SYNTHESIS OF 4-ALKYLTHIO-1,3-DITHIOLE-2-THIONES

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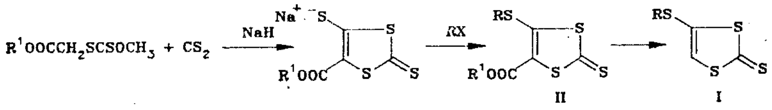
4-Methylthio-1,3-dithiole-2-thione (I, R = CH_3) was isolated as one of the side products in extremely low yield in the methylation of products of the reduction of carbon disulfide with sodium amalgam [1]. We have developed a preparative method for the synthesis of 4-alkylthio-1,3-dithiole-2-thiones by hydrolysis of esters of 4-alkylthio-1,3-dithiole-2-thione-5-carboxylic acid (II), which were obtained, in turn, in analogy with the method in [2].



The acid formed in the hydrolysis of ester II is unstable and undergoes decarboxylation during the reaction to give dithiolethiones I in 75-85% yields. Thus the hydrolysis of ester II [R = R^1 = CH_3; mp 143-144°C; PMR spectrum ($CDCl_3$): 2.60 (3H, s, SCH_3), 3.84 (3H, s, OCH_3); UV spectrum, λ_{max}, nm (log ε) (ethanol): 385 (4.32), 355 sh, 233 (4.26), 230 sh: IR spectrum (Nujol), cm^{-1}: 1690 (CO), 1090, 1065 sh, 1050, 1040, 1025 (SCSS); R_f 0.66 (Silufol, benzene)] leads to I [R = CH_3; mp 71-72°C (71.4-71.8°C [1]); UV spectrum, λ_{max}, nm (log ε) (ethanol): 376 (4.09), 310 sh, 271 (3.67), 232 (3.90); R_f 0.84 (benzene)]. Ester II (R = CH_3, R^1 = iso-Pr) is hydrolyzed under these conditions after 5 h (80% yield) in the case of refluxing in a mixture of equal volumes of acetic and concentrated hydrochloric acids (28 h, 78%) and acetic and concentrated hydrobromic acids (8 h, 84%). Refluxing esters II in pyridine with lithium bromide is even more effective (R = R' = CH_3, 1h, 86%).

LITERATURE CITED

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2. M. Augustin, W. Dölling, and A. Vogt, Z. Chem., No. 9, 333 (1983).

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