〔J. Org. Chem., **50**, 1512 (1985)〕

Pyrimidines. 54. Ring Transformation of 5-(2-Carbamoylvinyl)uracil Derivatives to 5-Carbamoylpyridin-2-ones. KOSAKU HIROTA*, YUKIO KITADE, KAORU SHIMADA, YOSHIFUMI MAKI

Reaction of 5-formyluracil derivatives with (carbamoylmethylene)triphenylphosphorane led to the formation of both the corresponding(Z)- and (*E*)-5-(2-carbamoylvinyl) uracil derivatives(1 and 2). Upon treatment of the Z isomers (1) with ethanolic sodium ethoxide, a mononuclear heterocyclic rearrangement occurred easily to give 5-(ethoxycarbamoyl)pyridin-2-ones (3) and 5-(*N*-substituted carbamoyl) pyridon-2-ones (4). Under the analogous conditions, the *E* isomers (2) were converted into (3) and (4) together with 5-(*N*-substituted carbamoyl)-1-methylpyridin-2-ones (5). Addition of water to the reaction mixture accelerated the conversion of (2) into (5). Conceivable reaction sequences for the present pyrimidine-to-pyridine transformations are discussed.

〔Chem. Pharm· Bull., **33**, 4212 (1985)〕

Nucleosides. II. Direct Synthesis of 5-Substituted 2′, 5′-Anhydro-1-β-D-arabinofuranosyluracils from Uridine Derivatives. KOSAKU HIROTA*, YUKIO KITADE, TETSUO TOMISHI, YOSHIFUMI MAKI

Reaction of 5-substituted 2′,5′-dichloro-2′,5′-dideoxyuridines with methanolic sodium hydroxide under reflux afforded the corresponding 5-substituted 2′,5′-anhydro-1-β-D-arabinofuranosyluracils (1) in high yield. On the other hand, reaction of 5-substituted uridines with the Vilsmeier-Haack reagent ($POCl_3$/DMF) followed by treatment with methanolic sodium hydroxide under reflux led to directly the formation of the corresponding anhydrouridines (1) in good yield. The latter method is much more practical and convenient for the preparation of 2′,5′-anydrouridines (1),

〔Nucleosides & Nucleotides, **4**, 681 (1985)〕

Nucleosides. Part 3. Synthesis of 2-N-Substituted 1-β-D-Arabinofuranosylisocytosine Derivatives by the Reaction of 2′, 5′-Dichloro-2′, 5′-dideoxyuridine with Amines. KOSAKU HIROTA*, YUKIO KITADE, TETSUO TOMISHI, YOSHIFUMI MAKI

Reaction of 2′, 5′--dichloro-2′, 5′-dideoxyuridine (1) with ammonia and benzylamine afforded the corresponding 2-*N*-substituted 1-(5-chloro-5-deoxy-β-D-arabinofuranosyl)isocytosine derivatives (2). Reaction of (1) with ammonia, methylamine, cyclohexylamine, and benzylamine followed by treatment with methanolic sodium methoxide gave the corresponding 2-*N*-substituted 1-(2,5-anhydro-β-D-arabinofuranosyl) isocytosine derivatives (3). Reaction mechanisms for the formation of (2) aud (3) are discussed.