ANOMERS IN THE SYNTHESIS OF IMIDAZOLE NUCLEOSIDES BY THE SHAW METHOD

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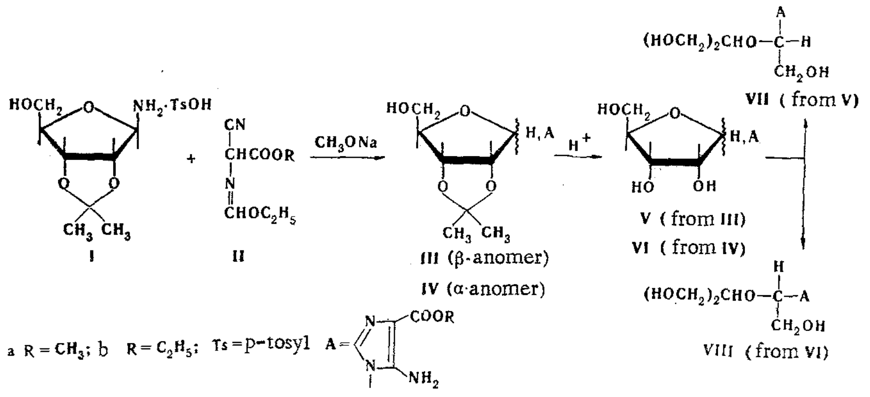
According to the data in [1], closing of the imidazole ring in the reaction of ribosylamine I with imidate IIa proceeds with the formation of only the β-anomer of imidazole nucleoside IIIa.



We have found that the reaction between amine I and imidates II gives both anomers II and IV. As compared with the signal of the same proton in IIIa,b, the signal of the anomeric proton in nucleosides IVa,b is shifted to weaker field (compare with [2]). When the pair of anomers is treated with acid, both are cleaved to ribose and the same base. Compounds VIIb and VIIIb, obtained from nucleosides Vb and VIb by the method in [3], have $[\alpha]_D^{24}$ +53° and −63°, respectively. These data prove the α-anomeric structure of nucleosides IV.

TABLE 1. Properties of Nucleosides III and IV

Compound	mp, deg C	Empirical formula[a]	λ_{max}, nm(ε)[b]	$\delta_{1\text{-}H'}$ ppm[c]	R_f[d]	Yield, %
IIIa	159—160[e]	$C_{13}H_{19}N_3O_6$	269 (12800)	5,77	0,73	18
IVa	191	$C_{13}H_{19}N_3O_6$	269 (12700)	5,87	0,58	19
IIIb	171—172	$C_{14}H_{21}N_3O_6$	269 (13200)	5,76	0,76	20
IVb	178—179	$C_{14}H_{21}N_3O_6$	269 (13800)	5,89	0,63	22

Note. [a] The results of elementary analysis correspond to the compositions given. [b] In water. [c] In dimethyl sulfoxide. [d] Silufol UV-254, chloroform–methanol (4:1). [e] According to the data in [4], this compound has mp 161°.

EXPERIMENTAL

Synthesis of Nucleosides III and IV. A total of 8.0 ml of an 0.5 N solution of sodium methoxide in methanol and a solution of 1 g (0.006 mole) of imidate II [4] in 20 ml of ether were added successively to a solution of 1.44 g (0.004 mole) of amine I [1] in 60 ml of methanol, after which the mixture was heated at 50° for 30 min and allowed to stand overnight. A mixture of anomers III and IV, which was separated by chromatography on silica gel (see Table 1), was isolated on the OH⁻ form of Dowex 1 × 2 (by the method in [5]).

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