

THIRD SYMPOSIUM ON THE CHEMISTRY AND TECHNOLOGY
OF HETEROCYCLIC COMPOUNDS OF FOSSIL FUELS

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The Third Symposium on the Chemistry and Technology of Heterocyclic Compounds of Fossil Fuels, which was organized jointly by Donetsk State University and the Institute of Physical Organic Chemistry and Coal Chemistry of the Academy of Sciences of the Ukrainian SSR, was held from May 24 to May 26, 1978. In the five years that have elapsed since the second symposium the volume of scientific research devoted to the refining of fossil fuels has increased substantially, and the theoretical and experimental level of this research has been raised.

Representatives of scientific centers of the country engaged in research on the chemistry and technology of heterocyclic components of petroleum and coal tar – scientists from Moscow, Kiev, Donetsk, Kharkov, Riga, Sverdlovsk, Tomsk, Irkutsk, Tashkent, Ufa, Dnepropetrovsk, etc. – and workers from the coal-tar-chemical industry participated in the activities of the symposium. Five plenary papers, more than 80 sectional papers, which were presented in two sections, and ~80 display communications on the chemistry and technology of nitrogen-containing and sulfur-containing heterocyclic compounds and the possibilities of their use in the national economy were presented to the participants for discussion.

A paper by S. N. Baranov entitled "Prospects for the use of heterocyclic compounds of fossil fuels in the national economy," in which the increase in the source of raw heterocyclic compounds due to the increasing volume of mining of fossil fuels was demonstrated, was presented in a plenary session. The resources of sulfur-containing compounds due to the refining of sulfurous petroleums and gases have increased particularly significantly. The source of raw heterocyclic compounds has been expanded appreciably due to the refining of heavy petroleum fractions and low-temperature carbonization of tars, as well as a result of the putting into operation of new coal-tar-chemical factories. The volume of mining and refining of sulfurous petroleums and coals of new deposits in the eastern regions of the USSR – a large-tonnage source of sulfur and sulfur compounds – is increasing steadily.

A review of the most important research to find methods for the use of pyridine and quinoline bases, indole, and carbazole was given in the paper. It was shown that the resources of pyridine bases are considerably greater than the need for them in the country and that a portion of them are being exported. The proposed methods for the production of the herbicide khloramp (Institute of Organic Chemistry of the Ukrainian SSR) and katapin, which are capable of absorbing some of the resources of pyridine and picolines, are currently at the introductory stage. On the basis of a comprehensive analysis of the use of nitrogen- and sulfur-containing compounds isolable by refinement of fossil fuels, it was concluded that the use of mixtures without isolation of the individual nitrogen- and sulfur-containing fractions holds some promise. Despite the success in the synthesis of vinylcarbazole and the production from it of plastics with valuable properties (Tomsk Polytechnic Institute, V. P. Lopatinskii), the large-tonnage product of the coal-tar-chemical industry – carbazole – is not being utilized at all adequately.

The fluctuating demand for one or another chemical product requires that chemists exert serious anticipatory research both on the methods for the preparation of various derivatives and on the technology for their production. A heterylation method, i.e., the introduction of heterocycle residues in various nucleophilic organic compounds in the presence of acid chlorides or active metals (Donetsk State University), was examined as a promising method for the synthesis of diverse heterocyclic compounds.

A great deal of attention in the work of the symposium was directed to problems involved in the utilization of sulfur-containing compounds, the resources of which reach tens of millions of tons, that undergo combustion with fuel and contaminate the atmosphere with sulfur dioxide. A detailed analysis of the state of research on sulfur-containing components of various petroleums of the Soviet Union was given in a paper by V. F. Kam'yanov. Efficient technological schemes for the isolation of thiophene and benzothiophene from coal tar fractions were proposed in papers by a number of researchers from the Institute of Organic Chemistry of the

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Academy of Sciences of the USSR, Donetsk Polytechnic Institute, and VNIIREAKTIVÉLEKTRON (Donetsk). Unfortunately, there were no papers promising their rapid large-tonnage utilization in the national economy.

The necessity for desulfuration of fuels in a short time leads to surplus sulfur, hydrogen sulfide, and other simple sulfur compounds, and syntheses of unsaturated heterocyclic sulfur-containing compounds on the basis of acetylene, vinyl chloride, and the simplest sulfur compounds are therefore attracting attention. Polymeric materials obtained on the basis of such sulfur-containing monomers have valuable properties (Irkutsk Institute of Organic Chemistry of the Academy of Sciences of the USSR, M. G. Voronkov). Considerable interest during the symposium was generated by papers devoted to the study of the reactivities of heterocyclic components of coal tar and petroleum. A. K. Sheinkman (Dnepropetrovsk) in his name and in the name of T. V. Stupnikova (Donetsk) in a plenary paper presented a thorough analysis of the modern state of the chemistry of heteroaromatic cations and discussed their own achievements in this area. He noted his communication on the discovered dual reactivity of N-acyl derivatives of dihydropyridines, quinolines, and isoquinolines with respect to several organic cations. The result of this discovery was a new method for the synthesis of stable N-acyl salts of heteroaromatic cations.

R. S. Sagitullin (Moscow) presented a plenary paper in which he discussed rich material on new rearrangements of nitrogen heteroaromatic systems - pyrimido[1,2-a]indoles to α -carbolines, pyrazol[1,2-a]pyrimidines to pyrazolo[3,4-b]pyridines, indolizines to indoles, isoquinolines to α -naphthylamines, pyrimidines to 2-aminopyridines, and pyridines to anilines. These transformations represent a new type of molecular rearrangement that involves opening of the electron-deficient ring under the influence of bases with cleavage of the carbon-nitrogen bond and subsequent formation of a new ring at the electron-surplus portion of the molecule to give a carbon-carbon bond.

The last two plenary papers were devoted to an examination of the modern state of the chemistry of betaines (R. O. Kochkanyan, Donetsk) and to the prospects for the use of carbazole in the chemical industry (V. P. Lopatinskii, Tomsk).

The topics discussed in the sectional sessions were extremely diversified. As compared with the previous symposia, there was a significant increase in the specific weight of display papers (~30%). As in the previous symposia, a great deal of attention in the papers was directed to the development of methods for the synthesis of heteroaromatic compounds from products obtained by refinement of coal and petroleum, as well as to the study of their reactivities. Many papers devoted to methods for the construction of heterocyclic systems were presented in the symposium; various cycloaddition reactions have been widely used in this respect. For example, P. B. Terent'ev (Moscow) reported 1,3- and 1,4-cycloaddition reactions on the basis of vinylpyridines; these reactions lead to derivatives of quinoline, isoquinoline, azacinnolines, pyrrolocinnolines, etc. Yu. M. Volovenko (Kiev) reported the synthesis of amino and keto heterocycles on the basis of substituted acetonitriles. N. N. Przheval'skii (Moscow) reported the Fischer synthesis of indoles and pyrroles from azines via a scheme involving sigmatropic (3,3) rearrangements. A. A. Zeikan' presented material on the synthesis of sulfur derivatives of tetrabromopyridine and a study of their reactivities.

New methods for the introduction of substituents in the ring of heteroaromatic compounds were examined in a number of communications. Thus V. V. Men'shikov (Moscow) in his name and in the names of A. N. Kost and R. S. Sagitullin presented a paper on the direct amination of the pyrrole portion of the indole molecule, and T. V. Stupnikov discussed nucleophilic substitution of a hydrogen atom in the indole ring with the use of an intermediate 3-acylindoleninium cation. Interest was aroused by a communication by B. P. Zemskii (Donetsk), who discussed the synthesis and reactions of some nitrogen ylids-anhydro bases of pyridylindoles.

A substantial portion of the symposium consisted of research involving the study of reaction mechanisms. Here one must above all note L. M. Litvinenko (Donetsk), who presented papers on the effect of the structure of nitrogen bases on their reactivities. As in the previous symposia, a large number of papers were devoted to applied research: the search for new physiologically active preparations, metal-corrosion inhibitors, stabilizers of polymeric materials, herbicides, etc.

The symposium undoubtedly promoted the exchange of information, the familiarization of a large number of chemists with the modern state of research and urgent industrial problems, and the revelation and coordination of the most important and promising research trends.