

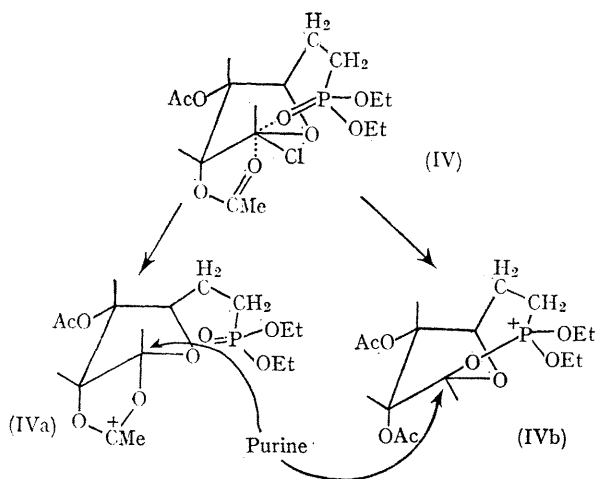
at C(5) react with chloromercuri-*N*-benzoyladenine to give only one anomer, assumed to be the β -(*trans*)-anomer⁸ on the basis of the *trans* rule.⁶ It seems unlikely that the present result is due to steric interference alone. There

may be interaction between the oxygen of the diethyl phosphonate group and C(1) (IVb) that results in the predominant formation of the α -anomer.[†]

Since the anomeric mixtures were difficult to separate by any of the usual procedures, the anomer ratios were estimated from the ¹H n.m.r. spectra of the reaction mixtures. The C(1')proton signal of a *cis*-furanosylpurine occurs downfield from that of the corresponding *trans*-furanosylpurine.^{4b} Treatment of the anomeric mixture (IIb) with methanolic sodium methoxide at reflux for 30 min. gave 9-(5,6-dideoxy-6-di-*O*-ethylphosphono- α,β -ribo-hexofuranosyl)adenine (IIIa). The α -anomer of (IIb), separated from the mixture by silica gel chromatography, was converted by treatment with methanolic ammonia (18 hr.; 100°) into a separable mixture of 9-(5,6-dideoxy-6-di-*O*-ethylphosphono- α -*D*-ribo-hexofuranosyl)adenine [α -(IIIa)] and 9-[5,6-dideoxy-6-(*O*-ethylphosphono)- α -*D*-ribo-hexofuranosyl]adenine [α -(IIIb)].

This work was supported by the Southern Research Institute, the C.F. Kettering Foundation, and the Cancer Chemotherapy National Service Center, National Cancer Institute, National Institute of Health.

(Received, October 28th, 1968; Com. 1468.)



† A Stuart-Briegleb model of this sugar indicates that such interaction would involve no steric strain.

¹ W. Sowa and G. H. S. Thomas, *Canad. J. Chem.*, 1966, **44**, 836.

² W. S. Wadsworth, jun., and W. D. Emmons, *J. Amer. Chem. Soc.*, 1961, **83**, 1733.

³ T. Sato, T. Simadate, and Y. Ishido, *J. Chem. Soc. Japan*, 1960, **81**, 1440. Many subsequent papers by these and other authors have described variations of the method.

⁴ (a) J. A. Montgomery and K. Hewson, *J. Medicin. Chem.*, 1966, **9**, 354; (b) 1968, **11**, 48.

⁵ L. Pichat, P. Dufay, and Y. Lamorre, *Compt. rend.*, 1964, **259**, 2453.

⁶ B. R. Baker, *Ciba Foundation Symposium Chem. Biol. Purines*, 1957, 120.

⁷ H. M. Kissman and B. R. Baker, *J. Amer. Chem. Soc.*, 1957, **79**, 5594, reported a case in which a α : β anomer ratio of 3 : 19 was obtained. At this time they stated "it should be emphasized that experience to date indicates that anomers having the C(1)-C(2) *cis* configuration are not often observed; and when they are observed, they are present in only minor quantities." Since that time the *trans* rule, with the addition related above, has appeared to be universally applicable. [G. T. Rogers and T. L. V. Ulbricht, *J. Chem. Soc. (C)*, 1968, 1929, have reported that the reaction of the silver salt of hypoxanthine gives an α : β ratio of 1 : 4.]

⁸ E. J. Reist, R. R. Spencer, and B. R. Baker, *J. Org. Chem.*, 1958, **23**, 1958; R. F. Nutt and E. Walton, *J. Medicin. Chem.*, 1968, **11**, 151.