HETEROCYCLIC CONFERENCE IN THE GERMAN DEMOCRATIC REPUBLIC

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A heterocyclic conference organized by the chemistry section of Leipzig University and the chemical society of the German Democratic Republic (GDR) was held from October 11 to 15, 1976, in Kuhlungsborn [a small village near Rostok (GDR)]. Approximately 100 scientists participated in the work of the conference. In addition to the German chemists, representatives of the USSR, Czechoslovakian SSR, Poland, Romania, Yugoslavia, England, France, and the Federal Republic of Germany (FRG) presented papers. Ten plenary and 28 discussion papers devoted to methods for the synthesis of N-, O-, S-, Se-, and P-containing heterocycles, the investigation of their reactivities, physicochemical properties, and structures, and quantum-mechanical calculations of their molecules.

A plenary paper by M. Tisler (Yugoslavia) dealt with a study of the reactivities of heterocyclic diazo compounds and the synthesis from them of more complex heterocyclic systems. An interesting example of a three-ring heterocycle — imidazo[4,5-e]tetrazolo[4,5-c]-1,2,3-triazine — that contains a chain of six nitrogen atoms was presented in the paper. This heterocycle is in equilibrium with two tautomers — an azide and a diazo compound.

V. Czuba [Polish People's Republic (PPR)] reported the synthesis of all possible naphthyridines and their transformations, directing particular attention to the spectroscopic methods for the identification of the isomeric systems.

K. Hafner (FRG) in a paper entitled "synthesis of heterocycles from ethynylogs of acid amides, urethanes, and ureas" reported the synthesis of new difunctional acetylene derivatives of the $R_2NC\equiv CCOR'$ type [R = CH_3, C_2H_5; R' = H, CH_3, CH_3O, and $(CH_3)_2N$] that have extensive synthetic possibilities. Numerous transformations of these compounds to derivatives of pyrazole, oxetane, 1,2,3-triazole, 2,3-dihydrofuran, 3-aza-4-pyrone, and other heterocycles were presented.

A plenary paper by J. Elguero (France) was devoted to the azide-tetrazole equilibrium in a number of derivatives of five-membered nitrogen heterocycles. An analysis of the literature data made it possible to derive a number of principles regarding the effect of solvents, temperature, and structure of the heteroresidue on the state of the equilibrium between the azide and tetrazole and its rate of establishment. Correlations of the experimental data and the results of calculation of the tautomer molecules by the methods of quantum chemistry were made.

Reactions involving cycloaddition of benzofuroxans and their conversion to isobenzimidazoles, as well as reactions of the latter with tetracyanoethylene and secondary amines, were examined in a plenary paper by G. Sushitsky (England). He reported new types of dyes and charge-transfer complexes (CTC) of isobenzimidazole derivatives. O. Met-Kon (England) presented a report dealing with how one can use different methods for the conversion of singlet and triplet nitrenes for the synthesis of new heterocycles. Many graphical examples of generation of the corresponding nitrene — by selection of the starting compounds and solvents, irradiation, and the application of chemical carriers of quanta energy — were presented.

The position occupied by pyrylium salts among other aromatic six-membered rings from the point of view of their physical and chemical properties was determined in a plenary paper by A. T. Balaban (Romania). He also reported the results of a study of H-D exchange in a number of alkylpyridines and the difference that could be observed in the reaction of α-CH_3- and α-CD_3-pyridines with lanthanide shift reagents. A new explanation of the "secondary isotope effect" consists in the fact that the deciding factor here is the difference in the volumes of the H and D atoms.

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Discussion papers by German chemists were devoted to new methods for the synthesis of quinolines, thiazoles, and triazoles, the preparation of new heterocycles [for example, 1,2,4,6-thia(IV)triazine and 1,2,4,6-phospha(V)triazine], the study of reactivities, and the physicochemical properties and structures of new heterocyclic systems and their derivatives.

I. Beger reported methods for the utilization of industrially accessible products of nitrosochlorination of olefins for the synthesis of thiazoles and 1,3,4-thiadiazines. A new route to thiophenes and their condensed derivatives consists in treatment of compounds of the $RCOCH_2CN$ type with carbon disulfide and sodium hydride and subsequent reaction with compounds with an activated methylene group (V, Rudorf and M. Augustin). J. Liebscher and H. Hartman found an original approach to selenium-containing heterocycles. They treated salts of the $RCCl{=}X{-}CH{-}\overset{+}{N}R_2,\ Cl^-$ type, formed from methylene ketones or acetonitriles and formamidochloride, with NaSeH or NaSeCN. This method enabled them to obtain selenophenes, isoselenazoles, selenopyrylium salts, selenazines, and selenodiazines. The reaction of N-aryleneamines ArNHCR=CHR with Arnold reagents or intramolecular cyclization of amides $ArNHCR{-}CRCONR_2$ under the conditions of the Vilsmeier—Haack reaction leads to quinoline derivatives (H. Lettau). 4-Aminoquinolines were obtained by intramolecular Friedel—Crafts reaction from nitriles ArNH-X-Y-CN; it was found that this method could be extended to cinnolines and quinazolines (H. Schaefer and K. Gewald).

The relationship between the chemical structure and the absorption of light by heterocyclic 1,2-enediols was established in a paper by M. Weissenfels and A. Lippman. To ascertain the origin of the bands in the electronic spectra the authors drew upon the concept of an unbonded interaction between the unshared electron pairs of the nitrogen and oxygen atoms and were able to correlate the experimental data with the results of calculations of the molecules by the MO LCAO Pariser—Parr—Pople (PPP) method. H. Hartman correlated diverse polar cycloaddition reactions leading to heterocycles from the position of orbitally controllable reactions. The author's conclusions make it possible to construct the optimum strategy for the synthesis of new structures. K. Weiss, P. Birner, and B. Wil performed quantum-mechanical calculations of the reactivities of pyridinelike heterocycles. By comparing the experimental results with the results of calculation of their molecules by means of the newest and earlier methods they found the limits of applicability of each of these methods.

The behavior of some heterocyclic "push—pull" systems, particularly those that contain a "push-substituted" or "pull-substituted" exocyclic methylene group [ROOC(CN)C=, RO(RS)C=, etc.], with respect to nucleophilic reagents was examined in a paper by H. Kristen, K. Pesek, and K. Vogel. L. Mögel and V. Schrot reported the synthesis of new thia- and dithiacycloalkenes and the results of a study of their stereochemistry and aromatic character. R. Spitzer, S. August, B. Dobner, and V. Schrot proposed a method for the synthesis of 6,6'-bis-1,3-thiazinyldenes and related thia heterocycles from 1,3-thiazine-6-thione. H. Dorn presented a method for the unambiguous establishment of the structures of isomeric hydrazine derivatives on the basis of NMR and IR spectral data.

The results of an investigation of diverse aryldiazines containing long-chain alkyl groups were presented in a paper by H. Zaschke. The aim of the study was to search for new compounds that form liquid crystals. The author was able to find preparations of practical value that have low melting points and a broad nematic range and to uncover anomalies in the appearance of the nematic and smectic modifications.

E. Kleinpeter, S. Berendt, and R. Borsdorf investigated selenazolones containing a 2-dialkylamino group by PMR spectroscopy and calculated the energy barrier to its rotation.

Transmission of polar effects of substituents through furan and vinylfuran systems was reported in a paper by A. Krutosikova (Czechoslovakian SSR). E. Kisa and M. Potacek (Czechoslovakian SSR) Reported the synthesis of 2-arylbenzotriazoles. V. Sliwa and J. Mlohowsky (PMR) reported methods for the attachment of a pyridine ring to polynuclear nitrogen heterocycles.

Soviet scientists presented four papers at the conference. V. M. Mamaev illuminated some problems in the synthesis and reactivities of pyrimidines and the problem of transmission of electronic effects of substituents through the pyrimidine ring. S. A. Vartanyan reported new methods for the synthesis of keto derivatives of six-membered nonaromatic O-, N-, and S-containing heterocycles and their interconversions. A plenary paper by G. N. Dorofeenko was devoted to new preparative methods for pyrylium, 4-ethoxychromylium, flavylium, and isoflavylium salts. He also touched upon problems in the synthesis of complex pyrylia-containing condensed heterocycles and reported new pyranyl radicals and cation radicals that were encountered during a study of the reduction of pyrylium and dipyrylium cations. M. Yu. Kornilov dealt with the application of pyrylium and dipyrylium cations. M. Yu. Kornilov dealt with the application of lanthanide shift and relaxant reagents in the PMR spectroscopy of functional derivatives of some nitrogen- and oxygen-containing heterocycles. An analysis of the peculiarities of the computer calculation of the position of the lanthanide ion in the adducts was given in the paper.