CHRONICLES

# SIXTH INTERNATIONAL SYMPOSIUM ON THE CHEMISTRY OF ORGANIC SULFUR COMPOUNDS

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The possibility of the development of new methods for the large-tonnage utilization of sulfur for economic and health needs is determined to a considerable degree by advances in the synthesis of organic sulfur compounds, fundamental research, and the development of theoretical concepts regarding the nature of sulfur and its compounds. For this reason, international symposiums devoted to the chemistry of organic sulfur compounds began to be held regularly in 1964. The sixth such symposium was held July 1-5, 1974, in Bangor (England).

Approximately 350 individuals from 26 countries participated in the work of the symposium. The greatest number of participants were from England, France, Italy, the United States, and the Federal Republic of Germany. The Soviet delegation consisted of eight individuals.

Thirteen plenary and ~130 sectional papers were presented at the symposium. The sectional papers were divided into four sections: theoretical and structural chemistry, mechanism and stereochemistry, synthesis, and heterocycles.

As a rule, the program of the symposium provided for the discussion of exclusively theoretical aspects of the chemistry of organic sulfur compounds.

The contents of the plenary papers presented at the conference best reflect the principal tendencies of the development of organic sulfur compounds. Of these papers no less than half, to one or another degree, touched upon either stereochemical problems, problems involved in the synthesis of complex strained structures that do not contain sulfur, or approaches to the synthesis of natural compounds proceeding from readily accessible highly reactive types of sulfur compounds (α,β-unsaturated sulfides, mercaptals, sulfur-containing ylids, thienyllithium compounds, etc.). A great deal of attention was directed to the structure and nature of chemical bonds in compounds such as unsaturated sulfones, diverse types of aromatic sulfur-containing systems, and compounds having S—N bonds, and also to the creation of fundamentally new types of organic sulfur compounds.

A paper presented by K. Mislow (USA) on the synthesis and properties of thiabenzene — a new type of aromatic compound with tetravalent sulfur that has interesting physical and chemical properties — was of great theoretical interest. In particular, compounds of this kind are quite unstable and rapidly undergo sigmatropic rearrangement. A fundamental point is the author's conclusion regarding the high probability of a pyramidal configuration of the sulfur atom in these compounds.

The extensive utilization of diverse physical methods of investigation including all forms of spectroscopy (UV, IR, NMR, and ESR), x-ray diffraction analysis, dipole moments, mass spectroscopy, and photoelectron spectroscopy was characteristic of most of the communications presented at the symposium. Thus, for example, a large amount of data on the electron-diffraction determination of the structures of an interesting series of conjugated systems of thiathiophenes and their derivatives was presented in a paper by Professor A. Hordwig (Norway).

The extensive use of the methods of quantum chemistry in the field of organic sulfur compounds distinguishes this symposium from the preceding symposiums, and the most up-to-

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date computational methods (ab initio, MINDO-2, and CNDO-2) were used in most of the studies.

One must note the papers presented by a group of prominent theoreticians — S. Wolfe, N. Epiotis, F. Bernardi, and I. Csizmadia. The root problem — namely, the reason for the differences in the reactivities of sulfur-containing and oxygen-containing compounds — was examined in these papers. The principal conclusion drawn on the basis of nonempirical quantum-mechanical calculations consists in the fact that the participation of the d orbitals of sulfur is not substantial and is not required for the explanation of its reactivity and anomalies. A model that explains the differences in oxygen- and sulfur-containing compounds in terms of the difference in the energies of the orbitals of the unshared pairs, the difference in the X—S and X—O antibonding σ orbitals, and, finally, the difference in the magnitudes of the overlap integrals, was proposed.

Many of the papers were devoted to conformational aspects. However, they either examined special cases of the conformational behavior of concrete systems or did not have significance precisely for sulfur-containing compounds (for example, a discussion of the "gear effect").

The chemistry of sulfur heterocycles and the chemistry of S-derivatives of diverse heterocyclic systems were extremely extensively represented at the symposium. A considerable number of communications in other sections and most of the plenary papers were also devoted to this area in addition to the subject matter of the individual section. The overwhelming majority of the papers touched upon the synthesis of heterocyclic systems, for the most part condensed systems. Considerable attention was directed to the preparation of sulfur derivatives of the pyridine and pyridazine series and also to the synthesis of sulfur- and nitrogen-containing heterocycles — thiazolo, pyridazines, thiazoles, aminothiazolidines, thiadiazoles, etc.

Tetravalent sulfur compounds — sulfuranes — constitute a new trend in the chemistry of organic sulfur compounds. Interesting information regarding the reactivities of monocyclic sulfuranes was reported by J. Martin (USA).

A great deal of attention was directed to the chemistry of oxidized sulfur compounds — sulfinic acids, sulfones, and sulfoxides — and also to the chemistry of sulfur ylids, sulfonium salts, reactive intermediates of the "sulfene" type, and also sulfur-containing ion radicals. β-Sulfonylimines, nitro-substituted tosylates, thiohydroxamic acids, isothiocyanates, etc., also generated interest.

However, it should be noted that most of the sectional papers contained the application of known synthetic methods or reactions for the construction of new compounds. Thus, they were basically developments of already-existing synthetic methods. Nevertheless, new preparatively convenient reagents were proposed in a number of the papers. Thus, for example, the paper presented by O. Oldenziel and A. Van Leysen (the Netherlands) was promising in a synthetic respect. The authors proposed a new reagent for the synthesis of heterocycles — "tosmik" (tolylsulfonylmethyl isonitrile). This stable odorless substance has nucleophilic and electrophilic centers and is therefore capable of cycloaddition of substances containing double bonds to give diverse heterocycles.

However, this research trend is broad in scope, i.e., the synthesis of a large number of new heterocyclic structures, even though by known methods, is dictated by the strategy involved in the development of this field and its dedication to practical goals — the search for new pharmacological agents, pesticides, extraction agents, etc.

Thus the high theoretical and methodological level of the plenary papers and a large amount of factual material on the synthesis of diverse sulfur-containing systems (mainly heterocyclic systems) made it possible for those present at the symposium to form an overall idea regarding the state of this problem, and this is the aim of such symposiums.

The next (seventh) symposium on the chemistry of organic sulfur compounds will be held in 1976 in Hamburg.