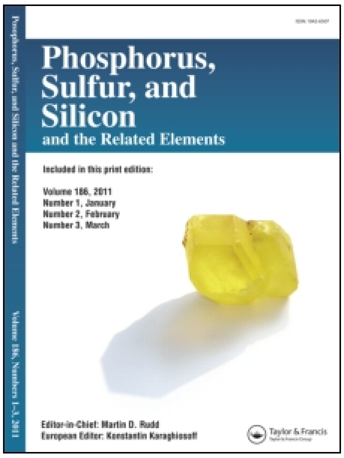

Phosphorus, Sulfur, and Silicon and the Related Elements

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A review of: “Topics in Organic Sulphur Chemistry, edited by M. Tisler. University Press, Ljubljana, Yugoslavia, 1978. i 413 pp. paperback. $15, including postage; purchase from Tisler, Oddelek Za Kemijo, Univerze of Ljubljani (Dept. of Chemistry, University of Ljubljana), Murnikova 6-P. 0. B. 537, 61001 Ljubljana, Yugoslavia.”

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Book Review

TOPICS IN ORGANIC SULPHUR CHEMISTRY, edited by M. Tišler. University Press, Ljubljana, Yugoslavia, 1978. i + 413 pp. paperback. $15, including postage; purchase from M. Tišler, Oddelek Za Kemijo, Univerze V Ljubljani (Dept. of Chemistry, University of Ljubljana), Murnikova 6-P. O. B. 537, 61001 Ljubljana, Yugoslavia.

This volume consists of the 14 plenary lectures given at the 8th International Symposium on Organic Sulphur Chemistry held in Portorož, Yugoslavia, in June of 1978. Emphasis is on classes of sulfur compounds and their reactions, but theory and technique are represented as well. The prompt appearance of the volume in less than six months after the meetings sets a commendable standard. Though a paperback, the book is well made, should withstand use well, and lies flat when opened without snapping back at one's nose. Typescript is used, but its uniformity obviates distraction; blurring of some of the figures, on the other hand, is a bit annoying. The style also is pleasingly uniform, although it would have been nice if, for once, the ever-recurring question of *sulphur vs. sulfur* had been resolved, perhaps by an international coin-toss. A leisurely conversational tone makes the book quite readable and contrasts strikingly with the style of a cablegram so often seen in conference reports. Value is enhanced by well-laid backgrounds and an average of 37 references per section. There are some four-dozen typographical errors, along with a few wrongly numbered compounds, but these mostly are trivial slips.

The flavor of the volume may be suggested by supplementing a listing of the topics and authors with brief comment. *Conjugative Effects of the —SR and* $\overset{\diagdown +}{\underset{\diagup}{S}}R$ *Groups* (F. Bernardi): Combined use is made of SCF and one-electron MO calculations with molecules containing —SH and —$\overset{+}{S}H_2$ and their alkylated derivatives (i.e. sulfide and sulfonium groups). The role of 3*d* orbitals is negligible, but —SH may behave as a strongly conformationally dependent π acceptor. Also considered theoretically are conformational preferences and bonding properties of oxonium and sulfonium ylides, again without 3d orbital involvement, and stereochemical aspects of C—H bond acidification in thianium cations. *Epoxysulfones* (T. Durst): Epoxyalkyl phenyl sulfones can give carbocycles of different size with LDA *vs.* CH_3MgI, which then will undergo alkylation, and also loss of $PhSO_2$ by reduction or oxidation-elimination. α,β-Epoxysulfones can give carbonyls by migration of $PhSO_2$, or α-bromocarbonyls by loss of $PhSO_2$ using $MgBr_2$. *Photoelectron Spectra of Organic Sulfur Compounds—Some Aspects* (R. Gleiter): Electronic structures, often useful for MO pictures, are considered for sulfides, along with "through space" and "through bond" interactions in sulfur heterocycles (strongly dependent on conformation), spiro compounds, tetrathianes, π systems, thiocarbonyl compounds, and tri- or tetravalent compounds. "PE spectroscopy" can detect short-lived species, determine gas-phase equilibria, and identify products. *Synthesis and Reactions of Some New Sulfur Transfer Reagents* (D. N. Harpp, K. Steliou): Structures XS_nX react with RSH to give RSS_nSR, with best results when X is an azole. The latter ($n = 1$) also give sultines with suitable diols. *Organic Synthesis with Sulphones* (M. Julia): Many illustrations are given of the usefulness of —SO_2— for linking synthons by single or double bonds, producing olefins (often stereoselectively), and achieving stereoselectivity through bulkiness or crystallizing tendency. *1,3-Dipolar* $|2\pi + 2\pi|$*-Cycloadditions* (G. L'abbé): X—Y cleavage of an intermediate $\overline{XYC}{=}Z$ gives 1,3-dipolar isomers that react with 2π—unsaturated compounds to give five-membered heterocycles. *The Chemistry of Condensed Thiophenes: Thienothiophenes, Selenophenothiophenes and Related Systems* (V. P. Litvinov): Considered are syntheses of varied bicyclic heteroaromatic systems containing S, Se, O, and N, the extent to which the five-membered rings involved retain individuality, and how arrangement of heteroatoms affects physical and chemical properties; the bicyclic systems are more reactive than the monocyclic counterparts. *Sulfuranes, Sulfurane Oxides and Persulfuranes—Structure-Reactivity Relationships in Compounds of 3-, 4-, 5- and 6-Coordinate Organosulfur* (J. C. Martin): Stability of the sulfurane $Ar_2S[OC(CF_3)_2Ph]_2$ is enhanced in a "five-membered ring effect" by 1,2-connections of the SOC systems to the Ar groups. Sulfur centers of this kind can be monoxidized (sulfurane oxides) or made common to two more five-membered rings (persulfuranes). Widely varying hypervalent compounds of such types are discussed. *New Reactions and Syntheses of Organic Compounds. Reactions of Sulfones with CCl_4 and Other Perhalomethanes in KOH-t-BuOH* (C. Y. Meyers): Perhalomethanes with KOH in *t*-BuOH α-halogenate sulfones *via* sulfonylcarbanions. Among adaptations are conversion of $(ArCH_2)_2SO_2$ to *trans* ArCH═CHAr (*via* monohalogenation and episulfone formation), modification of sulfones, and synthesis of alkynes, sulfonic acids, and other products. *Organic Sulfur-Phosphorus Compounds* (J. Michalski): Varied general features of sulfur four-coordinate phosphorus chemistry are illustrated by recent work, quite a bit of it stereochemical. *The Pummerer Rearrangements* (S. Oae): Reviewed are mechanistic evidence, clear-cut regioselectivity, stereospecificity, and inter- *vs.* intramolecular aspects, along with related reactions of reduction, thiolsulfinates, dithioacetic acid, and biological demethylation. *α-Diazo Sulfoxides* (C. G. Venier): Considered are preparation from sulfinyl chlorides and diazo compounds, along with use *in situ* to give α-halosulfoxides, cyclopropyl sulfoxides (with alkenes), a cyclopropene (with an alkyne), sulfinylcarbenes, and sulfinylcarbonium ions. *High-temperature Reactions of Hydrogen Sulfide and Thiols with Organic Compounds* (M. G. Voronkov and E. N. Deryagina): The Cl of aryl, thienyl or vinyl chlorides can be replaced using H_2S or ArSH, via HS· or ArS·, in gas-phase tube reactions at 500–650°C. Produced, often selectively and in good yield, are thiols and sulfides, which can be further converted to thiophenes, thianthrenes and thioxanthenes. *Trialkylsilylthioamides-Behavior and Reactions* (W. Walter and H. W. Luke): Trimethylsilylations (mostly at nitrogen) are discussed for various types of thioamides, along with various aspects of the products such as structure, rotamer aspects, properties (especially NMR) and reactions (with alkyl, acid and imidoyl halides, α-haloethers, tosyl isocyanate and diphenylketene, and of isomerization).

All in all, this book can be recommended for general readers who wish to obtain a feel for what has been going on lately in a number of active areas of organic sulfur chemistry, as well as for persons who are working in areas related to the topics and who would profit from the expertise of the review aspects.

L. FIELD