

NEW BOOKS

V. I. Minkin, L. P. Olekhnovich,
and Yu. A. Zhdanov

MOLECULAR DESIGN OF TAUTOMERIC SYSTEMS*

Reviewed by A. N. Kost

This book by authors from Rostov University is relatively small (300 pages and 407 bibliographic citations) and is original in content. The authors interpret the somewhat unnecessarily fashionable title selected by them as "design, plan, or construction." Terms of this sort have already begun to appear in the scientific literature, including the chemical literature, although in the technical literature and even in everyday usage the understanding of this term as "picture of design" has been already established. In fact, the reader finds in this book communications regarding the problem of tautomerism, carbonotropy (the migration of a carbon group), and the general principles of the construction of tautomeric systems, in which the authors use the conclusions of both quantum-mechanical studies and stereochemical studies based on the theory of graphs. Chapters on the mechanism of nucleophilic substitution (alkylotropic and vinylotropic tautomerism, etc.) and the mechanisms of nonspecific and photomechanical intramolecular tautomeric transformations are found at the close of the book. Let us note that the authors had to give a general formulation of the concept of tautomerism and had to define the limits of applicability of this term, having included in the general system prototropy, metallotropy, σ, σ transitions, π, π transitions, anionotropy, and all forms of valence tautomerism.

The authors deserve a great deal of credit for the general concepts developed in the book and their critical correlation of a large amount of experimental data (which, up until now, no one has attempted to do). The book is of interest to any qualified organic chemist; since the authors extensively use examples primarily from the chemistry of heterocyclic compounds, the book may be useful to many chemists engaged in research in this area who encounter tautomeric transformations, migrations of radicals, and many other rearrangement processes, the common character of which is made clear by the authors. The understanding of this common character may actually make it possible — and has already enabled the authors — to understand and predict previously unknown transformations of organic molecules.

The book is written on a good modern theoretical level but is not encumbered by computational material, and this makes it accessible to the qualified organic chemist.

*Izdatel'stvo Rostovskogo Universiteta, 1977.

Translated from *Khimiya Geterotsiklicheskikh Soedinenii*, No. 5, p. 707, May, 1979.

A. V. Fokin and A. F. Kolomiets

THE CHEMISTRY OF THIIRANES*

Reviewed by E. N. Prilezhaeva

This book fills a gap in the Soviet and world review literature, since it is the first monograph with a high degree of completeness that correlates the available data on the chemistry of thiiranes, their derivatives, and related organosulfur compounds. The book consists of three sections.

The comprehensive literature on the preparation of sulfur-containing three-membered heterocycles both from oxirane derivatives by replacement of the oxygen atom by a sulfur atom and by ring formation under homolytic or heterolytic conditions from organic compounds of various classes that contain or do not contain sulfur is systematized in the first section. The mechanisms of the corresponding processes are discussed. Data on the reactions of thiirane derivatives that proceed with the retention of the ring are also presented here.

Data on diverse physical properties of thiiranes are examined systematically in the second section, ideas regarding the structures and electronic natures of the bonds in three-membered heterocycles are discussed within a historical framework, and the authors' own ideas regarding these problems are expressed.

Reactions involving opening of the thiirane ring under the influence of nucleophilic and electrophilic reagents, reactions of thiiranes that are accompanied by splitting out of a sulfur atom, and reactions involving their conversion under homolytic conditions, primarily during irradiation, are analyzed in detail in the third section. Information on the practical utilization of thiirane compounds as starting compounds for the preparation of physiologically active substances, as monomers, etc., is presented in a brief chapter of the last section.

Another merit of the book is also the detailed examination of reactions in which thiirane complexes are formed as intermediates. All of the sections in the book are furnished with detailed bibliographies: The overall list of cited literature contains ~1400 citations, and the literature cited spans the period from 1975 to 1976.

One flaw of this useful book is its needless lengthiness and the copiousness of the repetitions in the sections involving the discussion of the theoretical problems and in the conclusions of the chapters and of the book as a whole.

Rather elementary information is frequently presented in detail; moreover, the book unfortunately does not have a reference to the concise and laconic analysis of the properties and reactions of three-membered heterocycles from the point of view of the perturbation theory of molecular orbitals in the recent monograph by Dewar and Dougherty.

*Nauka, 1978.

E. Ya. Lukevits (Editor)

ADVANCES IN THE CHEMISTRY OF FURAN*

Reviewed by V. G. Glukhovtsev

A monograph entitled *Advances in the Chemistry of Furan* has been published by co-workers in the Institute of Organic Synthesis of the Academy of Sciences of the Latvian SSR. Neither the small number of printed copies (1000), nor the arresting design of the book, nor the relatively low price of the book (1 ruble and 90 kopecks) taken all together are the reasons why it will evidently soon become a bibliographic rarity. The chief reason is that the need for a book that reflects the advances in the chemistry of furan is actually very great due to the vigorous development in this field, which also involves a number of allied branches of organic chemistry and technology. The comprehensive monograph by A. Dunlop and F. Peters published in the U.S.A. in 1953 has now finally become obsolete, and the enormous amount of new data has only been partially recorded in a few books and reviews devoted to individual problems in the chemistry of furan.

The book is divided into 10 chapters, each of which is written by outstanding investigators engaged in research on the corresponding specific problem. It includes material that is of interest not only to specialists in the chemistry of furan. Thus the first three chapters (authored, respectively, by Ya. Ya. Bleidelis, Yu. Yu. Popelis, and R. A. Gavar) contain a great deal of factual material, much of which is presented in tables, that will undoubtedly be of interest to both specialists engaged in the chemistry of furan but also to those engaged in x-ray diffraction analysis and NMR and EPR spectroscopy. The fourth chapter, which was written by Ya. P. Stradyn and is devoted to the electrochemical (primarily polarographic) reduction of furan compounds, will also be of interest to specialists in various branches of chemistry. Several aspects of organic catalysis as applied to furan compounds — catalytic oxidation and oxidative ammonolysis (by V. A. Slavinskaya and D. R. Shimanskaya and L. O. Golender) — are examined in chapters 5 and 6. The chapters by K. K. Venter (chapter 7) and N. O. Saldabol (chapter 8), in which data on the nitration and other electrophilic substitution reactions in the furan series are presented, are extremely interesting for chemists engaged in organic synthesis. R. A. Zhuk (the author of chapter 9) examines mainly methods for the synthesis of purine and pyrimidine bases that include a tetrahydrofuryl substituent and their biological activity. In the final chapter (authored by E. Ya. Lukevits and N. P. Erchak), which is devoted to furan derivatives of group IV elements — silicon, germanium, tin, and lead — the authors examine not only methods for the synthesis of these compounds and their physical and chemical properties but also discuss their practical applications. This chapter may serve as an example of a concise exposition of the material, since the structures of the substances and their properties are examined here in the aggregate. The book is basically written in a concise and clear fashion, but it does contain material that might have been presented in a more abbreviated manner. Thus, for example, the titles of all of the papers are presented in the bibliography. This undoubtedly facilitates the reader's evaluation of the citations presented, but the list of literature (1019 citations) occupies a fourth of the monograph. The lists of literature for the individual chapters are placed at the end of the book, and the citations in them are arranged in an unusual manner: They are not arranged in the order of their mention in the text but rather in alphabetical order, sometimes with respect to the names of the authors and sometimes with respect to the titles of the papers (when there are more than three authors), and this makes it difficult to use the list as an author index. In fact, the very brief name index could have been omitted, since it does not reflect the principal trends in the research being done in the chemistry of furan and is arbitrary in nature. Since the

*Zinatne, 1978.

chapters were written by different authors, a certain amount of repetition of material, such as, for example, with respect to the nitration of furan derivatives, was inevitable in a number of cases.

The most significant reproach that can be made with respect to the book under review here is the fact that many types of transformations that are important in the chemistry of furan and have recently been subjects of research were omitted from it. It is sufficient in this connection to mention the specific ability of furan compounds to undergo the Diels-Alder reaction, which is currently being widely used both to obtain diverse substituted furans and to effect their conversion to compounds of other series: new synthetic possibilities associated with the application of substitutive addition; original methods for changing the orientation of electrophilic substitution that are bound up with the problem of the synthesis of β -substituted furans; the extensive application of metallation in the synthesis of furan compounds; the investigation of the reaction of furans with free radicals and carbenes; research on nucleophilic substitution in the furan series; the catalytic hydrogenolysis of the furan ring at the C-C bond, etc. The monograph contains virtually nothing with regard to the extensive research on the synthesis of physiologically active compounds of the furan series carried out by A. L. Mndzhoyan et al. The material on hydrogenated furans is presented very sparingly and, if one may say so, spottily. In particular, there is not even any mention of such industrially important processes as the cleavage and polymerization of the tetrahydrofuran ring. Let us note in this connection that important studies have been made by Soviet authors with respect to all of the research trends mentioned above, but this research is not reflected in the book under review, in which even citations to the available review papers that deal with some of the indicated problems are absent.

The material in the book is limited essentially to an account of the principal trends in the research being carried out in the Institute of Organic Synthesis of the Academy of Sciences of the Latvian SSR on the chemistry of furan and individual problems of a general nature (x-ray diffraction analysis, NMR spectra, and polarography). It is difficult to take exception to this selection of material when one takes into account the fact that the book is dedicated to the memory of S. A. Giller, but this limitation should have been stipulated in the preface and perhaps even in the title of the monograph.

There is no doubt that the creation of a monograph that fully reflects the advances in the chemistry of furan will continue to remain a problem for the future and that its achievement may probably be realized only by the joint efforts of representatives of various schools of researchers.