THIRD ALL-UNION SCIENTIFIC CONFERENCE ON THE CHEMISTRY AND TECHNOLOGY OF FURAN COMPOUNDS

M. V. Shimanskaya and V. G. Kul'nevich

An all-union conference devoted to the problems in the chemistry and technology of furan compounds was held in the Krasnodar Polytechnic Institute (KPI) from October 4 to October 5, 1978. Representatives from research institutes, universities, and industrial enterprises of a number of cities participated in the conference.

In his opening address to the conference the rector of KPI, Professor K. A. Daragan, noted that in the 15-yr period that has elapsed since the second conference on the chemistry of furan great advances have been made in this field. One of the new centers that is doing effective research involving the chemistry and technology of furan compounds is the department of organic chemistry and the problem laboratory of KPI. Professor Daragan also noted the great significance of the fundamental research of P. A. Moshkin, Yu. K. Yur'ev, A. A. Ponomarev, S. A. Giller, A. L. Mndzhoyan, and A. P. Terent'ev, in memory of whom those present were silent for a moment, with respect to ensuring the development of this trend in organic chemistry.

A total of 18 review and 100 display papers were presented at the conference. In review papers from KPI Professors V. G. Kul'nevich, L. A. Badovskaya, and Z. I. Zelikman presented the results of a study of various transformations of furfural and the substances formed from it, demonstrated possible ways to use a number of the products in the national economy, and accurately defined the problems involved in the mechanisms of the most common reactions of furfural, particularly the reactions with oxygen, hydrogen peroxide, and polyols. The authors have developed a number of practical recommendations, viz., a method for the stabilization of furfural during storage, a method for the synthesis of crotonolactone and succinic acid from substandard furfural and still residues from its manufacture, etc.

Methods for the synthesis of diverse trisubstituted ethylenes with a furan ring as one of the substituents were demonstrated in a paper presented by A. Jurasek (Slovakian Polytechnic Institute, Bratislava). The problems dealing with the stabilities of the carbanions and the transfer of the polar effects of substituents attached to the aryl grouping in sulfones and sulfides of 5-nitrofurans were discussed during a comparison of the pK_a values, rates of formation of the carbanions, and the chemical shifts in the NMR spectra. Literature data and the authors' own observations regarding the lack (according to x-ray diffraction data) of deviations from planarity of the five-membered ring for hydrogenated and substituted furan derivatives were presented in a paper by Ya. Ya. Bleidelis and A. A. Kemme (Institute of Organic Synthesis, Academy of Sciences of the Latvian SSR). On the basis of a study of the ^{13}C NMR spectra of carbonyl compounds of furan and thiophene, as well as their complexes with $AlCl_3$, L. I. Belen'kii and I. B. Karmanova (Institute of Organic Chemistry, Academy of Sciences of the USSR) revealed differences in the transmission of the effects of a substituent through heterorings as a function of the position of the substituent. They showed that the chemical behavior of substituted furans and thiophenes is determined by the ring heteroatom, which they regard as a unique activating "internal function" that directs the attacking agent to the α position.

The peculiarities of the electrical reduction of nitrofurans as compared with other heterocyclic and aromatic and aliphatic nitro compounds and the effect of the nature of the reaction medium were reported in papers by Ya. P. Stradyn' and R. A. Gavar (Institute of Organic Synthesis, Academy of Sciences of the Latvian SSR). The individual steps in the electrical reduction of nitrofurans were uncovered, the EPR spectra with different hyperfine structures (hfs) of the products of one-electron reduction were recorded and the density of the unpaired spin of the anion radicals obtained was compared with the results of quantum-chemical calculations. It was shown that the transmission of the effect of substituents

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through the furan ring is greater by a factor of 1.16 than through the benzene ring for electrical reduction reactions. It was assumed that there is an analogy with processes that take place under enzymatic reduction conditions.

M. V. Shimanskaya (Institute of Organic Synthesis, Academy of Sciences of the Latvian SSR) examined the effect of modified vanadium-molybdenum catalysts and the presence of substituents in the furan ring on the quantitative indexes of catalytic partial vapor-phase oxidation. The significance of the adsorbability and the character of the orientation of the molecules undergoing oxidation on the surface, as well as the ease of removal of the side chain, was emphasized. Infrared spectroscopic data on the structure of the surface intermediate product of oxidation of furan to maleic anhydride were presented.

The peculiarities of the reaction of 5-halofurans (with activating groups in the 2 position) with secondary amines were demonstrated in papers by V. N. Novikov, S. V. Borolaev, and L. D. Babeshkina (Rostov University). The complex mechanism of the reaction with 2-formyl-5-halofurans was established, and pathways for the formation of both the products of halogen substitution and the products of simultaneous addition of amines to the carbonyl group through a stable intermediate that evidently has the structure of a three-membered quasi-aromatic system were uncovered.

A. F. Oleinik and K. Yu. Novitskii (S. Ordzhonikidze All-Union Scientific-Research Pharmaceutical-Chemistry Institute, Moscow) compared two methods for the synthesis of arylfurans (by the formation of a furan ring or by the introduction of an aryl residue in a furan compound) and made a detailed study of the reaction of diazonium salts with furan derivatives that contain electron-acceptor substituents. A large number of 2-substituted 5-arylfurans were synthesized, the reactivities of 5-arylfurans in electrophilic substitution reactions were studied, and a decrease in the reactivity because of interaction of the furan ring with the electron system of the benzene ring was established. Substances that display considerable biological activity were discovered.

N. O. Saldabol (Institute of Organic Synthesis, Academy of Sciences of the Latvian SSR) presented the results of a study of the electrophilic and radical substitution reactions of furylazoles and demonstrated the significance of the effect of the nature of the azole and the heteroring annelated with it, as well as the strength of the electrophilic agent and the reaction conditions, on the order of substitution in the furan or azole ring. Destructive oxidation of the furan ring under the influence of a nitrating mixture on 2-(5-bromo-2-furyl)- and 2-(5-nitro-2-furyl)imidazo[1,2-a]pyrimidines was observed.

Ways to use free-radical reactions for the preparation of tetrahydrofuran (THF) derivatives and the conversion of the latter to bifunctional aliphatic compounds were shown in a paper by V. G. Glukhovtsev and G. I. Nikishin (Institute of Organic Chemistry, Academy of Sciences of the USSR). The generation of free tetrahydrofuryl and tetrahydrofuroxyl radicals under the influence of various agents and their transformation in reactions involving interradical recombination, detachment of hydrogen from the solvent, addition to multiple bonds, and isomerization with ring opening were examined. The reactions of furan and alkylfurans with free radicals were examined, and the effect of the nature of the radicals and the structure of the furan compound on the character of their reaction was discussed.

E. Ya. Lukevits (Institute of Organic Synthesis, Academy of Sciences of the Latvian SSR) presented a wealth of material on the syntheses and properties of three types of furan derivatives of silicon, germanium, and tin and showed that there is a deshielding effect of the vacant d orbitals of the element on the π-electron system of furan when there is a direct bond between the furan ring and a group IV element; only their electron-donor effect is displayed when the heteroorganic substituents are one or two methylene groups away from the furan ring. A decrease in toxicity when a phenyl group is replaced by a furyl group in silatranes was established. The dissimilar physiological effects of some organosilicon derivatives of furan were disclosed.

I. I. Ibragimov (Sumgaitsk Branch of the Institute of Petrochemical Processes, Academy of Sciences of the Azerbaidzhan SSR) demonstrated the promising character of the use of the Kondakov reaction for the creation of industrial methods for the preparation of 2-alkylfurans. He showed that the yields of 2-alkylfurans increase as the molecular weights of the acid chlorides that undergo reaction with allyl or methallyl chloride increase.

The growth and prospects for the future growth in the development of the manufacture of furfural, furfuryl and tetrahydrofurfuryl alcohols, the FA monomer, and other binders based on furfural, tetrahydrofuran, and polifurit were examined in a paper by N. G. Semanov (VTO Soyuzgidrolizprom, Moscow). He emphasized the advisability of finding new ways to produce tetrahydrofuran and improving the technological process involved in the production of furfural in order to utilize more fully the raw material and coordinate the energies of a number of scientific-research centers in the country in order to accelerate the solution of these problems. Yu. M. Mamatov (Fergana Division of the Scientific-Research Institute of Plastics) reported data on the synthesis of monomers based on furfural and furfuryl alcohol and enumerated the areas of application of polymeric materials that contain a furan link.

In a resolution adopted by the conference it was proposed that research involving the synthesis and study of the properties of new furan compounds be developed more extensively in order to search for promising physiologically active substances for medicine and agriculture. It is important to create modern continuous technology for the production of furfural, tetrahydrofuran, and furfuryl and tetrahydrofurfuryl alcohols, to develop technology for the production of furan compounds from petrochemical raw material, and to search for ways to create new polymeric materials from furans. Attention was directed to the need for a search for efficient ways to recover and utilize furfural and other furan substances that are present in gaseous discharges and waste waters.

The participants in the conference proposed that the next conference on this topic be held in Riga in 3-4 yr.

PROSPECTS FOR GROWTH IN THE PRODUCTION OF FURFURAL AND ITS DERIVATIVES

M. V. Shimanskaya

"The present state of and methods for the improvement and raising the level of the economic efficiency of the production of furfural and its derivatives by complex refining of pentosan-containing raw material" was the topic of the joint session of the all-union scientific council for the problem of the utilization of pentosan-containing raw material of the Academy of Sciences of the Latvian SSR and the section of the hydrolysis industry of the scientific-technical council of Glavmikrobioprom SM SSSR that was held in Moscow on December 5-6, 1978.

Of the 22 communications presented in this session, 15 were devoted to the problems involved in the improvement of the technology and quality of production and economic indexes in the production of furfural and seven were devoted to the technological processes involved in the refining of furfural.

The principal trends in the development of the manufacture of furfural were set forth in a paper by the assistant chief of Glavmikrobioprom N. S. Maksimenko. In addition to the utilization of the traditional forms of pentosan-containing raw material, primarily plant by-products, in the production of "large amounts" of furfural (we are referring here to factories with a capacity of 10,000-12,000 tons) — he projected the utilization of wood from deciduous trees, in which case the process is based on a two- or one-phase method with hydrolysis in continuously operating apparatuses. Organization of the refining of part of the furfural in furfural factories is proposed.

In the papers a great deal of attention was directed to the problems involved in the improvement of the technological processes for extraction of furfural from hydrolyzates and self-evaporation vapors, increasing the quality of technical-grade furfural, improvement of the economic indexes of its production, and reducing the losses of furfural with manufacturing effluents and waste products. In communications dealing with the technology of the manufacture of large-tonnage products of refining of furfural (furfuryl alcohol, tetrahydrofurfuryl alcohol, furan, tetrahydrofuran, polifurit, and synthetic resins based on the FA monomer, as well as other furan derivatives and preparations for agriculture and medicine that are based on furfural) attention was directed to the problems involved in increasing the

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