

cyclization of hydrazones, and oxidative degradation of hydrazones. Chapter 10 (22 pages, 3 Tables, 197 references) reports on two methods for the reduction of hydrazones: polarography and chemical reduction. Chapter 11 (16 pages, 121 references) describes some additional reactions of hydrazones; *inter alia*, the interesting transhydrazonation and 1,4-elimination reactions.

The biological applications of hydrazones are treated in Chapter 12 (25 pages, 2 Tables, 163 references). The hydrazone derivatives that are reported to be drugs show activity against tuberculosis, inflammation, and other bacterial diseases. Potent herbicides, insecticides, and fungicides are also discussed.

The book concludes with a Subject Index and a Table of Contents, but an Author Index is not provided. Despite the new nomenclature proposed, there is a tendency to adhere to the Rules of IUPAC Nomenclature; however, several deviations were noted.

In general, the monograph is scientifically sound, and contains an abundance of structural formulae that are adequate. The book was written by specialists actively involved in the field, as evidenced by numerous references (57) to them in Chapters 1, 3, 6, 7, and 10. The monograph also cites the work of their colleagues, and gives references to less-common Russian periodicals.

The book constitutes a valuable, companion volume to recent chapters on phenylhydrazones and osazones of carbohydrates, and synthesis of polyhydroxyalkyl heterocycles [H. S. El Khadem (Ed.), *Synthetic Methods for Carbohydrates*, ACS Symposium Series 39, American Chemical Society, Washington, D.C., 1977]; however, translation of this Russian book into English would require some updating.

National Bureau of Standards,  
Washington, D.C. 20234

ALEXANDER J. FATIADI

*Khimiya Hydrazonov* (Chemistry of Hydrazones), edited by YU. P. KITAEV, approved by the A. E. ARBUZOV Institute of Organic and Physical Chemistry, Kazan, Academy of Science USSR, "Nauka" Publishers, Moscow, 1977, 204 pages, 14 × 21.5 cm, paperback, 1300 copies published, Rubles 1.40 (~\$2.00).

This well-written monograph, containing references to the middle of 1976, is a supplement to a recently published book on the subject, *Hydrazones*, by Yu. P. Kitaev and B. I. Buzykin [for a review, see *Carbohydr. Res.*, 67 (1978) C22]. According to the editor's introduction, the new monograph reflects the rapid growth in the number of known compounds having the hydrazone structure that are of theoretical interest (*e.g.*, in photoelectron,  $^{14}\text{N}$  quadrupole resonance, and X-ray diffraction studies). A similar demand for new hydrazone derivatives has also been observed in the applied fields of organic synthesis and analytical chemistry, and in the medicinal, pharmaceutical, and agricultural industries. Consequently, this book is designed for study by a wide range of research chemists and chemical engineers.

The monograph consists of seven contributed chapters written by experts

actively involved in the field; the authors and the editor are to be congratulated on their success in this enormous endeavor.

Chapter 1 (Electronic Structure of Hydrazones, V. V. Zverev, M. C. Elman, and Yu. P. Kitaev, 39 pages, 17 Tables, 65 references) deals with the fundamental analysis of the electronic structure of hydrazones and open-chain azines, as determined by photoelectronic and ultraviolet spectroscopy, and quantum chemistry. In hydrazones, the energy of a molecular orbital and the degree of overlap of the upper occupied atomic orbitals [ $n\pi$ ,  $n\sigma$ ,  $\pi(b_1)$ ,  $\pi(a_2)$ , and  $\pi(\text{C}=\text{N})$ ] depend significantly on the stereoconfiguration of the molecule. Free rotation about the N–N bond changes the character of the upper occupied atomic orbital, leading to  $n\pi \rightarrow n\sigma$  transition. Hence, the observed nearness in energies of the  $n\sigma$  and  $\pi(\text{C}=\text{N})$  atomic orbitals is a result of rotation about the N–N bond, whereas coplanarity of the phenyl ring with the hydrazino group is responsible for the different orbital energies in  $\pi(b_1)$  or  $\pi(a_2)$  orbitals. The observed transition in the longer-wavelength region for hydrazones can be explained by an electron transfer from the amino nitrogen atom to the imino group. The chapter, which also cites and interprets the electronic spectra of many protonated and iodomethylated complexes, may be supplemented by study of a recent spectroscopic article (photoelectronic and e.s.r. techniques) on the conformations of four-membered-ring hydrazines and hydrazine radical cations [S. F. Nelsen, V. E. Peacock, G. R. Weisman, M. E. Landis, and J. A. Spencer, *J. Am. Chem. Soc.*, 100 (1978) 2806, and references cited therein].

Chapter 2 (Basicity of Hydrazones, V. V. Zverev, T. N. Pylaeva, and L. V. Ermolaeva, 32 pages, 17 Tables, 96 references) examines theoretical and experimental results concerning the basicity and the protonation center of hydrazones: as is shown, there is little difference in the energy of protonation as between amino and imino nitrogen atoms. However, there is a linear relationship between the pK values and ionization potentials of simple hydrazones. Unlike those of the amines, the pK values of hydrazones increase with the number of alkyl groups in the molecule. The chapter also discusses the proton affinity of amines in the gas phase, and the basicity of amines in solution: and the basicity values of hydrazones and amines, as determined by the Pople–Santry–Segal method, are compared with those obtained by other methods.

Chapter 3 (Hydrazones in Coordination Chemistry, T. V. Troepolskaya and E. N. Munin, 33 pages, 251 references) discusses at length the complex-formation and chelation of hydrazones with a variety of transition-metal ions. The most stable complexes are formed with hydrazones incorporating additional ligands (*e.g.*, OH, SH,  $\text{CO}_2\text{H}$ , and  $\text{NH}_2$ ), to give five- and six-membered, chelate rings; the coordination ability of the hydrazono group alone is insufficient for formation of a stable, metal complex. Applications of modern techniques for the determination of the structure of hydrazone chelates are also surveyed.

Chapter 4 (Sulfonylhydrazones, F. K. Izmailova, B. I. Buzykin, and R. K. Vasil'eva, 15 pages, 108 references) deals with the chemistry of hydrazones of the type  $\text{RCX}=\text{N}-\text{NYSO}_2\text{R}'$  ( $\text{R}=\text{Ar}$ ,  $\text{X}-\text{H}$ :  $\text{Y}=\text{H}$ , alkyl, or aryl); the most studied in

this series is the group of tosylhydrazones (derivatives of  $p\text{-MeC}_6\text{H}_4\text{SO}_2\text{NHNH}_2$ ). Because of the lability of the N-S bond, hydrazones of this type are widely used in synthetic organic chemistry, photochemistry, and the dye industry, and in the preparation of alkanes, alkenes, carbenes, and diazonium compounds; the chapter is provided with ample examples of all of these chemical transformations.

Chapter 5 (Substituted Azines, B. I. Buzykin and G. D. Leshnina, 33 pages, 153 references) is devoted to the synthesis and chemistry of azines having substituents at the carbon atom of the azine group: halogen,  $\text{N}_3$ , CN, NHR,  $\text{NRR}'$  ( $\text{R}, \text{R}' = \text{H}$ , alkyl, aryl, or heterocyclic, and  $\text{R}^2\text{CO}$ ),  $\text{NHNRR}'$ ,  $\text{N}=\text{NR}$ , OH, SH, OR ( $\text{R} = \text{alkyl, aryl, or heterocyclic}$ ),  $\text{CO}_2\text{R}$ , and  $\text{SO}_2\text{R}$ ; tautomerism, rearrangements, and the synthesis of heterocyclic compounds from substituted azines are also described.

Chapter 6 (Hydrazones of Carboxylic Acid Hydrazides, B. I. Buzykin, N. G. Gaztdinova, and L. P. Sysoeva, 56 pages, 144 references) presents a broad overview on hydrazono-hydrazides. This includes methods of preparation, and physical (u.v., i.r., and n.m.r. spectroscopy) and chemical properties (substituent effects and cyclization reactions) of a series of hydrazones of carboxylic acid hydrazides called "hydrazidines"; some comments on the nomenclature, classification, and industrial applications of hydrazono-hydrazides are also included.

Chapter 7 (Formazans as Analogs of Hydrazones, B. I. Buzykin, 16 pages, 54 references) is concerned with a detailed comparison of the physical and chemical properties of formazans with those of a variety of hydrazones. Similarity in the chemical behavior of formazans and hydrazones sharing identical substituents has been demonstrated. Buzykin considers that acceptance of formazans as members of the hydrazone family may be helpful in the design and synthesis of novel formazans and hydrazones. A discussion of the nomenclature and classification of formazans is also presented. This chapter may be supplemented with a recent study of the acid strength of formazans in ethanolic solution [J. B. Gill, H. M. Irving, and A. Prescott, *J. Chem. Soc. Perkin Trans. 2*, (1977) 1683, and references cited therein].

The book concludes with a Table of Contents and a detailed summary of each individual chapter, but a Subject Index and an Author Index are not provided. Despite the new nomenclature suggested, there is a tendency to adhere to the IUPAC Rules of Nomenclature.

In general, this book is an excellent, scientifically sound, "little" (but comprehensive) monograph, containing an abundance of high-quality, structural formulas.

The book is indispensable to all organic, analytical, and physical chemists interested in hydrazine chemistry: any reader working with phenylhydrazones and osazones of carbohydrates will also benefit from it. The reviewer is not aware of any similar recent book on the chemistry of hydrazones published in the West; translation of this book into English is highly recommended.