LETTERS TO THE EDITOR

CONDENSATION OF THIORHODANINE WITH ELECTROPHILIC REAGENTS

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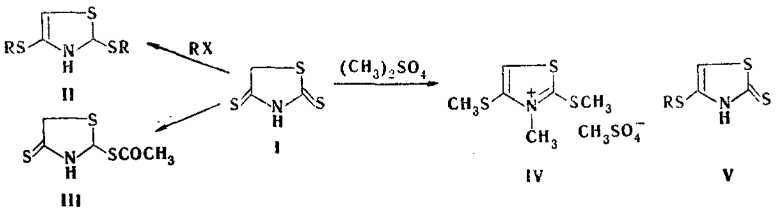
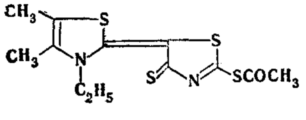
We have subjected thiorhodanine to reaction with some electrophilic reagents (chloroacetic acid, acetic anhydride, 2-chlorobenzoxazole, and dimethyl sulfate), as a result of which we have developed a new general method for the synthesis of thiazole derivatives with substituted thiol groups in the 2 and 4 positions simultaneously. In the case of dimethyl sulfate the reaction was accompanied by the formation of a quaternary thiazolium salt (IV).



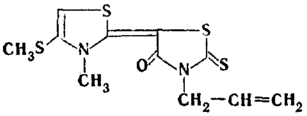
II a $R=CH_2COOH$; b $R=COCH_3$; c R=2-benzoxazolyl

In the case of acetyl chloride the reaction takes place only in the 2 position at 60-65°C (30 min) and leads to 2-acetylthiothiazolidine-4-thione (III) with mp 131°C (from chloroform) in 70% yield.

In contrast to the isomeric V, III contains an active methylene group in the 5 position that is capable of undergoing reaction with quaternary salts of 2-methyl derivatives of nitrogen heterocycles to give 2-acetylthio-5-(3-ethyl-4,5-dimethylthiazolin-2-ylidene)thiazolidine-4-thione (VI) with mp 226°C and λ_{max} 468 nm (in alcohol) in 49% yield.



VI



VII

The PMR spectrum of III in $CDCl_3$ contains a singlet at 1.21 ppm from the CH_3 group of a thioacetyl residue and a singlet at 3.69 ppm (5-CH_2). The condensation of thiorhodanine with other electrophilic reagents was carried out by mixing equimolar amounts of the components. 2,4-Bis(dicarboxymethylthio)thiazole (IIa) was obtained from thiorhodanine and chloroacetic acid by heating at 80-90°C for 90 min in the presence of 10% aqueous NaOH. The reaction mixture was neutralized to pH 6 with hydrochloric acid and worked up to give a product with mp 162°C (from alcohol) in 54% yield. PMR spectrum ($CDCl_3$) of IIa: singlet at 1.44 and 1.4 ppm (CH_2 of the 2- and 4-carboxymethylthio groups) and singlet at 4.06 ppm (5-H). 2,4-Bis(acetylthio)thiazole (IIb) was obtained by heating thiorhodanine with acetic anhydride at 100°C for 2 h; workup gave a product with mp 178°C in 73% yield. PMR spectrum: singlets of methyl groups at 1.88 and 2.1; 3.94 ppm (5-H). Compounds IIa-c were converted to thiazolium salts by the action of dimethyl sulfate. In the case of 2,4-di(2-benzoxazolyl)thiazole (IIc), obtained from thiorhodanine and 2-chlorobenzoxazole at 20°C (in 52% yield, mp 119°C), the benzoxazole residue was replaced by a methyl group. This was proved by condensation of the product of quaternization of IIc with N-allylrhodanine. The resulting merocyanine VII [3-allyl-5-(3-methyl-4-methylthiothiazolin-2-ylidene)thiazolidine-2-thion-4-one], which was obtained in 68% yield and had mp 263°C (from alcohol) and λ_{max} 425 nm (in alcohol), was identical to the compound obtained from IV. No melting-point depression was observed for a mixture of this product with the dye obtained from IV. The results of elementary analysis of all of the compounds were in agreement with the calculated values.

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