NEW DIRECTIONS IN THE CHEMISTRY OF THIOPHENE*

Reviewed by A. N. Kost

This book, which was published at the very end of 1976 and is the result of the work of a collective of authors from the Institute of Organic Chemistry of the Academy of Sciences of the USSR on the chemistry of thiophene, will undoubtedly attract the attention of a large number of organic chemists, particularly those who are engaged in research on the various aspects of the reactivity of the heteroaromatic ring. The research of the school of Ya. L. Gol'dfarb on the chemistry of thiophenes is widely known and, with respect to more or less special problems, has been examined in review papers. A review of the state of the problem and of the advances made in the last 20 years (i.e., after the publication of the fundamental monographs and review papers on the chemistry of thiophene) from the positions of the scientific collective proper with primary examination of the results and the as-yet unsolved problems included in the range of interests of this scientific school is given in this book, edited by Ya. L. Gol'dfarb (the authors include L. I. Belen'kii, E. P. Zakharov, M. A. Kalik, V. P. Litvinov, F. M. Stoyanovich, S. Z. Taits, and B. P. Fabrichnyi). This range of interests is, by the way, very extensive and includes the general principles of the electrophilic substitution reactions of the hydrogen atom in the aromatic ring (including the change in the orientation and the rearrangment processes that take place during protonation or under the influence of Lewis acids), the principles of metallation with subsequent development with respect to the synthetic utilization of the resulting organometallic (primarily lithium) compounds, and the development of methods for the synthesis of condensed models on the basis of the thiophene ring with a detailed physicochemical characterization of the newly created heteroaromatic system, and two very important trends based on the general principle of the initial introduction of a necessary substituent in the thiophene ring and subsequent decomposition or opening of this ring. Numerous syntheses of aliphatic amino acids and lactams (by reductive desulfuration of the corresponding thiophene acids or their derivatives) and a number of other aliphatic compounds have been developed on the basis of these principles, and, even more important, a general and extremely flexible method for the preparation of macrocyclic structures on the basis of intramolecular alkylation or acylation of the thiophene ring and subsequent desulfuration was created.

We note immediately that the book is a good publication. It is printed in a convenient type, and the structural formulas and reaction schemes are well executed (which substantially facilitates understanding of the text). The carefully compiled bibliography, which is presented for each chapter (and even for the preface) and contains more than 1500 citations, is virtually free of repetitions. The thoroughness of the literature treatment of the material substantially increases the value of the book, which may be of service for handbook purposes. For this reason it is provided not only with a sufficiently detailed table of contents but also with a detailed subject index.

It is natural that the various chapters were written by different authors whose area of interests determined the character of exposition of the material. One's attention is directed to the first chapter, in which L. I. Belen'kii (who, together with Ya. L. Gol'dfarb, performed the general editing of the book) in the case of the chemical properties of the thiophene ring essentially gives an example of the general principles of the study of heteroaromatic character from the point of view of chemical reactivity and the rules of orientation during electrophilic substitution. In conjunction with the material in chapter IV, which was written by V. P. Litvinov mainly from the point of view of the physicochemical and quantum-chemical characteristics of condensed heteroatomic rings and the simplest derivatives, the reader receives a useful manual for investigators doing research on the chemistry of heteroaromatic structures. If the data from chapter II (in which a general examination of the problems of metallation in a series of heterocycles is given in the case of the formation of lithium derivatives and subsequent reactions) are added here, this front is expanded to an even greater extent.

The interest of the book's compilers in the problems of the directed search for new ligands for the preparation of chelate compounds and, correspondingly, in the study of some tautomeric systems (first and

* Izd. Nauka (1976).

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foremost aldimines) is somewhat more specific. Until recently, analytical chemists or physical chemists were primarily engaged in the search for ligands and in the investigation of chelate compounds, although there has long been a need for qualified organic chemists in this sector of our science. Chapters III and IV will therefore be very useful to many chemists with diverse scientific interests.

As I have already stated above, the specific scientific direction of the Ya. L. Gol'dfarb school is the original solution of the problem of the synthetic utilization of the discovered principles of the introduction of substituents in the thiophene ring for the subsequent decomposition of this ring by desulfuration. In other words, an original method has been created for the incorporation in an organic molecule of a four-carbon fragment – if necessary one with a ready-made substituent, including such an important functional grouping as an amino group. These studies constitute an excellent example of an elegant and effective solution of a major problem of synthetic organic chemistry. One may be certain that the publication of a book in which a generalized examination of the results and developed methods is given should entail the extensive application for scientific research and perhaps industrial purposes (where problems of fine organic synthesis are solved) of this original approach. This is of particular importance, since the problem of the isolation of thiophenes from the corresponding sulfurous petroleum oils has already been fundamentally solved, and the expedient utilization of thiophene has become an urgent problem. The authors of the book have demonstrated the effectiveness of this method for the preparation of diverse amino acids and macrocycles. One may be certain that many other models also will follow.

The publication of this book can only be welcomed. For many of our readers it should be an indispensable manual in their daily work.

K. M. Akhmerov

CATALYTIC AMMONOLYSIS AND AMINATION OF ACETYLENIC HYDROCARBONS*

Reviewed by A. N. Kost

One of the directions of the chemistry of acetylene that has been developed mainly in the postwar period is the catalytic ammonolysis of acetylenic hydrocarbons by the Chichibabin method. The products of this reaction are nitrogen-containing heterocycles, amines, nitriles, and other compounds that are widely used in industry.

Until recently there were no monographs in which the literature on the ammonolysis and amination of acetylenic hydrocarbons was systematized and correlated. Akhmerov's book is an attempt to achieve this sort of correlation as applied to the joint catalytic transformations of acetylene with ammonia and amines.

The synthesis, properties, and transformations of acetonitrile – the starting material for pyridine bases and other compounds – are described in the first chapter. The synthesis and some transformations of nitrogen-containing compounds (pyridine bases, pyrrole, etc.) are presented in the second chapter. The third chapter is devoted to the amination of acetylenic hydrocarbons.

The book contains a review of the original literature (~400 citations) prior to 1973; the large contribution of Soviet scientists to the development of this area of chemistry is graphically demonstrated. The text is illustrated with reaction schemes, tables, and graphs; this makes it possible for one to readily orient oneself with respect to the problems discussed. There is sometimes a lack of continuity and logic of exposition of the material, and there are repetitions. The author, drawing upon the mechanism of the reaction of acetylene with ammonia, suggests the idea that the reaction between the indicated reagents has radical-chain character, but he does not present convincing proof in favor of his conclusions. In view of the breadth of the topic, the chapter on the synthesis of pyridines and pyrroles does not completely encompass the problem. The book is therefore of less interest to specialists in the chemistry of heterocycles than to chemists engaged in research on acetylenic hydrocarbons.

* Tashkent, FAN (1976).

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