

(mp > 300°); ¹H nmr (DMSO-d₆): δ 3.7 (s, 3H, CH₃), 6.10 (s, 2H, NH₂, deuterium oxide exchangeable), 6.90 (s, 2H, NH₂, deuterium oxide exchangeable), 11.10 (br, 1H, NH, deuterium oxide exchangeable); uv: (pH 7) λ max nm (ε × 10⁴), 269 (1.8); (pH 1), 264 (2.2); (pH 11), 282 (1.0), 296 (2.1).

Anal. Calcd. for C₇H₈N₆O₃·H₂O: C, 34.71; H, 4.16; N, 34.70. Found: C, 34.97; H, 4.25; N, 34.85.

That the oxazolo[5,4-*d*]pyrimidine derivative was indeed isolated from the reaction; rather than a possible 8-aminopurine derivative, was substantiated by the ¹H nmr spectra of **4a**. The triplet observed for the 4-NH and the doublet observed for the methylene of the benzylamino moiety confirms the formation of an oxazolo[5,4-*d*]pyrimidine ring system as the product of the reaction. Under deuterium exchange conditions the methylene splitting pattern collapses to a singlet. In addition, an oxazolopyrimidine to purine rearrangement could be accomplished by treatment of the oxazolo[5,4-*d*]pyrimidine **4a** with potassium bicarbonate in methanol under reflux and anhydrous conditions to effect the rearrangement to the purine (methyl 9-benzylguanine-8-carbamate) in 87% yield (mp 321-322° dec); uv: (pH 7) λ max nm (ε × 10⁴), 266 (3.4); (pH 1), 259 (3.6); (pH 11), 264 (2.8), 273 (2.6), 289 (2.7).

Anal. Calcd. for C₁₄H₁₄N₆O₃: C, 53.50; H, 4.49; N, 26.74. Found: C, 53.21; H, 4.57; N, 26.60.

The cyclization is believed to proceed *via* formation of a reactive carbodiimide intermediate, similar to that reported for the cyclization of *o*-aminophenyl aryl and alkyl thioureas [14]. That the purine ring system was not formed in these reactions may be due to the delocalization of the

lone pair of electrons on the 4-amino group decreasing the basicity and nucleophilicity of this moiety. This procedure for the cyclodesulfurization of the methoxycarbonyl-thioureido adduct should be adaptable to the synthesis of other bicyclic heterocyclic systems such as, purines or thiazolopyrimidines and additional studies in this area are in progress.

REFERENCES AND NOTES

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