SEVENTH INTERNATIONAL SYMPOSIUM ON THE CHEMISTRY OF ORGANIC SULFUR COMPOUNDS

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The Seventh International Symposium on the Chemistry of Organic Sulfur Compounds was held July 12-16, 1976, in Hamburg. Representatives of 27 countries (273 individuals, including two delegates from the USSR) were present at the symposium. Twelve plenary papers and ~ 110 papers in four simultaneously operating sections, which did not have any special trend although the papers were grouped into separate sessions with respect to their thematic relatedness, were presented.

Each of the plenary papers was read by a representative of one of the countries in which a given research trend is being developed quite intensively (one paper from each country), namely, from Austria, England, Denmark, Italy, Canada, the Netherlands, the Polish People's Republic (PPR), the USSR, the USA, France, the Federal Republic of Germany (FRG), and Japan.

Of these papers, three had a biochemical trend: "Participation of thiol ethers in metabolitic reactions" (F. Linen, FRG), "Mercapto amino acids encountered in nature. Synthesis and model experiments" (U. Schmidt, Austria), "Some studies associated with the biosynthesis of penicillin" (S. Wolfe, Canada). Three papers were devoted to stereochemistry: "Stereoselective transformations in some groups of tri- and tetracoordinated sulfur compounds" (A. Kiaer, Denmark), "Recent achievements in the stereochemistry of sulfinyl compounds" (M. Mikolajczik), Poland), and "Sulfur-containing nucleophiles in the study of the regio- and stereospecificity of reactions involving addition to an acetylenic bond" (E. N. Prilezhaeva, USSR). One paper was devoted to the use of quantum-chemical methods in the study of the structure of organic sulfur compounds ["MO theory of sulfur-containing molecules and the problem of the participation of the d orbitals" (N. Epiotis, USA)], and another was devoted to the nature of the sulfur–metal bonds in a large number of compounds ["Organic sulfur compounds with S–metal bonds" (R. Ricci, Italy)]. Finally, four papers illuminated new synthetic aspects and mechanisms of reactions of various groups of organic sulfur compounds: "Sulfones, sulfoxides, and sulfonium salts. Investigation of reaction mechanisms. Use and synthesis" (C. Sterling, England); "Formation of ylids and their rearrangements in the reactions of carbenes with compounds of divalent sulfur" (V. Ando, Japan); "Synthetic aspects of the chemistry of sulfines" (B. Zwanenburg, Holland); "The thiocarbonyl group: reactions with diazoalkanes and organometallic compounds. The thio-Claisen rearrangement" (D. Paquet, France).

The sectional paper (accompanied by a 40-min film) of A. Carpentier (England) entitled "Some key data on the utilization and consumption of sulfur" which was devoted to the problem of the industrial utilization of elementary sulfur and its simplest compounds that have become accessible owing to the incorporation of methods for the desulfuration of petroleum products, can, in fact, also be considered to be a plenary paper. The following data on sulfur production were also presented: Of the 49 million tons produced in 1974, the USA produced 11.6, Canada produced 8.2, the USSR produced 7.7, Romania produced 3.8, Japan produced 2.8, France produced 2.0, Spain produced 1.2, the FRG produced 1.1, and other countries produced 3.5 million tons.

Vis-a-vis the general theoretical trend of the plenary papers, one observed a tendency to formulate problems in the utilization of organic sulfur compounds and in the study of their biological role. This tendency was manifested to a somewhat lesser extent in the topics of the sectional papers. Of these, ~75 elucidated new methods for the synthesis of and reactions of organic sulfur compounds, including those employing kinetic methods and the study of the mechanisms of processes: 24 communications analyzed the application of various physical methods in the chemistry of organic sulfur compounds (including photoelectronic and microwave spectra, various diffraction methods, high-resolution NMR spectra, dipole moments, etc.), four were devoted

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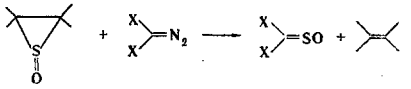
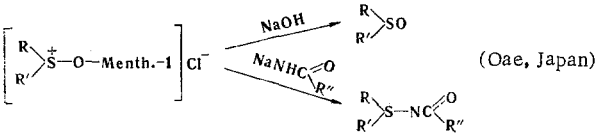
to photochemical transformations, five were devoted to quantum-chemical calculations, and 11 were devoted to stereochemical studies. Ten communications were devoted to the chemistry of biologically important organic sulfur compounds.

It should be noted that the organizing committee of the symposium received 26 sectional and one plenary paper from scientists from the USSR, but in addition to Prilezhaeva's plenary paper, only the sectional paper of M. A. Ryashentseva entitled "Synthesis of 2- and 3-methylthiophenes from H_2S and C_5 hydrocarbons," which stimulated a great deal of interst and lively discussion, was read. In addition to the countries that traditionally actively participate in these symposia (Italy, France, England, the FRG, and the USA), one may note the increased, as compared with previous symposia, participation of the PPR, which attests to the development of this branch of chemistry in socialist Poland.

In analyzing the content of the papers one should note the continuing interest in highly reactive organic sulfur compounds and particles, sulfonium compounds, ion radicals based on sulfur compounds, sulfur-stabilized anions, sulfenes, compounds with tri- and tetracoordinated sulfur, etc. Within the framework, of interest is the paper by Shine (USA) on adducts of cyclic ion radicals involving double and triple bonds, the paper by Hoppe (FRG), who demonstrated the possibility of the use in synthesis of normal and branched amino acids stabilized by carbanions from alkylaminomonothio- and alkylaminodithiocarbonates, the paper by Modena (Italy), devoted to the isomerizations of N-acylazasulfonium salts, etc.

The chemistry of compounds with sulfinyl groups continues to generate great interest; this was also reflected in the topics of the plenary papers (three of them were devoted in some measure to sulfoxides). Of the sectional papers of this kind, one may note the following, which were devoted to original reactions of sulfinyl compounds or to their synthesis:


(Maccaniani, Italy)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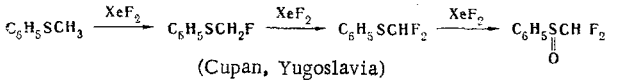
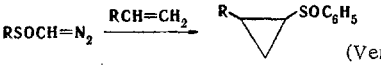
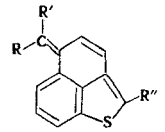

(Cupan, Yugoslavia)


(Venier, USA)

As always in these symposia, a great deal of attention was directed to the chemistry of heterocyclic sulfur-containing systems – thiophene, nitrogen-containing rings, polycondensed systems with several sulfur atoms, etc., – in all, 50 communications. Of these, more than 15 were devoted to the chemistry of thiophenes, including the synthesis of condensed systems of the thienofulvalene (I) (Neidlen, FRG) and thienopyridine (II) types (Pedersen, Denmark) and a method for the photolysis or pyrolysis of azides III (Iddon, England). Also of interest were communications by Guanti and Rosini (Italy) regarding new isomerizations during nucleophilic substitution reactions of thiophenes and benzothiophenes with electron-acceptor substituents.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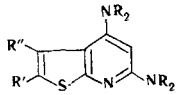
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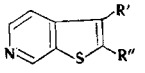
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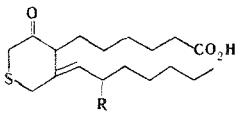
Methods for the syntheses of and reactions of new trithiaadamantanes (Fredga, Sweden), thia analogs (IV) of prostaglandins (Millir, England), thiabenzenes (Hori, Japan), dithiapyridinoparacyclophane (V) (Galushko, Poland), and other heterocyclic systems were also illuminated.



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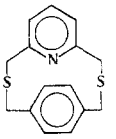
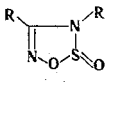


V

A number of communcations were devoted to novel or exotic heterocyclic systems containing diverse heteroatoms, such as, for example, 1,2,3,5-oxathiadiazole S-oxides VI (Dondoni, Italy), heteropentalenes of the VII and VIII types, obtained from thiourea (Beer, England), thiaziridineimines IX (Labbe, Belgium), thiadiazoloazaines X (Tisler, Yugoslavia), etc.



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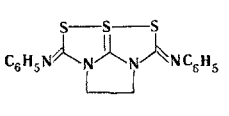

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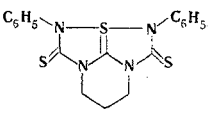

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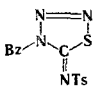

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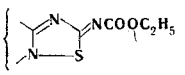
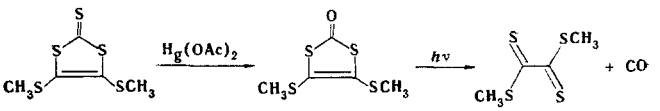


X

One might also note the communcations devoted to the study of various physicochemical characteristics of heterocycles: Problems involving their acidities and basicities (Doranzan, France), the bond orders in them (Parkanyi, USA), their electronic structures (Schweig, FRG), problems involving their tautomerism and stereochemistry, etc.

A number of papers were devoted to compounds containing bonds between sulfur and other elements, such as, for example S–S, P–S, Sn–S, and N–S bonds, and demonstrated the interest in further syntheses. A large amount of attention was directed to the study of the conformational equilibria of S-containing alicyclic compounds.

Among the photochemical studies, a convenient method for the synthesis of tetrathiooxalates (Hartke, FRG) seems of great interest:



Also of interest are the photoisomerization of substituted trithiapentalenes with opening of one of the rings (Pedersen, Denmark), the photoaddition of thiochromone to benzene (Steel, Canada), and the photoisomerization of thio-containing spiropyrans to photomerocyanines (Garniet, France). It should be noted that photochemical studies in the area of sulfur-containing organic molecules have not yet been adequately represented.

Most of the papers presented in the symposium were of a high level. The discussions in the sectional sessions were, as a rule, quite lively.

The Eight International Symposium on the Chemistry of Organic Sulfur Compounds will be held in the summer of 1978 in Yugoslavia (Ljubljana).