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

with a substituent in the benzene ring were obtained by condensation of furyl-substituted glyoxals, glyoxylic acids, and their derivatives with substituted o-phenylenediamines; the conditions for the primary formation of one of the isomers were found. It is shown that the character of the substituent in the o-phenylenediamine, the nature of the α-dicarbonyl component, and the pH of the medium affect the direction of the reaction. It was established that, in addition to nitrofurylquinoxalines, 2-(5-iodo-2-furyl)quinoxaline has high antibacterial activity.

Institute of Organic Synthesis, Academy of Sciences of the Latvian SSR; scientific supervisor N. O. Saldabol.

STUDY OF THE SYNTHESIS OF PYRIDINE AND SOME OF ITS METHYL HOMOLOGS BY GAS-PHASE CATALYTIC CONDENSATION OF CARBONYL COMPOUNDS WITH AMMONIA

V. A. Shikhanov

An experimentally substantiated mechanism for the gas-phase condensation of carbonyl compounds with ammonia that makes it possible to predict the direction of reactions for the formation of pyridine bases from virtually any (with respect to structure) carbonyl compound and ammonia is proposed. It was established experimentally for the first time that the catalytic centers of the aldol condensation of carbonyl compounds and their Michael reaction, which precede the formation of the pyridine bases during their gas-phase synthesis, are the aprotic acid centers; the protic acid centers are the most active catalytic centers in the cyclization of the intermediates to alkylpyridines. Some side reactions that occur during the synthesis of pyridine and its homologs were revealed and investigated. Kinetic studies of the synthesis of pyridine and 3-methylpyridine by gas-phase condensation of acetaldehyde, formaldehyde, and ammonia on an industrial aluminosilicate catalyst were carried out. A fundamental technological scheme for the synthesis and isolation of pyridine and its homologs is recommended.

Scientific-Research Institute of Monomers for Synthetic Rubber; scientific supervisor A. P. Ivanovskii.