USE OF α -CHLOROACRYLONITRILE IN THE SYNTHESIS OF NUCLEOSIDES

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When we refluxed 2-amino- β -D-arabinofurano[1',2':4,5]oxazoline (I) with α -chloroacrylonitrile in a ratio of 1:1 or 1:2 in alcohol, we unexpectedly found that the reaction does not stop with the formation of 2,2'-anhydro-1-(β -D-arabinofuranosy1)-5-chloro-5,6-dihydrocytosine (II); a second molecule of α -chloroacrylonitrile immediately undergoes reaction, and this is followed by splitting out of hydrogen chloride and the formation of 6-chloro-5-amino-2,2'-anhydro-3-(β -D-arabinofuranosy1)-3,4-dihydropyrido[2,3-d]pyrimidine (III) and 4a-chloro-6-cyano-2,2'-anhydro-3-(β -D-arabinofuranosy1)-3,3,4a,5-tetrahydro-6H-pyrrolo[2,3-d]pyrimidine (IV) in 35% overall yield.

Compounds III and IV were separated by successive crystallization from n-propyl alcohol and 90% ethanol. Compound IV was obtained in 6% yield and had mp 178-179°C (ethanol) and $\alpha_D^{2°}$ -42.4° (c 0.25, dimethylformamide). Compound III was obtained in 17% yield and had mp 238°C (dec., ethanol), $\alpha_D^{2°}$ -305.2° (c 0.25, dimethylformamide), and a molecular weight of 312 (by mass spectrometry).

A singlet of an NH₂ group at 5.85 ppm, a singlet of a pyridine ring CH group at 7.22 ppm, and a singlet of a CH₂ group of an unsaturated pyrimidine ring at 4.45 ppm are observed in the PMR spectrum (d₆-DMSO) of III. In the case of IV, the signal of the protons attached to C₄ appears at 4.02 and 3.76 ppm in the form of a characteristic AB quartet (²J = 13 Hz). The 5-CH₂ group is displayed in the form of a multiplet at 2.5-2.9 ppm. The signal of the



proton attached to C₆ at 5.00 ppm is observed in the form of a double doublet (${}^{3}J$ = 1.5 and 5.2 Hz).

A characteristic band at 2250 cm⁻¹ (C = N) is observed in the IR spectrum of a mineral oil suspension of IV. UV spectrum (water), $\lambda_{max}(\varepsilon)$: 332 (8620) (III) and 250 nm (12000) (IV).

Found for III: C 46.0; H 4.2; Cl 11.9; N 18.3%. C₁₂H₁₃ClN₄O₄. Calculated: C 46.1; H 4.2; Cl 11.3; N 18.3%. Found for IV: C 45.7; H 4.2; Cl 11.4; N 18.2%. C₁₂H₁₃ClN₄O₄. Calculated: C 46.1; H 4.2; Cl 11.3; N 18.3%.

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