POLISH–SOVIET SYMPOSIUM

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The advances in the chemistry of heterocyclic oxygen compounds were the subject of discussion in the Polish–Soviet symposium devoted to the 60th Anniversary of the Great October Socialist Revolution, which was held in Torun (Poland) September 22-24, 1977.

Twenty one scientists from the USSR, 75 scientific workers and Polish college teachers from Bydgoszcz, Warsaw, Wroclaw, Gdansk, Gliwice, Kielce, Cracow, Lodz, Torun, and Czestochowa, as well as five scientists from Bratislava (Czechoslovakian SSR) and two from Rostock (German Democratic Republic) participated in the symposium, which was organized by the Institute of Chemistry of N. Copernicus University. Representatives of the Polish Academy of Sciences and party workers and statesmen from the western area of Poland participated in the work of the symposium.

In his opening remarks to the symposium, the president of the organizing committee Professor T. Lesiak (Torun) appraised the contribution of the scientific centers of the USSR and Poland in research on oxygen-containing heterocyclic compounds. Professor A. N. Kost (Moscow State University) brought greetings from Soviet scientists and noted the fruitfulness of collaboration between Soviet and Polish scientists.

Problems involved in the synthesis, transformations, and structures of furan, pyran, and 1,3-dioxane derivatives were the center of attention in the symposium. A total of seven plenary papers were presented, and more than 50 communications were delivered in the sections.

In his plenary paper entitled "Advances in the chemistry of pyrylium salts," G. N. Dorofeenko (Rostov-on-Don) presented valuable material on the synthesis and transformations of pyrylium and chromylium salts and salts of analogous heteroaromatic cations. Of particular interest is the author's general method for the synthesis of condensed structures; this method made it possible, by recourse to the appropriate compounds with a pyridine ring, to find a method for the preparation of isoquinoline and carboline derivatives, analogs of natural alkaloids, etc.

L. Skulski (Physicochemical Laboratory of the Medical Academy, Warsaw) in his own name and in the name of M. Wojciechowski made a thorough analysis of the existing interpretations of tautomeric transformations, developed their own approach to the study of tautomerism in solutions (which stipulates the formation of intermediate ambident anions or cations in solution), and critically examined the identification of dual reactivity and polyreactivity with the presence of tautomerism.

A. N. Grinev (Moscow) cited valuable material on the synthesis of diverse 4-, 5-, and 6-hydroxybenzofuran derivatives using the classical reactions of the aromatic series. D. L. Rakhmankulov (Ufa) demonstrated the prospects for the use of the Prins reaction in the synthesis of conjugated diene hydrocarbons on the basis of 1,3-dioxanes. A number of homogeneous and heterogeneous catalytic transformations of 1,3-dioxacyclanes were examined, and the principles of the effect of the structure of the substrate on the reactivity were ascertained.

Professor Z. Jezmanowska (Institute of Fundamental Chemical Sciences, Medical Academy, Lodz) reported the reaction of benzo-γ-pyrones with hydroxylamine and phenylhydrazine, the conversion of isoxazoles to coumarins, and analogous reactions with other nucleophiles. [Correspondingly, W. Basinski (from the same institute) in a sectional section presented a paper on the reaction of isomeric methylfavones with hydroxylamine.]

S. S. Zlot-skii (Ufa) examined the transformations of 1,3-dioxacyclanes under the influence of free-radical donors and demonstrated the applicability of a radical-chain mechanism with quadratic termination in peroxide radicals for the oxidation of cyclic acetals. A number of examples of free-radical substitution reactions in this series were presented.

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W. J. Steč and R. W. Kinas (Center of Molecular and Macromolecular Studies, Polish Academy of Sciences, Lodz) demonstrated on the basis of measurements of the spin–spin coupling constants that the axial–equatorial orientation of the substituents in the 1,3,2-dioxaphosphorinane molecule depends on their nature. The steric interactions of the substituents attached to the ring carbon atoms with the substituents attached to the phosphorus atom and the interaction of the electron pairs of the endocyclic oxygen atoms with the exocyclic heteroatoms attached to phosphorus affect the conformation of the molecule in six-membered amido esters of phosphoric, thiophosphoric, and selenophosphoric acids.

L. A. Badovskaya and V. G. Kul'nevich (Krasnodar) reported the results of investigations of the mechanism of the reaction of furfural with hydrogen peroxide. The α-hydroxyperoxides of furan aldehydes, formyloxyfuran, and oxodihydrofuran were recorded. A convenient synthesis of furancarboxylic, acylacrylic, and acylpropionic acids and their derivatives was developed, and a new technological process for the preparation of succinic acid was proposed.

M. V. Shimanskaya (Riga) presented data obtained by her and A. Ya. Karmil'chik and S. A. Giller on relative reactivities in the transformations of furfural and methylfurfural on the surface of oxide and metal catalysts. Schemes of the mechanisms of these reactions were examined, and the practical realization of contact processes with pilot-plant equipment was reported.

V. Glukhovtsev (Moscow) cited a large amount of experimental data on the effect of the nature of the functional groups on the rate and direction of reactions involving addition to tetrahydrofurans and their oxidation, the properties and reactions of tetrahydrofuran peroxides, and new syntheses based on these peroxides. K. Yu. Novitskii (Moscow) reported the synthesis of arylfurans by means of the Meerwein reaction. A communication by V. A. Zefirova and R. A. Karakhanov (Moscow), who studied the synthesis and reactions of furylcyclopropanes, and a paper by R. Kad, V. Knoppova, and J. Kovač (chemistry department, Slovakian Higher Technical School, Bratislava) on the synthesis and properties of sulfur-containing furfural derivatives from 5-halo-2-formylfurans were also devoted to the chemistry of furan. R. Skowronski, R. Nazarski, and I. Skolimowski (State University, Lodz) reported on the results of conformational analysis of 2,2,5,5-tetramethyltetrahydrofuran derivatives by means of IR and NMR spectroscopy in comparison with crystallographic data.

J. Kovač and D. Vegh (chemical technology department, Slovakian Polytechnic Institute, Bratislava) presented several variants of the synthesis of 5-nitro-2-furylvinyl halides from 3-(5-nitro-2-furyl)acrylic acid. They developed a method for the exchange of the labile halogen in these compounds by other groupings and investigated the conditions for the detachment of hydrogen halide and the preparation of 5-nitro-2-furylacetylene. A. Jurasedk, J. Kovač, and M. Kovač reported the addition of diazomethane to α,β-unsaturated sulfones of the 5-nitrofuran series and the formation of the corresponding pyrazolines, which are converted by thermolysis to derivatives of tetrasubstituted ethylenes. A. Krutosikova and J. Kovač studied the reaction of 5-arylfuran-2-carbohydroxamic acid chlorides with enamines, which leads to isoxazolines or isoxazoles. In this series of communications from the laboratory of J. Kovač one's attention is drawn to the diversity of the models that contain a 5-nitrofuran grouping. Biological activity of the compounds obtained was established in a number of cases.

A number of communications regarding the practical application of furfural and some substances obtained from it are also related to the chemistry of furan compounds. Thus T. Lesiak and K. Mazeč (Institute of Chemistry, N. Copernicus University, Torun) demonstrated several methods for the conversion of furfural to diols and halo-substituted diols, which react with diisocyanates to give polyurethane resins with valuable properties, including in some cases the capacity for self-extinguishing. K. Stazinskaja and G. Derecki (Institute of Industrial Chemistry, Warsaw) discussed the synthesis of furan–formaldehyde and urea–furan–formaldehyde resins, particularly those based on 3-methylol derivatives of furans, which increase the rate of hardening of resins. The technology for the preparation of such resins for the casting industry was worked out. Z. Kin and H. Bardyga (J. and E. Sniadecki Technical-Agricultural Academy, Bydgoszcz) presented the results of the use of the products of condensation of furfural with acetone for the preparation of plastic concretes and organic mastics. Z. Kin also presented data on the industrial conditions for the prehydrolysis of beechwood and characterized the parameters of the technological process for the dehydration of pentoses to furfural. J. Jaworski from the same scientific center reported the chromatographic determination of furfural, methanol, and acetic acid in furfural-containing technical mixtures.

F. Godzejewicz and S. Skrowaczewska (Institute of Organic and Physical Chemistry, Wroclaw Polytechnic Institute) presented a new approach to the synthesis of pyrylium salts based on the alkaline cleavage of the product of the reaction of pyridine with 2,4-dinitrochlorobenzene and subsequent cyclization in the presence of perchloric acid. E. A. Zvezdina (Rostov) discussed data on the reactions of pyrylium salts with thionylaniline, azomethines, benzaldioxime, thiourea, phenyl isothiocyanate, etc. with subsequent recyclization to pyridinium salts and on the analogous synthesis of pyrimidine derivatives.

M. G. Voronkov, N. A. Keiko, L. G. Stepanova, and I. D. Kalikhman (Irkutsk) presented a paper on the reactivities of 2,5-dialkoxy(dialkylthio)-2,3-dihydro-γ-pyrans. R. Skowronski, T. Markowicz, R. Nazarski, and I. Skolimowski (State University, Lodz) discussed the synthesis and conformation of alcohols of the 2,2,6,6-tetramethyltetrahydropyran series.

G. Grynkiewicz, V. Pribe, and A. Zamojski (Institute of Organic Chemistry of the Polish Academy of Sciences, Warsaw) presented data on the catalytic reaction of tri-O-acetylgalactal with nucleophilic reagents and the effect of the composition of the catalyst and the nature of the solvent on the reaction. When stannic chloride ($SnCl_4$) in 1,2-dichloroethane at room temperature is used, alcohols or phenols give 2,3-unsaturated glycosides with an α-threo configuration in 50-80% yields. V. N. Odinokov, O. S. Kukovinets, and G. A. Tolstikov (Ufa) presented a large amount of experimental data on the ozonation of stereoisomeric bicyclo-[2.2.1]hept-5-ene-2,3-dicarboxylic acids and on the reduction and hydrolysis of the corresponding peroxides.

É. A. Karakhanov (Moscow) in a paper entitled "Cationoid intermediates in the transformations of condensed oxygen-containing heterocyclic compounds" correlated data on the catalytic dehydrogenation of 2,3-dihydrobenzofuran and chroman, on the mechanism of the reaction of the substrate with the active surface centers, and on the structure of the cationoid intermediates. According to the deuterium-exchange and mass-spectral data, the α-hydrogen atoms of 2,3-dihydrobenzofurans are closer to the surface of the aluminum silicate than the atoms in the 3 position.

P. Sawlewicz, M. Smulkowicz, P. Sowinski, and E. Borowski (Gdansk Technical University) presented a paper on the synthesis of 6-ketooctahydrobenzofuran by intramolecular cyclization. E. A. Viktorova (Moscow) examined the reaction of benzofurans with lithium in hexamethylphosphoric triamide (HMPT). The author assumes that the reaction proceeds as successive addition of two electrons to give the dianion. Its independent nucleophilic centers have comparable reactivities in nucleophilic substitution, and this leads to easy dialkylation.

E. Wojtanis, B. Sila, and T. Lesiak (Institute of Chemistry, N. Copernicus University, Torun) investigated the composition of the substances formed in the Rosenmund reduction of alkylbenzofuran-2-carboxylic acid chlorides and expressed assumptions regarding the mechanism of the process. E. Kossakowski and T. Zawadowski (Institute of Medicinal Sciences of the Medical Academy, Warsaw) presented data on the synthesis of pharmacologically interesting benzofuran and furochromone derivatives.

E. Jedlinski, J. Lukasik, M. Gibas, and J. Dudek (Institute of the Physical Chemistry and Technology of Polymers of the Silesian Polytechnic Institute, Gliwice) on the basis of PMR spectral data proposed a half-chair conformation for 2,4,5-trisubstituted dioxolanes. J. Maslinska-Solich (the same institute) investigated the reaction of maleic anhydride with 2-furyl-1,3-dioxanes, which leads either to copolymers or to adducts, depending on the structure of the 1,3-dioxane. A. Pjasecki and B. Burczyk (Institute of Organic Technology and Plastics, Wroclaw Polytechnic Institute) presented examples of the syntheses of cis and trans isomers of 2-alkyl-4-hydroxymethyl-1,3-dioxolane and also gave the characteristics of their surface activities. J. Beliawski, S. Witek, and A. Beliawski (the same institute) thoroughly demonstrated the possibilities of the synthesis and some of the transformations of cyclic acetals of the 1,3-dioxane type and their thio analogs and presented data on their herbicidal activity.

U. B. Imashev (Ufa) reported that the thermocatalytic cleavage of 4-alkenyl-1,3-dioxanes in the vapor phase is of technical value for the preparation of polyenes. A mechanism for the reaction was proposed and discussed. S. Kwiatkowski and W. Danikiewicz (Institute of Organic Chemistry and Technology of the Chemical Department of the Polytechnic Institute, Warsaw) presented data on the reaction of trans-2-bromocyclopentanol acetate with potassiomalonic ester, which leads to 1,3-dioxolanes.

W. Waclawek (Teachers Institute, Czestochowa) analyzed literature data on the conditions for manifestation of the dioxane effect and showed that the chief reason for the difference in the dipole moments determined in 1,4-dioxane and an inert solvent is complexing. E. Blazejewski, W. Moska, and E. Sichlinski (Gdansk University) examined various aspects of the use of 1,4-dioxane as a solvent for photochemical reactions.

M. Uger and A. Martvon (Chemical-Engineering Department of Slovakian Polytechnic Institute, Bratislava) reported the synthesis of 1,3,5-oxidiazine-4-thiones from phenyl isothiocyanate and arylazomethines. M. Oswencimska and S. Witek (Institute of Organic Technology and Plastics, Wroclaw Polytechnic Institute) presented a great deal of material on the synthesis of 4,4-dialkyl-2-oxomorpholines and their hydrolysis. A. Beliawska and S. Witek (the same institute) reported the synthesis of 1,3-oxazolidine derivatives with a —CONHR grouping attached to the nitrogen atom (the compounds are of interest as herbicides). E. B. Gaca, K. Chyziewicz, and S. Schodzinski (J. and E. Sniadecki Technical-Agricultural Academy, Bydgoszcz) presented a paper on the preparation of benzoxazoles, which are used in the synthesis of sensitizing dyes, by cyclization of o-aminophenol derivatives. E. Fischer (V. Pik University, Rostok) reported the synthesis of oxazolines, oxadiazoles, thiadiazoles, 1,1-dihydroxy-1,2,3,4-tetrahydrothiadiazole, and 1,2,3,5- or 1,4,3,5-oxathiadiazines from cyanamide. B. Lenarczyk, J. Kulicz, and M. Gabrysiewski (Institute of Chemistry of the Teachers College, Kielce) presented data on the formation by isoxazoles and 3,5-dimethyl-1,3,4-oxadiazole of unstable coordination compounds of the ML and ML_2 type with the ions of a number of transition metals. I. I. Ibragimov and A. N. Kost (Sumgait-Moscow) presented data on a new synthesis of substituted isoxazoles.

L. Szczepkowski, T. Lesiak, W. Nowakowski, J. Paninski, and S. Gernacki ("Organic-Zachem" Chemical Plant, Bydgoszcz, and N. Copernicus University, Torun) presented a paper on the synthesis of dimorpholinoalkenes — catalysts in the production of polyurethane foams. K. Kozlowski, Z. Kucybala, and E. B. Gaca (J. and E. Sniadecki Technical Agricultural Academy, Bydgoszcz) reported a new synthesis of 3-ethyl-3-thio-4-oxazolidone from ethyl isothiocyanate.

Several papers dealt with natural carbohydrates and complex polynuclear natural compounds. Unfortunately, there were no communications involving the chemistry of oxirane and oxetane presented in the symposium. The symposium undoubtedly not only promoted the exchange of information but also strengthened scientific collaboration between our countries.