NEW BOOKS

W. L. F. Armarego

STEREOCHEMISTRY OF HETEROCYCLIC COMPOUNDS.

PART 2. OXYGEN, SULFUR, MIXED N, O, AND S, AND PHOSPHORUS HETEROCYCLES*

Reviewed by L. I. Belen'kii

The second part of the monography by Armarego is devoted to the stereochemistry of oxygen and sulfur heterocycles, as well as heterocycles that contain two or three different heteroatoms (O, S, and N). The stereochemistry of phosphorus heterocycles is examined in the final chapter by Gallagher (University of New South Wales, Sydney). The book is constructed in the same way as Part 1, but the material is more condensed, since the overall volume of Part 2 is approximately equal to the volume of Part 1, whereas the number of subjects discussed is, of course, considerably larger.

The chapter devoted to oxygen heterocycles occupies ∿ 130 pages and contains more than 1000 literature citations. All of the principal classes of saturated oxygen heterocycles are examined in it. The stereochemistry of the opening of the epoxide ring, including cleavage of not only C—O but also C—C bonds, is discussed in detail. Data on the stereochemistry of the formation, configuration, and conformation of oxetanes, on their thermal decomposition to give olefins, and on the stereospecificity of the formation of 1,2-dioxetanes from olefins and singlet oxygen are presented in sections devoted to four-membered rings.

Of considerable interest is the section devoted to hydrogenated furans, particularly data on the stereochemistry of the formation of di- and tetrahydrofurans (both from furans and from compounds with an open chain) and the conformation of tetrahydrofuran, including the results obtained during a PMR study of some furanose derivatives. The stereochemistry of the formation and reactions of 1,3-dioxolanes is examined. Some of the problems in the stereochemistry of ozonides (1,2,3- and 1,2,4-trioxolanes) are also illuminated.

In the section pertaining to the sterochemistry of hydrogenated pyrans one's attention is especially drawn to the examination of the electrostatic interaction of substituents such as OH, OR, and Cl with the heteroatom which may lead to predominance of the less sterically favorable conformation with an axial orientation of the substituent in the 2 position (the "anomeric effect"). Condensed pyrans, including chromans, isochromans, and reduced xanthenes, various oxabicycloalkanes, and carcass structures of the oxatwistane and oxaadamantane type, are also discussed. In his examination of the stereochemistry of 1,3- and 1,4-dioxanes, Armarego particularly notes the conformational differences between them and cyclohexane due to the shorter length of the C—O bond as compared with the C—C bond. The material pertaining to the stereospecificity of the synthesis of 1,4-dioxanes is interesting. Six-membered cyclic peroxides (1,2-dioxanes) and condensed 1,3- and 1,4-dioxanes are also examined in the same section. A small section is devoted to 1,3,5-trioxanes and 1,2,4,5-tetroxanes.

The stereochemistry of oxygen heterocycles that include seven or more members is discussed in the final section of the chapter. Problems in the stereochemistry of hydrogenated oxepines, mainly in the case of condensed and bridged systems, are set forth concisely, and seven-membered cyclic formals are also examined. Data relating to the transannular reactions that take place with the participation of oxygen heterocycle or lead to the formation of an oxygen bridge in the carbocyle, to the stereochemistry of oxygen-containing ansa compounds, to crown esters, and, finally, to analogs of diphenic acids that include oxygen heterocyclic fragments are of interest.

The chapter devoted to sulfur heterocycles is smaller than the preceding chapter (it contains ∿ 80 pages of text and 540 literature citations). In many cases the author pursues

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their similarity to the oxygen analogs. In addition, the ability of sulfur to exist in higher valence states creates additional possibilities, which have been studied particularly thoroughly for chiral sulfoxides, in which the stereochemical problems are similar to those examined in Part 1 of the book for compounds with trivalent nitrogen. However, one should bear in mind that because of the substantially higher barrier to pyramidal inversion of the sulfoxide sulfur atom as compared with nitrogen (157 kJ/mole for dimethyl sulfoxide as against 24 kJ/mole in the case of triethylamine), the conformational analysis of cyclic sulfoxides, in contrast to nitrogen heterocycles, is virtually uncomplicated by inversion of the heteratom. Taking this into account, the author classifies the material in the same way as in the preceding chapters (on the basis of the ring size and the number of heteroatoms) without singling out sections devoted to sulfoxides and sulfones.

In the sections in which thiiranes and thietanes are examined, the data on the stereospecificity of the formation and opening of these systems and the configuration and conformation of thietanes, including the corresponding sulfoxides and sulfones, are most interesting. The following two sections are devoted to hydrogenated thiophenes (thiolanes and thiolenes) and the corresponding condensed systems. Here one's attention is drawn to the material pertaining to the stereochemistry of the synthesis of biotin, (2 + 2)-cycloaddition reactions of olefins and acetylenes involving addition to compounds of the thiophene and benzothiophene series, and the stereospecificity of the reduction of 2-acylsulfolanes and the thermolysis of Δ^3-sulfolenes. The two shortest sections are devoted to the stereochemistry of dithiolanes and trithiolanes. The data pertaining to lipoic acid, which has been studied in detail as a coenzyme and has been used to establish the absolute configuration of some optically active thiolanes, are most interesting.

The problems of the configuration and conformation of tetrahydrothiapyrans (thianes), including the stereospecificity of the formation of the corresponding sulfonium salts, the manifestation of an anomeric effect, the possibility of the existence of an intramolecular hydrogen bond with participation of the ring heteroatom, and, finally, the stereochemistry of the corresponding sulfoxides, sulfimides, and sulfoximides, undoubtedly occupy a central position in the next section, in which tetrahydrothiapyrans are examined. In the next three short sections one's attention is drawn to data on the conformations of 1,2-, 1,3-, and 1,4-dithianes, 1,2,3- and 1,3,5-trithianes, 1,2,4,5- tetrathianes, and pentathianes, since they clearly reveal the effect of substituents on the relative preferableness of the chair or twist conformation. Of no less interest is the material presented in the next section which characterizes the effect of the number and orientation of the sulfur atoms on the size of the barriers to ring inversion in thiepanes, 1,2- and 1,3-dithiepanes, and tri-, and pentathiepanes. The summary of data on the transannular interactions with the participation of the sulfur atom is also useful to readers. Sulfur-containing analogs of cyclophanes (the so-called thiophenophanes) and ansa compounds in which the sulfur atom is included in an ansa bridge are examined in rather great detail. Unfortunately, the author failed to include the extensive research on the first of these groups of compounds carried out by Ya. L. Gol'dfarb and co-workers. As a result, the material presented by Armarego on "thiophenophanes" is virtually limited to a reference to a review by Vogtle and Neuman published in 1972, and some of the additional references to earlier original papers are arbitrary in nature. The data on compounds with a sulfur atom in the ansa bridge are presented in a more thorough manner; however, here also the bulk of the literature citations pertain to 1968-1971, although several extremely interesting papers in this area are now being published every year. In particular, the problem of extrusion of SO_2 from a bridge, which is currently one of the most valuable methods in the synthesis of cyclophanes from their analogs, is not touched upon at all.

A special section is devoted to the stereochemistry of the reactions of thiabicycloalkanes. Where possible, the author makes a comparison with the corresponding carbocycles — compounds of the bicyclo[2.2.1]heptane, bicyclo[3.2.1]octane, bicyclo[2.2.2]octane, bicyclo[3.3.1]- and -[4.2.1]nonane, barbaralane, and adamantane series — and their heteroanalogs. A variety of material is collected in the final section. After a brief examination of the stereochemistry of thioxanthenes and thianthrenes, the author presents data on thiophene analogs of diphenic acids and 2,2'-disubstituted diphenyls, in which a sulfur atom is included in a bridge between the ortho positions that hinders free rotation and creates the possibility the existence of enantiomers. Data on heterohelicenes that include thiophene rings (from papers by Vinberg and co-workers) are presented at the end of the section, and the problem of their chiral character is examined. The fragment that closes the chapter, in which the

synthesis of thiapropellanes is discussed without any examiniation of their sterochemistry, seems somewhat strange.

A separate chapter of the monograph is devoted to heterocycles that contain two or three different heteroatoms. Heterocycles that contain nitrogen and oxygen, nitrogen and sulfur, and sulfur and oxygen are examined in its three major sections; in addition, heterocycles that simultaneously contain three different heteroatoms are discussed in the brief final section. The chapter occupies ∿ 60 pages, and bibliography contains 439 citations; on the whole, this chapter is written in an extremely concise manner due to both the smaller volume of the literature and the analogy between properties of these compounds and those of heterocycles that include identical heteroatoms.

Of the heterocycles that contain nitrogen and oxygen atoms, five-membered systems have been described in relatively greater detail; this is due to both their accessibility and their significance. The stereochemistry of the reactions of N-oxides of nitriles and nitrones with olefins, which lead to isoxazolines and isoxazolidines, respectively, and served as a basis for Huisgen and co-workers for the development of concepts regarding 1,3-dipolar cycloaddition, is examined in detail. Also of interest is the material pertaining to oxazolines and oxazolidines, particularly that which deals with the establishment of the absolute configurations of some compounds of this type. Of the six-membered systems, substituted morpholines are examined in greatest detail. Bicyclic and polycyclic compounds, as well as seven-membered and macrocyclic compounds with nitrogen and oxygen heteroatoms, are discussed in the final section.

In the following section one's attention is drawn to data on the stereochemistry of the formation of thiazolines and thiazolidines; however, reference mainly to reviews dealing with the stereochemistry of penicillin and related compounds are presented here. In his subsequent examination of reduced 1,3-thiazines, the author presents (also without details) citations of the principal research pertaining to cephalosporin, its total synthesis, and the conversion of the cyclic system of penicillin to the cephalosporin system. The discussion of the stereochemistry of biotin in the final part of the section devoted to heterocycles that include sulfur and nitrogen atoms seems completely unwarranted, since compounds with different heteroatoms in the same ring were examined prior to this, and, in addition, the necessary data on biotin were already presented in the chapter devoted to sulfur heterocycles (see above). In the brief section dealing with heterocycles that include sulfur and oxygen atoms the data on the stereochemistry of four-, five-, and six-membered sultones are evidently of greatest interest.

The long concluding chapter (∿ 90 pages and 443 literature citations), which is devoted to phosphorus heterocycles and includes some arsenic and antimony analogs, was written, as indicated above, by Gallagher. The format of this chapter differs from the format of the other chapters, primarily because of the ability of phosphorus to exist in different valence states with substantially different stereochemistries. All of the material of the chapter was therefore classified in conformity with coordination numbers of the phosphorus atom from two (for example, as in the case of phosphabenzene) to six (as in various anions of the PX^-_6 type) and, within these sections, in conformity with the number of anions in the heteroring. The principal exposition is found in the section that examines the ^{31}P and ^{13}C NMR spectroscopic data, which are extremely valuable for the study of the stereochemistry of phosphorus compounds.

An extremely high barrier to pyramidal inversion is characteristic for trivalent phosphorus compounds. This leads to the possibility of separation of phosphates into their optical antipodes and the relative stability of the latter, which is fully manifested also in the case of heterocycles. Separation into the antipodes is easily realized for phosphonium salts, and the compounds of tetravalent positively charged phosphorus have therefore been studied extremely thoroughly. The stereochemistry of pentavalent phosphorus, for which orientation of the substituents at the apexes of a trigonal bipyramid is most characteristic, is particularly complex; the existence of 10 pairs of enantiomers is, in principle, possible in the case of five different substituents. The situation is simplified substantially in the case of heterocycles: this explains their extensive application as subjects for the stereochemical studies of pentavalent phosphorus. One cannot help but note that the last chapter clearly deviates from the content of the monograph and is intended not so much for heterocyclic chemists as for those engaged in research on the stereochemistry of Group V elements, primarily phosphorus.

In conclusion, it should be stated that the rigid formal scheme adopted in the monograph enabled the author to examine voluminous and extremely diverse material. At the same time, this scheme is not the only possible scheme or the most convenient for the reader, since it leads to inevitable fragmentation of related material dealing with different heterocycles over separate sections and chapters. Thus, for example, the heterocyclic analogs of cyclophanes are examined among nitrogen, oxygen, and sulfur heterocycles, and finally, among heterocycles that contain different heteroatoms. This, of course, does not show the entire picture, although the chemistries of these compounds, particularly the stereochemical aspects, have very much in common, of which one is easily convinced in the light of the review by Newcomb and co-workers published in Chemical Reviews in 1977.

There are also substantial deficiencies in the selection of the material. In particular, the data on the stereochemistry of heteroaromatic compounds are scanty, whereas one might have hoped to find information on the geometry of the principal heteroaromatic systems and an examination of some stereochemical problems specific for them in this book. These problems include, for example, the problem of the rotational isomerism of acyl- and alkenyl-substituted heterocycles, which is currently being studied intensively by various methods, in particular by means of NMR spectroscopy and measurement of the dipole moments.

Finally, in a number of cases the exposition is excessively laconic and may serve more as a bibliographic source than as a selection of specific information. However, it was difficult to avoid this, considering the large volume and great diversity of the material. Despite these shortcomings, Armarego's monograph will undoubtedly be useful for readers interested in the stereochemistry of heterocyclic compounds.

Ole Buchardt (editor)

PHOTOCHEMISTRY OF HETEROCYCLIC COMPOUNDS*

Reviewed by A. N. Kost

This book is devoted to a research area that is undergoing vigorous development. The only review that encompasses the entire field was published in 1970.[1] Of course, one can find examples related to the chemistry of heterocycles in a monograph by Schönberg,[2] but this monograph has already become obsolete. Review papers that deal with special problems of the photochemistry of heterocycles (for example, see footnotes [3] and [4] below) have been published; however, they cannot give an idea of the general front of science in this field.

The book begins with a brief chapter on the theory of the excited state. The second chapter deals with three- and four-membered rings; the reader will find interesting material in this chapter, particularly in the part that deals with the photochemical isomerization reactions of oxiranes and azirines. The authors note that the epoxidation of cyclic unsaturated hydrocarbons with subsequent photochemical isomerization has become a convenient synthetic method for the synthesis of lactones. One of the authors (Professor Padva) has himself made a substantial contribution to this field of chemistry, and the material is therefore presented informally.

The conversion of adducts of the azanorbornadiene type to azepine derivatives, the migration of substituents in the pyrrole ring, reactions involving ring opening or contraction (the formation of cyclopropenes or cyclopropanes) in furans and analogous transformations of thiophenes, the photoisomerization of pyrazoles to imidazoles, and the interconversions of oxazoles and isoxazoles (and, correspondingly, thiazoles and isothiazoles) are most interesting topics in the chapter on the photoisomerization of five-membered rings.

The chapter on the photoisomerization of six-membered structures is brief. Here only the fundamentals of the transformations of pyridines and condensed structures having a pyridine ring, other azines (pyrimidines and pyrazines), derivatives of pyran and pyrylium salts, a number of models with several heteroatoms (for example, purines), as well as several compounds with silicon atoms in the ring, are set forth. The research of the editor of this book, O. Buchardt, on the photochemistry of N-oxides of the heteroaromatic series is represented here in a rather modest fashion, although the publications of J. Streith, the author of the chapter, that appeared simultaneously or later are cited extremely thoroughtly (see footnote [5] for reviews of these studies).

The chapter on the phototransformation of multimembered rings with different degrees of unsaturation is extremely diversified with respect to its content. Data on azepines and benzodiazepines (primarily a decrease in the ring) are presented most systematically. In this chapter the reader will find information on the transformations of eight- and nine-membered rings, cyclophanes, and even multimembered structures with silicon, phosphorus, and mercury atoms in the ring, the decomposition of which as a rule proceeds with elimination of the heteroatom.

*Wiley, 1976.

[1] S. T. Reid, Advances in Heterocyclic Chemistry, Vol. 11, Academic Press (1970), p. 1.

[2] A. Schönberg, Präparative Organische Photochemie, Springer Verlag, Berlin (1958).

[3] A. V. El'tsov, V. M. Grebenkina, and V. S. Kuznetsov, Khim. Geterotsikl. Soedin., No. 3, 437 (1974).

[4] A. Castelano, G. P. Cato, A. Lablache-Cambier, B. Planckart, and G. Alan, Khim. Geterotsikl. Soedin., No. 7, 867 (1974).

[5] F. Bellamy and J. Streith, Heterocycles, 4, 1391 (1976); J. Streith, Heterocycles, 6, 2021 (1977).

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A chapter on the photochemical cleavage of heterocycles under severe conditions is presented after the discussion of photoisomerization processes and similar transformations in which the principal part of the skeleton of the molecule is retained. The conversion of pyrazolines to cyclopropanes, the cleavage of tetrahydropyridazines and isopyrazoles, the splitting out of CO_2 from lactones, the decomposition of cyclic peroxides, etc., are included here. A great deal of attention was directed to evaluation of the stereospecificity of the processes.

Photochemical oxidation is described in Chapter 7, in which the authors give a short introduction dealing with the mechanism of photooxidation and the role of sensitizers, after which they examine the oxidation of furan, pyrrole, and imidazole rings and the oxidation of indoles and purines. Material on sensitized and unsensitized photooxidation is presented separately.

A presentation of examples of photoreduction in which an attempt is made to unify the reported instances of reduction in the excited state of a molecule by means of several typical schemes of mechanisms having a reaction through a step involving one-electron transfer in common follows directly after this chapter. The photochemical alkylation of the pyridine ring with simultaneous dimerization and analogous processes for quinolines, isoquinolines, acridine, phenazine, purines, etc. are examined.

The book closes with a discussion of examples that are finding industrial application. Included here are photochromic dyes of the spiran type, substances for the photostabilization of polymers (for example, quinazoline derivatives), optical bleaches, chemiluminescent substances (such as the well-known luminol), photopolymerization processes (for example, those observed for vinylcarbazole), sensitization, a photographic process without silver, etc.