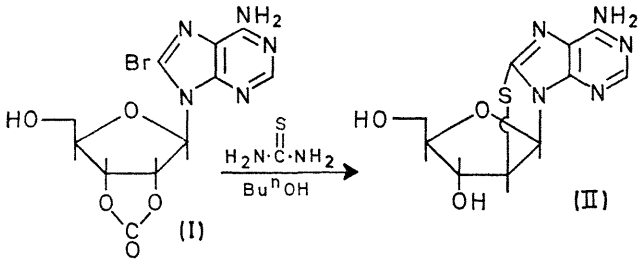
Novel Synthesis of 8,2′-Thioanhydropurine Nucleosides

By K. K. OGILVIE* and L. SLOTIN

(*Department of Chemistry, University of Manitoba, Winnipeg, Manitoba, Canada*)

Summary The synthesis of 8,2′-thioanhydroadenosine illustrates a new general route to the synthesis of 8,2′-thioanhydropurine nucleosides.

ANHYDRONUCLEOSIDES are important analogues of natural nucleosides. 8,2′-Anhydropurine nucleosides are key intermediates in the synthesis of many biologically active compounds and have provided new routes for the synthesis of nucleotides.[1,2] We have recently devised a very simple route to these molecules as illustrated by the synthesis of 8,2′-thioanhydroadenosine (II).



A mixture of 8-bromoadenosine,[3] diphenyl carbonate, and sodium hydrogen carbonate was heated at 150 °C in dimethylformamide for 30 min.[4] The product, 8-bromoadenosine 2′,3′-carbonate (I) was isolated (70%) by chromatography, m.p. 159—162 °C, λ_{max} (EtOH) 263·5 nm (ϵ 14,100); the i.r. spectrum and elemental analysis were consistent with structure (I).

A mixture of the carbonate (I) and thiourea in n-butanol was heated under reflux for 5 h. The product, (II) (66%), was isolated by chromatography and crystallized from water. Compound (II) was identical in all respects (u.v., n.m.r., and mass spectra,[5] chromatography) to authentic 8,2′-thioanhydroadenosine prepared by the method of Ikehara.[3]

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[1] M. Ikehara, *Accounts Chem. Res.*, 1969, **2**, 47.
[2] M. Ikehara, S. Uesugi, and M. Vasumoto, *J. Amer. Chem. Soc.*, 1970, **92**, 4735.
[3] M. Ikehara and M. Kaneko, *Tetrahedron*, 1970, **26**, 4251.
[4] A. Hampton and A. W. Nichol, *Biochemistry*, 1966, **5**, 2076. No bis-5′-carbonates were detected in our work.
[5] M. Ikehara, Y. Tamura, and M. Ikeda, *J. Heterocyclic Chem.*, 1970, **7**, 1377.