SYNTHESIS OF 2,3,4,5-TETRAHYDROPYRIMIDO[2,1-b]-BENZOTHIAZOLES

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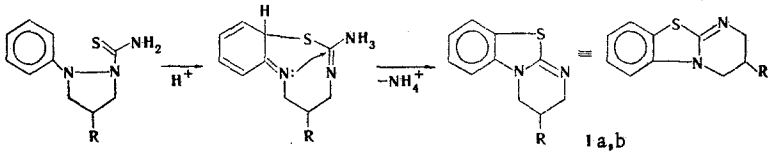
1-Thiocarbamoyl-2-phenylpyrazolidines are cyclized to give 2,3,4,5-tetrahydropyrimido[2,-1-b]benzothiazoles, the structure of which was proved by mass spectrometry.

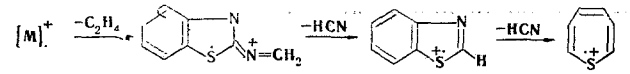
It is known that arylthiosemicarbazides on heating in acidic media are capable of cyclizing to 2-aminobenzothiazoles [1, 2]. We have been able to show that three-ring 2,3,4,5-tetrahydropyrimido[2,1-b]-benzothiazoles (I) can be similarly synthesized from 1-thiocarbamoyl-2-phenylpyrazolidines. The reaction apparently proceeds via a Fischer prototropic rearrangement, but in our case the aromatic ring attacks the sulfur atom rather than the carbon atom.



Ia,b

Ia R=H; b R=CH_3

The mass spectrum of Ia confirms the assigned structure:



m/e 19 | *m/e* 162 (32%) | *m/e* 135 (51%) | *m/e* 108 (15%)

The formation of compounds of the I type is simultaneously a proof that an amino group rather than a hydrazine nitrogen atom is eliminated in the process.

EXPERIMENTAL

2,3,4,5-Tetrahydropyrimido[2,1-b]benzothiazole (Ia). A mixture of 3.8 g (0.02 mole) of 1-phenylpyrazolidine hydrochloride and 4 g (0.04 mole) of potassium isothiocyanate was heated in 10 ml of absolute alcohol on a water bath for 12 h, after which it was cooled, and the precipitate was removed by filtration, washed repeatedly with ice water, and recrystallized from alcohol to give 2.5 g (58%) of 1-thiocarbamoyl-2-phenylpyrazolidine with mp 165°. Found: C 58.4; H 6.2%. $C_{10}H_{13}N_3S$. Calculated: C 58.2; H 6.3%. UV spectrum (in ethanol): λ_{max} 250 nm (log ε 4.30). IR spectrum (in mineral oil): 3200-3400 cm^{-1}.

A solution of 1.2 g (0.006 mole) of 1-thiocarbamoyl-2-phenylpyrazolidine in 5 ml of absolute methanol saturated at 0° with hydrogen chloride was heated in a sealed ampule at 130° for 6 h, after which the mixture was evaporated, and the residue was chromatographed on a column filled with Al_2O_3 with successive elution with benzene and benzene–chloroform (2:1) to give 0.7 g (63%) of Ia with mp 123° (from octane). Found: C 63.0; H 5.4%. $C_{10}H_{10}N_2S$. Calculated: C 63.2; H 5.3%. UV spectrum (in ethanol): λ_{max}, nm, (log ε): 225 (4.62), 268 (4.00), 298 (3.73). IR spectrum (in mineral oil): 1615 cm^{-1}.

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3-Methyl-2,3,4,5-tetrahydropyrimido[2,1-b]benzothiazole (Ib). A mixture of 1.3 g (0.007 mole) of 1-phenyl-4-methylpyrazolidine hydrochloride and 1.25 g (0.013 mole) of potassium isothiocyanate in 4 ml of absolute alcohol was heated on a water bath for 10 h, after which it was worked up as in the preceding experiment to give 1.43 g (99%) of 1-thiocarbamoyl-2-phenyl-4-methylpyrazolidine with mp 143° (from alcohol). Found: C 60.2; H 6.8%. $C_{11}H_{15}N_3S$. Calculated: C 59.8; H 6.8%.

The cyclization was carried out as in the preceding experiment with 1.2 g of 1-thiocarbamoyl-2-phenyl-4-methylpyrazolidine. The eluate was evaporated, and the residue was vacuum-distilled to give 0.61 g (55%) of Ib with bp 204° (1 mm) and mp 72° (from octane). Found: C 65.2; H 6.3%. $C_{11}H_{12}N_2S$. Calculated: C 64.9; H 5.9%. UV spectrum (in ethanol), λ_{max}, nm (log ε): 225 (4.61), 268 (4.05), 297 (3.79). IR spectrum (in mineral oil): 1640 cm^{-1}.

The mass spectrum was recorded with an MKh-1303 spectrometer with admission of the sample into the ion source.

LITERATURE CITED

1. A. Hugershoft, Ber., 36, 3134 (1903).
2. K. Clusius and H. Weisser, Helv. Chim. Acta, 35, 400 (1952).