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INTERACTION OF CYANURIC CHLORIDE WITH ALKANE-THIOSULFONATES

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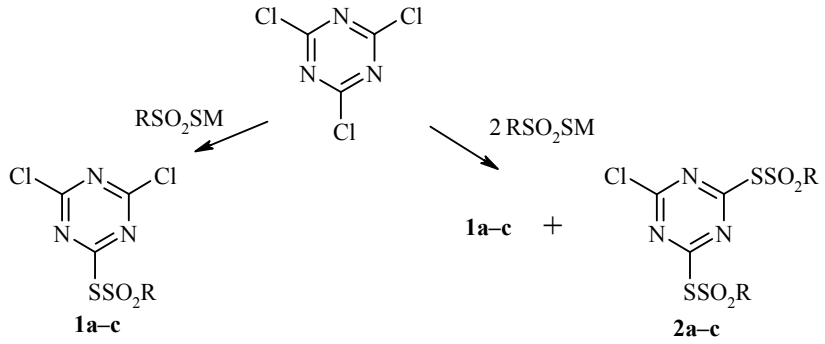
Substances with high herbicidal, insecticidal, and fungicidal activity are to be found among derivatives of *sym*-triazine [1]. With the objective of discovering new biologically active substances we have attempted to synthesize derivatives of *sym*-triazine with thiosulfonate fragments by reaction of cyanuric chloride with sodium or potassium salts of aliphatic thiosulfonic acids.



M = K, Na, **a** R = Me, **b** R = Et, **c** R = Pr

The esters of thiosulfonic acids **1a-c** were isolated in 36-45% yield from a molar ratio of the reagents in acetone at low temperature (-5 to 0°C). As a result of the reaction of cyanuric chloride with alkanethiosulfonates in 1:2 ratio at room temperature a mixture of mono- (**1a-c**) and disubstituted products **2a-c** was obtained. The products were separated thanks to their different solubility in diethyl ether. In the IR spectra of compounds **1** and **2** absorptions were observed in the regions 704-714, 804-812, 992-1112, and 1400-1560 cm^{-1}, characteristic of the triazine ring, and in the regions 840-854, 1156-1162, 1258-1262, and 1296-1300 cm^{-1} characteristic for the vibration of the C–Cl bond [2], and also in the 1115-1150 and 1310-1344 cm^{-1} regions which confirm the presence of the thiosulfonate unit.

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^{1}H NMR spectra of DMSO-d_6 solutions with TMS as internal standard were recorded on a Varian VXR-300 (300 MHz) machine and IR spectra were recorded with a Specord M-80 instrument.

Methanethiosulfonic acid 4,6-Dichloro-[1,3,5]triazin-2-yl Ester (1a). Yield 0.316 g (45.1%). Oil. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 3.7 (3H, s, CH_3). Found, %: C 18.09; H 1.38; Cl 26.85; N 15.83; S 24.18. $C_4H_3Cl_2N_3O_2S_2$. Calculated, %: C 18.47; H 1.16; Cl 27.25; N 16.15; S 24.65.

Ethanethiosulfonic acid 4,6-Dichloro-[1,3,5]triazin-2-yl Ester (1b). Yield 0.311 g (42.0 %). Oil. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.4 (3H, t, ^3J = 7.2, CH_3); 3.2 (2H, q, ^2J = 2.8, ^3J = 7.4, CH_2). Found, %: C 21.63; H 2.03; Cl 25.63; N 14.95; S 23.76. $C_5H_5Cl_2N_3O_2S_2$. Calculated, %: C 21.91; H 1.84; Cl 25.86; N 15.33; S 23.39.

Propanethiosulfonic acid 4,6-Dichloro-[1,3,5]triazin-2-yl Ester (1c). Yield 0.241 g (31.0 %). Oil. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 0.92 (3H, t, CH_3); 0.92 (3H, t, ^3J =7.4, CH_3); 1.59 (2H, m, CH_2CH_3); 3.79 (2H, ^3J = 8.7, CH_2SO_2). Found, %: C 24.63; H 2.67; Cl 24.25; N 14.17; S 21.83. $C_6H_7Cl_2N_3O_2S_2$. Calculated, %: C 25.01; H 2.45; Cl 24,61; N 14.58; S 22.25.

6-Chloro-2,4-bis(methylsulfonylthio)-*sym*-triazine (2a). Yield 0.325 g (35.8%); mp 28°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 3.48 (6H, s, $2CH_3$). Found, %: C 18.02; H 1.98; Cl 10.15; N 12.83; S 37.78. $C_5H_6ClN_3O_4S_4$. Calculated, %: C 17.88; H 1.80; Cl 10.56; N 12.51; S 38.19.

6-Chloro-2,4-bis(ethylsulfonylthio)-*sym*-triazine (2b). Yield 0.384 g (39.1%); mp 31°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.4 (6H, t, ^3J = 7.2, $2CH_3$); 3.2 (4H, q, ^2J = 2.8, ^3J = 7.4, $2CH_2$). Found, %: C 22.63; H 2.93; Cl 9.33; N 11.25; S 32.76. $C_7H_{10}ClN_3O_4S_4$. Calculated, %: C 23.11; H 2.77; Cl 9.74; N 11.55; S 35.25.

6-Chloro-2,4-bis(propylsulfonylthio)-*sym*-triazine (2c). Yield 0.32g (30.2%); mp 34°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 0.98 (6H, t, ^3J = 7.4, $2CH_3$); 1.92 (4H, m, $2CH_2CH_3$); 3.54 (4H, m, $2CH_2SO_2$). Found, %: C 27.23; H 3.87; Cl 8.75; N 10.47; S 32.43. $C_9H_{14}ClN_3O_4S_4$. Calculated, %: C 27.58; H 3.60; Cl 9.05; N 10.72; S 32.72.

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