NEW BOOKS

V. I. Ivanskii

CHEMISTRY OF HETEROCYCLIC COMPOUNDS*

Reviewed by A. F. Pozharskii and A. K. Sheinkman

At last a Soviet textbook on the chemistry of heterocyclic compounds has emerged into the light. It is intended for university students although it may of course be used by aspirants and students in other higher institutes of learning. In volume it significantly exceeds the books, published in this country in the past, by Katritsky and Lagowski, Paquette and also Joule and Smith although it is somewhat superseded by the classic handbook of Albert which, regretfully, has not been translated into the Russian language. There is no doubt that the textbook will rapidly disappear since the number of copies of it (8000) is small when the number of universities and the multitude of scientific centers occupied with problems of heterocyclic chemistry in the country is considered. Therefore the problem of the need for a second edition of the book may arise as a result of the latter circumstance and it is important to analyze its quality and shortcomings.

The book is constructed on a principle, already becoming standard for similar publications, i.e., the material in it is arranged according to the type of heterocycle in order of their complexity. Seemingly such an approach vindicates itself for initial instruction since it permits the student to form a clear concept of the actual physical and chemical properties of each heterocyclic system, and of the methods of making it which as a rule have their own characteristics. A weak aspect of such an approach is, however, unavoidable repetition but the main point is the transfer of conceptual problems of chemistry to a second scheme. The author of the book being reviewed attempts at the end of each chapter to summarize overall the physical and chemical properties of each class of heterocyclic compounds (azines, azoles, etc). In addition, at the beginning of the book, problems of the nomenclature of heterocycles and the principles underlying heterocyclization are expressed in separate small chapters. Although the chapters contain information on the methods of obtaining each type of heterosystem, these data do not exceed 12% of the whole size of the book, i. i.e., the main attention is paid to reactions of heterocyclic compounds. Here evidently there will be various points of view, but on the whole it must be admitted that within the framework of the present volume the author has succeeded in balancing the factual material available at the present time on the chemistry of heterocycles. In the book the chemistry of saturated, unsaturated, and aromatic heterocycles is reflected in a proper manner, such heterocycles as phenothiazine, azepine, diazepine, azocine, phosphobenzol, etc., which are important in practical or theoretical respects are considered. Attention is paid to electronic fine structure and the geometry of heterocycles, their relative stability, problems of practical application, and occurrence in nature. At the end of each chapter a list is given of the most important literature although some part of it is already obsolete or has lost its importance.

The main shortcoming of the textbook is that the author nevertheless has failed to reflect in a proper manner what is general in the chemistry of related heterosystems, to compare strictly their reactivities, and to throw light upon new concepts of heterocyclic chemistry. Thus the problem of the criteria of heteroaromaticity is really not touched upon in the book, consequently the student will find it difficult to understand the author when he compares the aromaticity of different heterocycles. Problems of the distribution of electron density in closely related heterosystems are not considered from a common position. This might well have been done on the basis of the concept of π-abundance and π-deficiency about which there is nothing in the book. From the methodological point of view it is also incorrect that the author, in comparing heterocycles, uses data of quantum mechanical calculations carried out by different methods.

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*Vysshaya Shkola, Moscow (1978).

Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 8, pp. 1138-1139, August, 1979.

0009-3122/79/1508-0935$07.50 © 1980 Plenum Publishing Corporation

There are very few quantitative data on reactivity in the book and those which are given may not always be in agreement. Thus, for example, the author writes that indole is more active than pyrrole in electrophilic substitution reactions, which in his words corresponds to a lower ionization potential for indole, but no actual data supporting this conclusion are given. Information available in the literature indicates the opposite. Pyrrole is two times more active than indole in the Vilsmeier reaction. Further, the activity of heterocycles on electrophilic substitution in the series pyrrole>indole>carbazole, furan>benzofuran>dibenzofuran, and thiophen>benzothiophen>dibenzothiophen changes in the opposite manner to the change in π-ionization potentials.

One of the most complex and important features in the account of the reactivity of azines is the explanation of why in individual cases the nucleophilic substitution reaction in bases and cations (e.f., pyridine, pyridinium cation) goes in the α-position in one and in the γ-position in the other. Here it should be pertinent to refer to the concept of hard and soft acids and bases, and to the ambident nature of heteroaromatic molecules (bases, cations, anions). The absence of such an approach in the book renders incorrect in principle the attempt to treat the dual reactivity of tautomeric compounds (e.g., hydroxy- and aminopyridines) from their different existing forms (p. 266). The actual problems of tautomerism are expressed in the book in an extremely hazy manner.

There are also errors of a factual nature in the book. Thus for benzoxazole the Chichibabin reaction is not characteristic (p. 184), the equilibrium anine ⇄ imine in 2-aminoimidazoles is shifted to the left and not to the right (p. 159), on p. 255 the arrows are incorrectly placed for the electron shifts, it is incorrect to name 4-substituted 1-acyl-1,4-dihydropyridines cryptosalts (p. 250), it is incorrect that the synthesis of purine is not the subject of special investigations (p. 413). It is impossible to agree with the curious term "aromaticity of position" which is used repeatedly in the book. The idea of aromaticity refers to a conjugated system as a whole. Again the term "complex heterocycles" is unfortunate and is even the title to chapter VII devoted to purine and pteridine. It should also be recorded that it is scarcely expedient to put into a textbook data on the index of free valency. Meanwhile there are many important data not found in the book in the proper form. In particular the synthesis of pyridines from aldehydes and ammonia according to Chichibabin, the metallation reaction in the furan and thiophen series, the diene properties of oxazole, and nucleophilic substitution in halofurans and halothiophens belong to that class.

Regretfully the comments expressed do not exhaust all the shortcomings of the book and for their complete analysis one would be obliged to increase the size of the review. What has been mentioned indicates that the book of V. I. Ivanskii, in spite of several positive aspects, is very raw and may scarcely pretend to the role of a basic university textbook on the chemistry of heterocycles. It should be recommended only as an additional educational manual. It is suggested that a second edition of this book is not expedient and the modern Soviet textbook on the chemistry of heterocycles must still be written.

ANNOTATIONS OF DISSERTATION WORK IN THE AREA OF THE CHEMISTRY OF HETEROCYCLIC COMPOUNDS

CONVERSIONS IN THE PYRIDINE SERIES UNDER THE ACTION OF NUCLEOPHILES

G. G. Danagulyan

The dissertation is devoted to a study the action of nucleophilic reagents on monocyclic and condensed pyrimidine systems. The rearrangement of the condensed system pyrazolo[1,5-a]-pyrimidine into derivatives of pyrazolo[3,4-b]pyridine has been accomplished and proceeded under the action of alkali. The structural factors necessary to achieve such a conversion have been clarified. In particular it was shown that the introduction of an electron accepting substituent (nitro group) into the pyrimidine nucleus or an electron-donating substituent into the pyrazole ring promoted recyclization. It was demonstrated that the discovered isomerization goes through the stage of forming an anionic sigma complex. Not only condensed systems but also monocyclic pyrimidines are able to rearrange into pyridine derivatives. The recyclization has been accomplished for the first time of the methiodides of 2-alkylpyrimidines into the corresponding 2-methylaminopyridines proceeding under the action of alcoholic solutions of aliphatic amines. It was shown that the rearrangement of 2-aminopyrimidines into the corresponding 2-aminopyridines also proceeds without quaternization of the nitrogen atom in the presence of a strong electron acceptor in the pyrimidine ring. The recyclization of pyrazolo[1,5-a]pyrimidines is not only a new type of intramolecular rearrangement but is in principle a new method of obtaining pyridine derivatives.

Chemical Faculty, M. V. Lomonosov Moscow State University. Scientific directors: Doctor of Chemical Sciences Professor A. N. Kost, senior scientific collaborator R. O. Sagitullin.

HYDROGENATION AND ISOTOPE EXCHANGE WITH D_2O OF CONDENSED HETEROCYCLIC COMPOUNDS ON CATALYSTS CONTAINING METALS OF THE PLATINUM GROUP

A. G. Dedov

A systematic investigation has been carried out for the first time of isotopic exchange with D_2O and the hydrogenation of condensed heterocyclic compounds of the benzofuran, 2,3-dihydrobenzofuran, chromane, indole, and benzothiophen series and their hydrocarbon analogs in homogeneous and heterogeneous systems in the presence of catalysts containing platinum group metals. It was shown that the hydrogenation reaction and isotopic exchange with D_2O of condensed heterocyclic compounds on platinum metals has a set of general rules and may be considered within the framework of common ideas on the formation of π-complexes. A π-complex mechanism was proposed for the hydrogenation and for H—D exchange of heterocyclic compounds on platinum metals. The orientation of the investigated compounds on the catalyst surface is established on π-complex adsorption. The number of active centers and the proportion of active surface of platinum, palladium, and rhodium in the isotope exchange reaction were determined by ESR.

University Department of Petroleum Chemistry and Organic Catalysis, Chemical Faculty, M. V. Lomonosov Moscow State University. Scientific director: Doctor of Chemical Sciences É. A. Karakhanov.

Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 8, p. 1140, August, 1979.

0009-3122/79/1508-0937$07.50 © 1980 Plenum Publishing Corporation

1-ARYLTHIOSEMICARBAZIDES AND THEIR CONVERSION UNDER THE ACTION OF ACIDIC REAGENTS

N. Yu. Deeva

The action of various acidic reagents on 1-phenylthiosemicarbazides substituted at various positions on the benzene ring and at each of the three nitrogen atoms has been investigated for the first time. As a result conditions were found permitting the synthesis by this route of substituted 2-aminobenzothiazoles including the difficultly available 2-arylaminobenzothiazoles. The structure of the side products of the reaction was established and it was shown that for certain models fission of the nitrogen—nitrogen bond, as for hydrolytic splitting of the thioamide group, may block the desired process. Data were obtained in favor of the fact that the process of ring formation proceeds through the stage of an isothiouronium salt. It was shown that this rearrangement is a convenient method of synthesis of tetrahydropyrimidobenzothiazoles and the previously unknown 3-aminoalkyl-2-iminobenzothiazoles, the preparation of which by other methods seemed to be appreciably difficult and was impossible in several cases. A systematic study was carried out for the first time of the mass spectral behavior of a series of thiosemicarbazides, thiocarbamoylpyrazolidines, and 2-aminobenzothiazoles.

Chemical Faculty, M. V. Lomonosov Moscow State University. Scientific director: Doctor of Chemical Sciences Professor A. N. Kost.