4.14; N 6.39; S 29.24.

S-(α-Hydroxypropyl)-3-pyridinethiosulfonate (3ad). Yield 56%; mp 64-65°C (aqueous methanol). IR spectrum, ν, cm^{-1}: 3380 br (OH), 1602, 1578, 1475 (C=C_{Ar}), 1310, 1124 (SO_2). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 7.18-7.52 m (4H, C_5H_4N); 4.32-4.58 d (OH); 5.58 (1H, CHOH); 1.98 m (4H, 2CH_2); 1.12 q (3H, CH_3). Found, %: C 41.38; H 4.89; N 5.83; S 27.79. $C_8H_{11}NO_2S_2$. Calculated, %: C 41.20; H 4.72; N 6.01; S 27.46.

S-(α-Hydroxyethyl)-8-quinolinethiosulfonate (3bc). Yield 47%; mp 67-68°C (methanol). IR spectrum, ν, cm^{-1}: 3402 br (OH), 1318, 1140 (SO_2), 824, 786, 758 (quinoline ring). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.22 t (3H, CH_3); 4.48-4.62 d (OH); 5.48 (1H, CHOH); 7.71-7.85 m (3H, HAr); 7.65-9.03 m (6H, HAr). Found, %: C 48.79; H 4.29; N 5.33; S 23.99. $C_{11}H_{11}NO_3S_2$. Calculated, %: C 49.07; H 4.09; N 5.20; S 23.79.

S-(α-Hydroxypropyl)-8-quinolinethiosulfonate (3bd). Yield 57%; mp 57-58°C (methanol). IR spectrum, ν, cm^{-1}: 3402 br (OH), 1322, 1134 (SO_2), 844, 796, 758 (quinoline ring). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.24 t (3H, CH_3); 4.38-4.58 d (OH); 5.79 (1H, CHOH); 7.74-7.87 m (3H, HAr); 7.75-9.05 m (6H, HAr). Found, %: C 50.79; H 4.39; N 5.13; S 22.99. $C_{12}H_{13}NO_3S_2$. Calculated, %: C 50.89; H 4.59; N 4.95; S 22.61.

REFERENCES

1. B. G. Boldyrev, T. A. Chernenko, L. P. Slesarchuk, A. V. Sen'ko, and M. E. Yarish, *Zh. Org. Khim.*, **4**, 1953 (1968).