DIHYDROTHIAZINE-THIAZOLINE REARRANGEMENT

REVERSIBILITY OF THE PROCESS

V. M. Fedoseev, V. S. Churilin,
S. E. Tkachenko, and A. V. Kamaev

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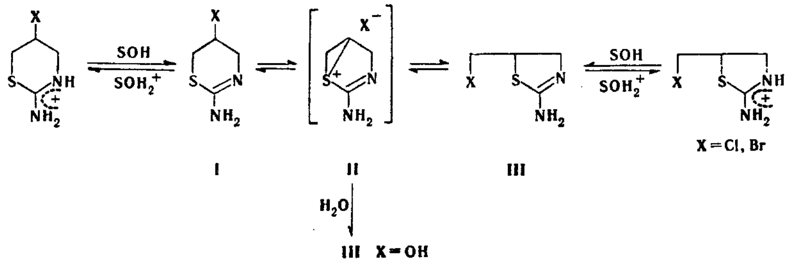
Rearrangement with ring contraction to give 2-amino-5-X-methyl-2-thiazolines (III, X = Cl, Br, OH) occurs in the hydrolysis of 2-amino-5-X-5,6-dihydro-4H-1,3-thiazines (I, X = Cl, Br) as a result of participation of the adjacent sulfur atom, which leads to the formation of intermediate episulfonium structure II. This does not exclude the possibility of the reverse reaction under the same conditions [1] for III (X = Cl, Br). We used thin-layer radiochromatography to study the solvolysis of ^{35}S-labeled* bromide III (X = Br) in water and 50% aqueous ethanol at 100°C. It was observed that in addition to the principal product [III (X = OH)], the reaction mixture contains bromide I (X = Br), the maximum amount of which reached 10-12%. In addition, solvolysis of the corresponding salts III (X = Cl, Br, I) in 50% aqueous ethanol at 100°C in the presence of a tenfold excess of ^{36}Cl-labeled sodium chloride gives, in addition to the usual substitution products, rearrangement product I (X = Cl), although only a small amount (up to 6%) is present in the mixture. However, in no case did we observe the formation of 2-amino-5-hydroxy-5,6-dihydro-4H-1,3-thiazine, the rearranged solvolytic product. The starting concentration of III was 0.1 mole/liter in all of the experiments.



LITERATURE CITED

1. V. M. Fedoseev, V. S. Churilin, S. E. Tkachenko, V. A. Lopatin, and A. V. Kamaev, Dokl. Akad. Nauk SSSR, 235, 1327 (1977).

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* The ^{35}S-labeled bromide III (X = Br) was obtained by bromination in alcohol of N-allyl-^{35}S-thiourea, which was synthesized by isotopic exchange.

M. V. Lomonosov Moscow State University, Moscow 117234. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 7, p. 997, July, 1978. Original article submitted February 2, 1978.