

Book Reviews

Organosulfur Chemistry: Synthetic Aspects.

Edited by P.C.B. Page. Academic: London, 1995, 277 pp, hardback. £ 55.00. ISBN 0-12-543560-6.

Organosulfur chemistry (synthetic aspects) is the first in a new series of books "intended to provide an in-depth coverage of topics of current interest throughout the whole range of organosulfur chemistry including bio-organic and physical organic as well as synthetic aspects."

This volume consists of 5 disparate chapters. Chapter 1 is entitled 'Optically active β -keto sulfoxides and analogues in asymmetric synthesis' and is written by Solladié and Carmen Carreño. It details the methods for the preparation of β -keto sulfoxides and their applications to total synthesis and is followed by several sections on alkenyl sulfoxides as dienophiles and dienes in synthesis. The authors have chosen a topic of considerable breadth and as such it has not been possible to provide a comprehensive review of this area. However, the authors own contributions in the area are well covered. This chapter might probably have been better divided into two separate chapters to cover both anion chemistry and cycloaddition chemistry of sulfoxides and then a fuller coverage of the area could have been given.

The second chapter is a scholarly account by Crich of homolytic processes at sulfur. This chapter provides a comprehensive review of the methods of generating and reactions of sulfur, sulfinyl and sulfonyl centred radicals and includes useful data for the important rates of radical addition and elimination reactions with alkenes. The Barton-McCombie reaction for removing alcohol and acid functions via thiocarbonyl derivatives is also discussed in this section.

Chapter 3 by Rayner provides a detailed and comprehensive review on various synthetic transformations involving thiiranium ion intermediates. Methods for generating thiiranium ions are provided and their subsequent capture by various nucleophiles (halides, carbon, oxygen, nitrogen, and sulfur nucleophiles) are discussed. Factors affecting the regioselectivity in ring

opening of thiiranium ions in both inter- and intramolecular reactions is also discussed.

Chapter 4 is an account by Wood on the chemistry of 1,3-dithioacetals. The first section discusses the importance of this group, not in synthetic chemistry, but in industrial chemistry as isosteres for cyclohexane and cyclopentane rings or as a super t-butyl group, or as a framework on which to hang other groups in precise orientations. This short section is a welcome addition to a book otherwise devoted to academic chemistry. The remaining chapter gives an account of the methods of preparation of 1,3-dithioacetals, anion chemistry and hydrolysis and seems to be very comprehensive. For example, tables of data are given for different reaction conditions for thioacetal formation, but without preferences for the best methods and a reader new to the subject may still not know which method to try first. In addition, the method using $\text{BF}_3 \cdot \text{OEt}_2$ with a dithiol and aldehyde/acetal is not given even though these were the original conditions described by Corey for the preparation of 1,3-dithiane.

Chapter 5 by Okazaki gives a comprehensive account of thioaldehydes. Methods for the preparation of thioaldehydes are discussed and as they polymerise readily their subsequent trapping is described. The author's own seminal contributions in the area are then described in the section on stable thioaldehydes and gives their structural properties and subsequent reactions.

Overall this book gives a useful account of organosulfur chemistry and highlights some of its important features that make it useful in synthesis. As the first book in the series of *synthetic aspects* of organosulfur chemistry, I would have liked to have seen perhaps a chapter on sulfur ylides. Also, I was somewhat disappointed that for a book which appeared towards the end of 1995 there were so few references after 1992 (Okazaki's excepting). Nevertheless, this book is certainly one that every departmental library should possess.

Varinder K. Aggarwal, Sheffield University, UK.

Symmetry: A Basis for Synthesis Design. By Tse-Lok Ho. Wiley: New York, 1995, 584 pp, hardback. £ 70.00. ISBN 0-471-57376-0.

Symmetry as defined by Webster (Webster's Ninth New Collegiate Dictionary, 1986) is "1. balanced proportions; also: beauty of form arising from balanced proportions; 2. the property of being symmetrical; esp.: correspondence in size, shape, and relative position of parts of opposite sides of a dividing line or median plane or about a center or axis; 3. a rigid motion of a geometric figure that determines a one-to-one mapping onto itself; and 4. the property of remaining invariant under certain changes ..." Thus from the simple title, one would assume (without additional input) that the textual material would deal with symmetry as related to stereochemistry in an Eliel-type context; in essence - one can not judge this book by its cover! In fact, this book could have more appropriately been titled: "Antithetical Approaches to Synthesis". By the injudicious use of prefixes and suffixes, "Symmetry" has been incorporated into 20 symmetry-related terms. In the introduction, the author interrelates the diverse "symmetry" related terms and attempts to delineate their relationship to synthetic organic chemistry. At times this mental exercise is obvious (or is it?): "Although it is likely that *symmetrical* substances are more readily constructed from intermediates of high *symmetry*, the synthesis of *unsymmetrical* molecules may also benefit from the use of *symmetrical* precursors, and vice versa." Also: "*Pseudosymmetry* refers to the presence of slight structural perturbations that cause an otherwise *symmetrical* molecule to be *asymmetrical*." And: "*Local symmetry* pertains to molecular segments but not the whole molecule." However, when one divorces oneself from the terms and focuses on the obvious antithetic approach to synthetic construction, starting with Chapter 2, the examples are a plethora of interesting molecular puzzles that have been mastered by a host of clever chemists over the past several decades.

The pictorial dissection presented in the text is stimulating especially if one would say to a graduate student - 'please fill in the details between the structures'. Chapter 2 covers highly *symmetrical* molecules possessing predominately all carbon skeletons with a few natural products.

After this warm up section of rather simple molecules, the author disentangles the natural product world by the use of 2- and 3-carbon building blocks ("bricks"); 4-carbon bricks; *symmetrical* 5- and larger carbon aliphatic bricks; 5-membered ring synthons; 6-membered ring construction; miscellaneous other ring synthons; and last, but not least, the use of symmetrical heterocyclic bricks (Chapters 3-9, respectively). The wealth of examples incorporated in this book is an interesting compendium for both the graduate students, who wish to fill-in the blanks and attempt to match wits with the masters, as well as the masters, who wish to stimulate thoughts to alternate approaches; interestingly, the answers are all collected in the back of the book, since there are approximately 2,000 references.

Although I take jabs at the usage of the *symmetry* aspects, this collection of artistic approaches to discrete molecular structures has appeal to all those who wish to practice, or simply enjoy, the mental gymnastics associated with the connectology of molecular bricks.

George R. Newkome, The University of South Florida, Tampa Florida, U.S.A.

Biotransformations in Organic Chemistry, 2nd Edition. By K. Faber. Springer: Berlin, 1995, 356 pp, paperback. 58 DM. ISBN 3-540-58503-6.

This paperback is intended to provide a basis for a course in biocatalysis or to serve as an introduction to this field for professionals. Chapter 1 discusses the advantages and disadvantages of biocatalysts, in general, and those of isolated enzymes vs. whole cells followed by information on enzyme classifications and by a brief account of how enzymes control stereoselectivity. Chapter 2, which comprises 245 pages of this 356 page book, examines biocatalytic applications conducted in aqueous media and is organized according to the type of chemical transformation. The section on hydrolytic reactions covers amidases, esterases, proteases, lipases, epoxide hydrolases, and nitrilases and also includes informative discussions of matters such as the dependence of enantiopurity on % conversion, the "meso trick", and sequential

resolutions. Due to their simplicity, hydrolytic reactions have received the greatest attention by the synthetic community and, accordingly, this section of 120 pages is the largest in the book. The section on reduction reactions discusses the role of cofactors and provides examples of the reduction of aldehydes, ketones and C=C bonds using isolated enzymes or whole cells. The section on oxidation reactions includes the oxidation of alcohols and aldehydes as well as hydroxylation of alkanes and arenes, epoxidation of alkenes, oxidation of sulfides to sulfoxides, Baeyer–Villager reactions and, finally, dioxygenases which lead to allyl hydroperoxides from dienes and dihydroxycyclohexadienes from arenes. The 20-page section of carbon–carbon bond forming reactions focuses on aldol and acyloin reactions. The final three sections of approximately 10 pages each cover addition and elimination reactions including cyanohydrin formation, glycosyl-transfer reactions and halogenation and dehalogenation reactions. Chapter 3, entitled "Special Techniques", discusses the use of enzymes in organic solvents, particularly lipases in organic media of low water content, provides a nice summary of immobilization techniques, and short sections on modified enzymes and catalytic antibodies. The book concludes with a brief essay on the "State of the Art and Outlook"; this reviewer stands with the author in belief that the process of integration of biocatalytic techniques into synthetic organic chemistry will continue.

The author points out that in 1991, 8% of all papers published "in the area of synthetic organic chemistry contained elements of biotransformations". The author's wish list for the future

includes simpler models for predictions of stereochemical outcomes, reduction enzymes with complementary enantiospecificity, continuing developments in production of enzymes by genetic engineering and, in particular, the cloning and overexpression of enzymes found only in trace amounts or in sensitive organisms and in the development of synthetically useful mutant strains. The author missed the opportunity to better serve his clientele with the Appendix which includes only a one page list of abbreviations of enzymes and co-enzymes plus a simple list of 30 names of companies with home countries (e.g., Amano, Japan) of suppliers of enzymes. The index is in textbook style with only minimal entries.

This second edition of the Faber book, which cites literature through the end of 1993, follows closely on the heels of the 1994 Wong and Whitesides "Enzymes in Synthetic Organic Chemistry". These two highly readable books are of similar size and both clearly emphasize enzymatic steps of use in the synthesis with particular emphasis on the production of enantiomerically pure materials. The coverage by the two books is much the same; the Wong and Whitesides book has a greater array of examples of successful enzymatic reactions while the present book places a little more emphasis on the practical aspects to carrying out enzymatic transformations. This book admirably achieves its goal as an introduction to this field of growing importance.

Carl R. Johnson, Wayne State University, Detroit, U.S.A.

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