A. S. Sadykov, Kh. A. Aslanov,
and Yu. K. Kushmuradov

# ALKALOIDS OF THE QUINOLIZIDINE SERIES (CHEMISTRY, STEREOCHEMISTRY, AND BIOGENESIS)*

Reviewed by O. S. Otroshchenko

The results of research on one of the widely spread classes of alkaloids containing a quinolizidine system are correlated in this monograph. The compositions, properties, and structures of 125 alkaloids are described. The interest in plant bases of this type is explained by the unique character of their structure and the abundance of conformational and optical isomers. The quinolizidine alkaloids have therefore been the subject of numerous studies and reviews. However, in most cases the problems involved in the proof of their structures and in their biogenesis and physiological activity have not been examined sufficiently purposefully and interdependently. They have been described only in unconnected papers or dissertations. The authors of this monograph have attempted to fill this gap and have correlated the literature data and the results of their own research.

The monograph includes three interrelated and complementary chapters. Data on methods for the preparation of quinolizidine alkaloids and on methods for the establishment of their structure by both classical and modern physicochemical methods are presented in the first chapter. The reader's attention is directed to the problems involved in the modification of quinolizidine alkaloids, since this expands the possibilities for the study of the reactivities, electronic structures, and conformations and for finding methods for the practical application of these compounds. The principal subject of discussion deals with the most typical quinolizidine bases that are biogenetically interrelated and are most frequently detected together in plants. These bases include lupinine, cytisine, sparteine, matrine, and nupharine derivatives. These alkaloids are particularly widely distributed in the plants of Central Asia.

The second chapter includes a description of the stereochemistry and stereochemical transformations of mono- di-, and trisubstituted quinolizidine bases. The chemical stability of their conformations is also demonstrated.

The material presented includes not only the literature data; a large part of the data are the result of research carried out by the Tashkent school of bioorganic chemists under the supervision of Academician Abid Sadykovich Sadykov.

The third chapter is devoted to the biogenesis of quinolizidine alkaloids. The role of the latter in the life activity of plants is primarily illuminated here. It is also shown that lysine is the precursor of large groups of quinolizidine alkaloids, and the interconversions of the latter are demonstrated, etc.

The value of the monograph is also determined by the fact that it for the first time presents data devoted to quinolizidine alkaloids in a correlated form that is accessible to readers. It is written in simple language and is accompanied by numerous diagrams of the interconversions of the alkaloids. The primary literature sources presented are simultaneously a unique bibliographic index. The publication of the monograph should be regarded as timely, since it provides answers to most of the problems of specialists doing research on and seeking applications for natural compounds. This book is undoubtedly a valuable handbook for various types of chemists and biologists and for students specializing in this field.

---

*Nauka, 1975.

Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 11, p. 1572, November, 1977.

0009-3122/77/1311-1260$07.50

O. Ya. Neiland, Ya. P. Stradyn',
É. A. Silin'sh, D. R. Balode,
S. P. Valtere, V. P. Kadysh,
S. V. Kalnin',* V. É. Kampar,
I. B. Mazheika, and L. F. Taure

# STRUCTURE AND TAUTOMERIC TRANSFORMATIONS OF β-DICARBONYL COMPOUNDS†

Reviewed by R. É. Valter

This book is devoted to the results of physicochemical investigations of the structure and tautomerism of 1,3-dicarbonyl compounds. Principal attention is directed to cyclic 1,3-diketones. The traditional subjects of research of the Riga chemists of the school of Academician of the Academy of Sciences of the Latvian SSR Gustav Vanag (1891-1965) are found in this field of organic chemistry. The results of many years of research by the authors in the chemistry department of the Riga Polytechnic Institute, in the Institute of Organic Synthesis of the Academy of Sciences of the Latvian SSR, and in the Physicoenergy Institute of the Academy of Sciences of the Latvian SSR are presented. In addition to correlation of the results of their own experimental research, the authors have, on the level of modern physical organic chemistry, made a critical review of a large amount of literature data (the bibliography contains 835 citations) published in the last 10-15 yr.

The book contains seven chapters devoted to the individual problems and methods of investigation of 1,3-dicarbonyl compounds.

The results of studies of acidity, enolization, and other prototropic equilibria are correlated in the first chapter (O. Ya. Neiland and S. V. Kalnin'). The effect of the medium, structure, and conformation of 1,3-dicarbonyl compounds on their CH and OH acidities and enolizability is discussed. Methods for the determination of tautomeric equilibrium and acidity constants are examined.

The IR spectra of the diketone, enol, and anionic forms of 1,3-diketones are characterized in the second chapter (S. P. Valtere). Their relationship to the structure and conformation of 1,3-diketones and to external factors is examined.

The third chapter (O. Ya. Neiland, S. V. Kalnin', and V. É. Kampar) is devoted to the electronic absorption spectra of 1,3-dicarbonyl compounds. The subject of discussion of this chapter is the effect of substituents, the ring size and structure, and the formation of an intramolecular hydrogen bond and the influence of solvents on the π-electron systems of both tautomeric forms, the anion (including onium betaines), and the enolium cation of 1,3-dicarbonyl compounds.

A completely new area of investigation is reflected in the fourth chapter (V. É. Kampar and O. Ya. Neiland), which is devoted to charge-transfer complexes (CTC) of the anions and onium betaines of 1,3-dicarbonyl compounds. The spectroscopic and energy characteristics of the CTC and methods for the determination of the ionization potentials and electron affinities of the donor and acceptor components of these complexes are presented.

The electrochemical properties of 1,3-dicarbonyl compounds are examined in the fifth chapter (Ya. P. Stradyn' and V. P. Kadysh). Comprehensive data on the application of polarography and anode voltamperometry for the characterization of the diketone, enol, and anionic forms of cyclic 1,3-diketones are presented. The mechanisms of the electrochemical transformations of indane-1,3-dione, for the establishment of which nonclassical modifications of polarography, as well as ESR spectroscopy, were used, are discussed in detail. Examples of the electroanalytical methods for the determination of indane-1,3-dione derivatives are presented.

The results of the application of the method of dipole moments in the investigation of the ketone–enol tautomerism, three-dimensional structures, and electronic effects of substituents in cyclic 1,3-diketones are presented in the sixth chapter (Ya. P. Stradyn' and I. B. Mazheika).

---

*Deceased.

†Zinatne, 1977.

Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 11, p. 1572-1573, November, 1977.

0009-3122/77/1311-1261$07.50

The results of investigations of the principal electrophysical and photoelectric properties of indane-1,3-dione derivatives are set forth in the last chapter, written by specialists in solid state physics (É. A. Silin'sh, L. F. Taure, and D. R. Bolode). Their relationship to the molecular and supramolecular structures of the investigated substances is discussed.

On the whole, despite the absence of data on the use of such important physicochemical methods as nuclear magnetic resonance and mass spectrometry, the book gives lucid representations of the modern state of the theory of the structure and tautomerism of 1,3-dicarbonyl compounds and, simultaneously, the possibilities of the use of physicochemical experimentation in the investigation of these problems. In addition, it directs the reader's attention to the long-range research trends in this field of organic chemistry.