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THE THIAZOLO[2,3-b]THIAZOLIUM CATION - A NEW AROMATIC SYSTEM

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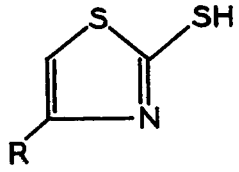
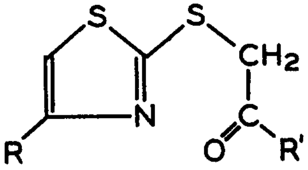
It is well known that the reaction of α-chloroketones with ammonium dithiocarbamate affords 2-mercaptothiazoles (I),[1] which in a basic medium react with an additional mole of the halide to afford the sulfides (II).[2,3]



II



II, R = R'
III, R≠R'

We wish to report that the cyclization of such sulfides (II) in concentrated sulfuric acid at 100° yields derivatives (IV) of the hitherto unknown aromatic thiazolo[2,3-b]thiazolium system.* 2-Thiazoacetonyl-4-methylthiazole (II, $R = CH_3$)[2]

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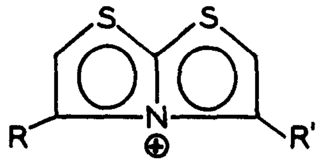
*The 2,3,5,6-tetrahydroderivative of the parent compound was prepared recently by two independent groups, W. Schulze, G. Letsch and H. Willitzer, *J. prakt. Chem.* [4], **19** 101 (1963), and S. Seto and Y. Ikegami, *Bull. Chem. Soc.* Japan **36**, 730 (1963).



IV, R = R'
V, R ≠ R'

affords in 97% yield the 3,5-dimethylthiazolo[2,3-b]thiazolium cation (IV, R = CH_3), isolated as the perchlorate, m.p. 362° (explosion), λ max (log ε): 221 (3.84), 292 (4.06) and 298 mμ (4.04). The spectrum was not altered after the salt had stood for 18 hr. in .001 M sodium hydroxide solution. The nuclear magnetic resonance spectrum (trifluoroacetic acid) was remarkably simple, a singlet at tau 7.06 and another at tau 2.43 with observed areas in the ratio 3.1/1.0. The perchlorate salt (IV, R = CH_3) was unaffected when treated with hydrogen at atmospheric pressure in the presence of Adams' catalyst.

The cyclization of 2-thiophenacyl-4-phenylthiazole (II, R = C_6H_5)[3] afforded a 91% yield of the diphenyl analog (IV, R = C_6H_5), m.p. of the perchlorate 228.5-229.5°.

The possibility that cyclization is preceded by rearrangement was eliminated by preparation of the 3-methyl-5-phenylthiazolo[2,3-b]thiazolium cation (V, R = C_6H_5, R' = CH_3; m.p. perchlorate 252-253°) by cyclization of 2-thiophenacyl-4-methylthiazole (II, R = CH_3, R' = C_6H_5; m.p. 80-81°), and by cyclization of 2-thioacetonyl-4-phenylthiazole (II, R = C_6H_5, R' = CH_3), m.p. dinitrophenylhydrazone (176-177°). The compounds described above have the expected composition.

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