SYNTHESIS OF ANALOGS OF OLIGOURIDYLIC ACID

D. É. Zarin'

The alkylation of silyl derivatives of uracils with diethyl bromomalonate and reduction of diethyl 1-uracilylmalonate were studied in order to obtain 1-(1,3-dihydroxy-2-propyl)uracil, which is the starting compound for the synthesis of symmetrical analogs of oligouridylic acid. The possibility of selective tritylation of one of the hydroxy groups in 1-(1,3-dihydroxy-2-propyl)uracil was established. Preparative methods for the synthesis of phosphate esters of 1-(1,3-dihydroxy-2-propyl)uracil were developed. The mechanism of the formation of a phosphoric acid diester bond in the synthesis of an analog was investigated by pulse ^{31}P NMR spectroscopy, and it is shown that the synthesis of the diester can be realized by means of both dicyclohexylcarbodiimide and 2,4,6-triisopropylbenzenesulfonyl chloride. In the reaction of the latter the formation of a triester also was recorded. The mechanism of the reaction does not differ substantially from the mechanism of natural dinucleoside monophosphates. Analogs of oligouridylic acid from the dimer to oligomers with a degree of polymerization ranging from nine to 10 were obtained by polycondensation of 1-(1,3-dihydroxy-2-propyl)uracil phosphate and were fractionated with respect to their molecular weights.

Institute of Organic Synthesis, Academy of Sciences of the Latvian SSR; scientific supervisor R. A. Zhuk.

NITRO AND AMINO DERIVATIVES OF 1-THIAINDENYL AND 1-THIAINDANYL SULFONES AND SYNTHESES BASED ON THEM

A. Kh. Kadyrov

The nitration of alkyl-1-thiaindene and 1-thiaindan 1,1-dioxides with concentrated nitric acid, mixtures of nitric and acetic acids, and potassium or ammonium nitrate and sulfuric acid was studied. Mononitro derivatives are formed in high yields in the nitration of 1-thiaindene and 1-thiaindan 1,1-dioxides with potassium or ammonium nitrate in sulfuric acid. The optimum conditions for the preparation of dinitro derivatives of 1-thiaindene 1,1-dioxides were worked out. Mononitro-1-thiaindene and 1-thiaindan 1,1-dioxides were reduced to the corresponding amines, and a number of the latter were synthesized. N-Arenesulfonamido-1-thiaindene 1,1-dioxides have spasmolytic activity, while 6-amino-1-thiaindene 1,1-dioxides have light- and heat-stabilizing properties for cellulose acetate.

V. I. Nikitin Institute of Chemistry, Academy of Sciences of the Tadzhik SSR; scientific supervisors Professor I. U. Numanov and I. M. Nasyrov.

STUDY OF THE NITRATING ACTIVITY OF A MIXTURE OF NITRIC ACID AND ACETIC ANHYDRIDE IN REACTIONS WITH FURAN COMPOUNDS

M. A. Trushule

This research is devoted to a study of the optimum conditions for the preparation of a mixture of nitric acid and acetic anhydride, its stability during storage, the peculiarities of its nitrating activity, and its safer use. Furan compounds were selected as model compounds. In solutions of acetyl nitrate in acetic anhydride

the unchanged nitric acid, like sulfuric acid, catalyzes the nitration reaction. When the nitration is carried out in acetic anhydride, oxidative acetoxylation of the furan ring to give 2,5-diacetoxy-2,5-dihydro- and 4,5-diacetoxy-4,5-dihydrofurans takes place to a small extent. The presence of free radicals in the freshly prepared nitrating reagent was observed for the first time. It is shown that the concentration of free radicals and the nitrating activity of the mixture of nitric acid and acetic anhydride increase markedly when strong acids are present. It is assumed that nitration with this mixture may proceed via a radical mechanism, as well as via an ionic mechanism. Promising methods for the nitration of furan compounds were developed, and an improved method for the preparation of 5-nitrofurfural diacetate was incorporated in industrial production.

Institute of Organic Synthesis, Academy of Sciences of the Latvian SSR; scientific supervisor K. K. Venter.

SYNTHESIS AND OXIDATION OF 1,4-DIHYDROPYRIDINES

Ya. R. Uldrikis

A series of studies of the synthesis and properties of 1,4-dihydropyridine derivatives were carried out. A convenient method for the preparation of 4-unsubstituted 3,5-dicarbonyl derivatives of 2,6-dimethyl-1,4-dihydropyridine was developed, and a number of compounds based on β-diketones and esters of β-keto carboxylic acids were synthesized. It is shown that one can use geminal diamines in place of an aldehyde in the Hantzsch synthesis. 1,4-Dihydroisonicotinic acid derivatives and monosubstituted amides of 2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylic acid were synthesized. The effect of substituents on the reactivities of 1,4-dihydropyridines in the case of chemical (in reactions with chloranil and compounds that contain an activated olefin bond), electrochemical, and enzymatic oxidation was investigated systematically for the first time. It is shown that the probable reaction center is the γ-carbon atom of 1,4-dihydropyridine. The synthesized compounds were used for extensive biochemical and biological studies, as a result of which the original antioxidant "diludin" (2,6-dimethyl-3,5-diethoxycarbonyl-1,4-dihydropyridine) for the stabilization of the carotene of fodders, which also acts as a stimulant of the growth of agricultural plants, was created and incorporated in agricultural practice. A method for the industrial preparation of diludin was developed and incorporated in production. Ready-made forms for introduction of the antioxidant into herbaceous meal were created.

Institute of Organic Synthesis, Academy of Sciences of the Latvian SSR; scientific supervisor G. Ya. Dubur.

DERIVATIVES OF GLYOXALS AND GLYOXYLIC ACIDS OF THE FURAN SERIES

A. Yu. Tsimanis

This research is devoted to a search for new methods for the synthesis of furyl-substituted glyoxals, glyoxylic acids, and their derivatives in order to obtain α-furylquinoxalines, among which compounds with high antibacterial activity have been observed. A new method for the preparation of 5-nitro-2-furylglyoxal aldoxime, which consists in the nitrosation of 2-acetyl-5-nitrofuran with alkyl nitrite in concentrated sulfuric acid, was developed. The E configuration and the preferred conformation of the synthesized furyl- and phenylglyoxal aldoximes were established. The oxidation of α-bromomethyl ketones with dimethyl sulfoxide (DMSO) was studied. It was established that glyoxylic acids and the products of their decarbonylation are formed along with the known products (glyoxals and methylthio esters of glyoxylic acids) in the course of the Kornblum reaction. Two new methods for the synthesis of glyoxylic acids, which consist in the oxidation of α,α-dibromomethyl ketones with DMSO or with aromatic N-oxides, are proposed. Isomeric α-furylquinoxalines