

more readily than the conjugate acids and that the reaction proceeds via a radical-chain mechanism. In the case of condensed systems the degree of shielding of the oxopyridine amide proton has a pronounced effect on the ability to undergo oxidation. The alkylation of 2-oxo-1,2,3,4-tetrahydropyridines, which have three nucleophilic centers, by means of alkyl halides was realized, and it was established that the nitrogen atoms and the carbon atom in the 3 position are more reactive. 2-Aminopyridines and condensed heterocyclic systems, viz., pyrazolo[3,4-b]pyridine and tetrazolo[5,1-a]pyridine, were synthesized through 2-chloropyridines. An original method for the synthesis of γ -butyro- and γ -spirobutyrolactones by bromination of the products of addition of N,N₁-disubstituted diamines to α,β -unsaturated ketones was developed. The synthesized derivatives of 2-oxopyridines and γ -butyrolactones have tranquilizing, hypotensive, and antioxidative activity.

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SYNTHESIS, STRUCTURE, AND SOME PROPERTIES OF HYDRAZONO AND HYDRAZINO DERIVATIVES OF PHTHALAZINE

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This dissertation is devoted to the study of the structures of the products of the reaction of 1-chlorophthalazines with hydrazine and its derivatives and to the synthesis and study of the structures and chemical and biological properties of various types of hydrazones of 2-methylphthalazans and phthalazinylhydrazones. New types of hydrazones, viz., various hydrazones of 2-methylphthalazones and 2H-phthalazones and N-methyl-N-phthalazinylhydrazones, as well as 1-arylazophthalazines, were synthesized. It was established from the set of physical (IR, UV, and PMR spectroscopy and the method of dipole moments) and chemical methods that the products of the reaction of 1-chlorophthalazines with hydrazine (as well as the products of condensation of these compounds with aldehydes and ketones) and nitroarylhydrazines exist in the form of phthalazone hydrazones. Several factors that affect the tautomeric equilibrium of the two forms of N,N-disubstituted derivatives were characterized. Erroneous data on the products of the reaction of hydrazine and methylhydrazine with 1-chlorophthalazines and on some of their derivatives (the medicinal preparation "budralazin") were rectified. It is shown that the transition from hydrazones of 2H-phthalazones to hydrazones of 2-methylphthalazones leads to a change in the geometry of the molecules. It was established that in the acid hydrolysis of N-methyl-N-(4-chloro-1-phthalazinyl)hydrazones a change in the nature of the substituents in the ylidene fragment gives rise to a change in the reaction center; this is explained by the difference in the three-dimensional and electronic structures of their molecules. It was observed that the compounds obtained have antihelminthic and chemosterilizing activity.

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SYNTHESIS OF 9-ALKENYLCARBAZOLES AND SOME ASPECTS OF THEIR REACTIVITIES IN CATIONIC POLYMERIZATION

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Methods for the preparation of new monomers based on carbazole were developed by means of reactions of carbazole with acrolein and the base-catalyzed isomerization of 9-allylcarbazole. In contrast to 9-vinylcarbazole, 9-alkenylcarbazoles that contain β -alkyl substituents attached to the double bond are not capable of forming high-molecular-weight products but give primarily cyclic dimers. The formation of oligomers is explained by the deactivating effect of the β -alkyl substituent; this was proved by a study of the relative

activities of 9-vinylcarbazole and trans-9-propenylcarbazole in the reaction with carbonium ions. Substantially lower activity of the cis isomers of 9-alkenylcarbazoles in cationic polymerization (dimerization) and in other electrophilic addition reactions was observed. It is shown on the basis of the experimentally found data on the relative thermodynamic stabilities of the cis and trans isomers of 9-propenylcarbazole and by means of structural models and the UV and ^{13}C NMR spectra that the difference in the activities of the isomers is due to a decrease in the degree of p- π conjugation in the cis isomer because of steric interactions between the substituents attached to the double bond. The photosensitive properties of some of the materials obtained on the basis of 9-alkenylcarbazoles were studied.

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SYNTHESIS AND STUDY OF THE PRODUCTS OF PHOSPHORYLATION OF HEXAHYDRIC ALCOHOLS AND HYDROXY CARBOXYLIC ACIDS

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This dissertation is devoted to the study of the peculiarities of the phosphorylation of structurally symmetrical acyclic polyhydroxy compounds, viz., d-mannitol, galactitol, and galactaric acid. The possibility of the formation of latticed diphosphites of hexitols that contain fragments of the 2,6,7-trioxa-1-phosphabicyclo[3,2,1]octane type as a result of the reaction of hexitols with phosphorus trichloride and tris(N-diethyl-amido)phosphite is demonstrated for the first time. The reaction of triethyl phosphite with hydroxy carboxylic acids with an α -carboxy group in the molecule leads to the formation of mixed or absolute phosphates (O phosphorylation). The reactivities of the hydroxy groups in hydroxy dicarboxylic acids and tricarboxylic acids is determined to a considerable extent by the competitive effect of the α - and β -carboxy groups: An increase in the effect of the β -carboxy group favors nucleophilic substitution of the hydroxy group by triethyl phosphite with the formation of a phosphonate (C phosphorylation). The assumption that the reactions of the hydroxy groups of hydroxy carboxylic acids, as well as some 1,2- and 1,3-diols, glycerol, and mannitol, with PCl_5 , which lead to C chlorination and O phosphorylation (the formation of dichlorophosphates), proceed through the intermediate formation of various types of dialkoxytrichlorophosphoranes was confirmed by the synthesis of the previously unknown cyclic dihydroxytrichlorophosphoranes from dihydroxymaleic and citric acids.

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ACYLATION OF NAPHTHOLS AND SOME HETEROCYCLIC COMPOUNDS WITH UNSATURATED ACID CHLORIDES AND PESTICIDAL PROPERTIES OF THE SUBSTANCES OBTAINED

Z. Sh. Enileeva

This research was devoted to the O acylation of naphthols and the N acylation of benzimidazolones with α, β -unsaturated acid chlorides. 1,3-Diacylbenzimidazolones were obtained in the reaction with benzimidazolone. The alkylation of 5-nitrobenzimidazolone with alkyl halides in the presence of bases in acetone solution was realized. A relationship between the herbicidal activity of the compounds obtained and their chemical structure was established. 5-Nitro-1,3-dialkylbenzimidazolones are highly effective herbicides.

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