NEW BOOKS

A. Katritzky and A. Boulton (editors)

ADVANCES IN HETEROCYCLIC CHEMISTRY*

Reviewed by L. I. Belen'kii

Volume 21 of this well-known publication contains eight review papers devoted to various aspects of the chemistry of heterocycles. Some of these papers can be regarded as supplements to already available reviews. This is true of the paper by Filler and Rao (USA), which correlates the data on the chemistry of oxazolones that have been published since the review by Filler in Volume 4 of the same plblication (1965). The bibliography contains 165 citations, of which more than half deal with the synthesis, reactions, and stereochemistry of 2-oxazolin-5-ones (azlactones). The material dealing with other types of oxazolones is less comprehensive. However, it is interesting to note the growing interest in 2-oxazolin-4-ones, among which one finds tranquilizers, antidepressants, and appetite suppressors.

The comprehensive review by Butler (Ireland) on the chemistry of tetrazole (112 pages and 681 literature citations) summarizes the data published from 1965 to 1976 and is regarded as a supplement to the chapter in Volume 8 of the series *Heterocyclic Compounds* edited by R. Elderfield. The review contains a special section that correlates the data from theoretical calculations, NMR and mass spectroscopy, and studies of molecular complexes of tetrazoles, including their crystal structures; the transformations of tetrazoles during photolysis and the properties of tetrazolinyl radicals are examined. Approximately one fourth of all of the literature cited in the remiew pertains to this section. Of principal importance in the section devoted to the synthesis of tetrazoles is research involving the preparation of biologically active 5-substituted tetrazoles. The ring—chain tautomerism of azidoazomethanes and tetrazoles and the synthesis and tautomeric transformations of condensed systems that include a tetrazole ring are examined at the end of the paper.

A paper by Kul and Lombardino (USA), which contains 63 pages and 241 bibliographic citations, is devoted to pyrrolodiazines with a "bridgehead" position, which have also been discussed in part in the review literature. However, this paper is the first in which all of the systems that have been assigned to this class — pyrrolo[1, 2-a]pyrimidines, pyrrolo[1, 2-c]pyrimidines, and pyrrolo[1, 2-a]pyrazines and pyrrolo[1, 2-b]pyridazines, including also partially or completely hydrogenated compounds — are examined. Of particular interest is 2, 3, 4, 6, 7, 8-hexahydropyrrolo[1, 2-a]pyrimidine (diazabicyclononene or DBN), which is a strong base with weakly expressed nucleophilic properties and is used as a catalyst for reactions of polyhydroxy compounds with polyisocyanates that lead to polyurethanes and for other processes; however, it is used in laboratory practice as a dehydrohalogenating agent for labile compounds. There is also a considerable amount of material on 1,4-diketooctahydropyrrolo[1, 2-a]pyrazines ("proline anhydrides"), which are formed in certain microbiological transformations and are easily synthesized.

A paper by Fringuelli, Marino, and Tatioi (Italy) includes an unexpectedly large amount of material (∿50 pages and 109 literature citations) dealing with tellurophene and related compounds. Data on 158 compounds described up to 1975, including tetrahydrotellurophenes and the corresponding condensed systems, are summarized in a special appendix. The authors make a detailed examination of the data on the geometry of the tellurophene ring, on various physical properties (the dipole moments and the UV, IR, Raman, NMR, and photoelectronic spectra), on the aromaticity of tellurophene, and on the conformations of substituted tellurophenes and discuss the chemical properties, primarily the electrophilic substitution and metallation of tellurophene. The properties of tellurophene are compared with the properties of furan, thiophene, and selenophene. Quantitative data are given for some of the reactions; in particular, in the case of electrophilic substitution the activity of the systems under considera-

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tion changes in the order thiophene $<$ selenophene $<$ tellurophene $<$ furan, i.e., the activity increases as the aromatic character of the heteroring decreases.

Data on the chemistry of four-membered cyclic peroxides — 1,2-dioxetanes — are summarized in a compact yet pithy paper by Adam (Puerto Rico). Although the first reliable data on the synthesis of such compounds were obtained less than 10 yr ago, the review contains ~200 literature citations. The principal methods for the synthesis of 1,2-dioxetanes — cyclization of α-substituted hydroperoxides with the elimination of hydrogen halide, water, etc., and the cycloaddition of singlet oxygen to the C=C bond — and the physical methods used for their characterization, which is especially valuable for such labile compounds, are examined. A special section is devoted to the role of 1,2-dioxetanes in chemical and biological reactions, mainly those involving the participation of singlet oxygen, and to the kinetics and mechanism of the transformations of these cyclic peroxides under themolysis, photolysis, and nucleophilic substitution conditions.

A large review by Barker (England) is devoted to the chemistry of thienopyridines. The principal methods for their preparation are similar to the classical syntheses of quinolines and isoquinolines; however, specific methods involving the formation of a thiophene ring are also known. The interest in the chemistry of isomeric thienopyridines as quinoline and isoquinoline analogs is due to the presence in the condensed system of electron-deficient pyridine and electron-surplus thiophene fragments. The effect of the replacement of an annelated benzene ring by a thiophene ring on the biological activity of analogs of compounds of the quinoline and isoquinoline series has also been studied extensively. Approximately one third of the 150 studies cited in the review are devoted to the latter problem. Finally, research on the synthesis of polymethine dyes that include thieno[2, 3-b]- and thieno[3,2-b]pyridine systems carried out by V. G. Zhiryakov and P. I. Abramenko is reflected in the review.

Data on methods for the preparation of isoxazolidines and their physical and chemical properties, as well as data on ways to use them, are summarized in a review by Takeuchi and Furusaki (Japan). The paper contains 210 citations to publications since 1918, when these compounds were described for the first time, with particular emphasis on publications appearing from the sixties to May 1974. The principal methods for the synthesis of isoxazolidines reduce to inter- or intramolecular cycloaddition of nitrones to olefins. The chemical and physical properties of isoxazolidines and data on the physiological activity of some compounds of this type and the properties of polymers that include isoxazolidine fragments are examined concisely in the review.

The review by Reinhoudt (Holland), which is not devoted to any individual class of compounds but rather to [2 + 2]-cycloaddition reactions and reversible processes, occupies a special place. Reactions of this sort have been the subject of intensive study in recent years, as attested to graphically by the bibliography of this review paper, which contains more than 300 citations to research published from the start of the sixties to 1974, inclusively. A characteristic example of the use of the reactions examined by the author is the construction of a β-lactam ring by the addition of ketenes to the double bond of the corresponding heterocycles, which makes it possible to realize the synthesis of penicillin, caphalosporin, and related systems. The reverse process, the so-called [2 + 2]-cyclo reversion, is not only of theoretical interest but also makes it possible to obtain some otherwise difficult-to-prepare compounds, particularly those with seven- and eight-membered rings. Substituted and condensed oxepines, thiepines, and azepines have recently been obtained by precisely this method. Two- and three-ring systems, which in turn are obtained by [2 + 2] cycloaddition of various acetylenic compounds to the corresponding substituted compounds and to benzannelated furans, thiophenes, and pyrroles, serve as the starting compounds for the cycloreversion. Voluminous material, which is set forth in ~70 pages, is classified with respect to the types of reactions: thermal cycloaddition, photochemical cycloaddition, and cycloreversion processes are examined in individual sections. The mechanisms and peculiarities of inter and intramolecular reactions and of processes involving the participation of various components — heteroaromatic compounds or nonaromatic heterocycles, on the one hand, and olefins, carbonyl compounds, acetylenes, and heterocumulenes, on the other — are discussed within each of these sections. The considerable theoretical interest, the great synthetic possibilities of [2 + 2]-cycloaddition and cycloreversion reactions, and the unquestionable difficulty in the selection of the appropriate literature material make this paper an extremely useful one. To a greater or lesser extent this is also valid for the rest of the papers in the collection, which will be received with interest by those engaged in research on the chemistry of heterocycles.