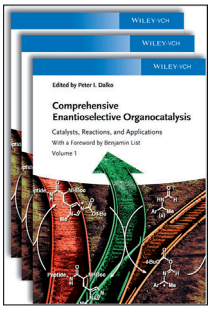

Comprehensive Enantioselective Organocatalysis
Edited by Peter I. Dalko.
3 Volumes. Wiley-VCH, Weinheim, 2013. 1160 pp., hardcover, € 449.00.—ISBN 978-3527332366

Comprehensive Enantioselective Organocatalysis

The field of organocatalysis has attracted a substantial number of players and has been developed in many creative dimensions. New and/or better catalysts and reactions are generated in many laboratories every day, and impressive breakthroughs occasionally appear in influential journals and scientific news media. It has become hard to keep track of the fast development of this field, even for insiders. For student beginners and for researchers outside the area, it might not be feasible to have a true picture of organocatalysis, even after an exhaustive literature search.

This three-volume handbook, *Comprehensive Enantioselective Organocatalysis*, edited by Peter Dalko with a foreword by Benjamin List, provides a convenient and comprehensive access to this field for both beginners and experienced players. For this new edition of an earlier manual on this subject, the editor has gathered over 90 authors who are experts in the field to summarize the main advances of organocatalysis, presented in 44 chapters. The editor and authors have done a marvelous job in organizing this rather complex and somewhat unstructured field in a reasonable way for readers. The catalysts, activation paths, reactions, and synthetic applications are detailed in the three volumes of the work.

In brief, Volume 1 introduces organocatalysts that are derived from amino acids and from non-amino-acid scaffolds. Readers can expect to find catalysts ranging from unmodified amino acids to designed oligopeptides and sophisticated supramolecular self-assembled structures. Volume 2 describes the activation modes of different organocatalysts, and the various methods to control catalytic reactivity and selectivity. On the basis of the interactions between the catalysts and the substrates, the editor has organized this part by a classification according to covalent and non-covalent catalysis. The discussion also introduces the tuning of reaction modes by controlling the environmental conditions (such as pressure, nano-scale cavities from porous structure, and water as reaction medium). Volume 3 focuses on reactions and synthetic applications of organocatalysis, including total synthesis. The topics covered include alkylations, nucleophilic additions to (and reduction of) carbon–carbon and carbon–heteroatom double bonds, and building of molecular complexity through ring formation, cascade catalysis, and multicatalysis. Free radical reactions, rearrangements, and kinetic resolutions are also discussed.

Given the complexity of the subject, readers should be prepared to see some unavoidable overlaps in different chapters written by different authors. The editor has achieved the best way of organizing the contents for such a sophisticated book.

Some aspects that are not covered in the present edition, but that a reader would probably have wanted to find included are: 1) a chapter summarizing the different reaction types of organocatalysis, with attempts at drawing their fundamental connections; 2) one or two chapters of commentary views identifying challenges in possible future directions of organocatalysis; 3) one or two chapters from scientists not in the organocatalysis field who can offer constructive criticism. I guess it will be quite hard to recruit authors for such chapters, for a future edition of this book.

In short, this is a useful book that one should read to find out about this field of research, or to become a player in it.

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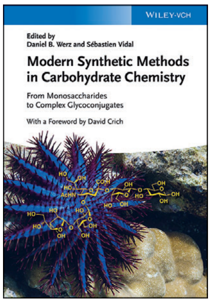

Modern Synthetic Methods in Carbohydrate Chemistry
From Monosaccharides to Complex Glycoconjugates.
Edited by Daniel B. Werz and Sebastien Vidal. Wiley-VCH, Weinheim, 2013.
406 pp., hardcover, € 139.00.—ISBN 978-3527332847

Modern Synthetic Methods in Carbohydrate Chemistry

Carbohydrates constitute the most abundant and functionally diverse organic compounds on the planet. Their extremely varied and elaborate structures are built on a myriad of monosaccharides, through various linkages and appendages. The chemical reactions of carbohydrates are determined largely by their functional groups and chirality, especially in terms of regio- and stereoselectivity. In fact, each type of the monosaccharides and glycosidic linkages is usually treated as a specific topic, and the synthetic chemistry of carbohydrates is a highly specialized field in the realm of synthetic organic chemistry. *Modern Synthetic Methods in Carbohydrate Chemistry*, edited by Daniel B. Werz and Sebastien Vidal, assembles a superb collection of state-of-the-art topics, which, as stated by David Crich in the foreword, "depend very heavily on the power and ingenuity of contemporary synthetic organic methodology".

The book consists of 12 chapters, all written by established experts in their topics. Chapter 1, from the research group of George A. O'Doherty, describes "De novo approaches" to the synthesis of chiral carbohydrates. It is counter-intuitive to synthesize carbohydrates, especially glycans, using achiral compounds as starting materials instead of the abundantly available monosaccharides, which already bear the required chiral centers. Nevertheless, the authors demonstrate, with sufficient examples, not only the feasibility but also the advantages of the de novo approaches, especially in the synthesis of carbohydrates that contain deoxy or unnatural sugar units. Chapter 2 focuses on the synthesis of aldoheptoses and aldoheptose-containing glycans. A plethora of reactions have been applied to the synthesis of these "rare sugars" from common pentoses and hexoses. The assembly of these units to form glycans that are relevant to the lipopolysaccharides (LPSs) of pathogenic bacteria, by providing the synthetic basis for antimicrobial agents or vaccines, is a topic of great current interest.

Chapter 3 is concerned with the formation of the non-natural glycosyl hydrazide and oxyamine linkages. These two highly chemoselective condensation methods have made it possible to synthesize glycoconjugates easily without resorting to the usually tedious manipulation of protecting groups. Chapters 4 and 5 focus on construction of the 1,2-*cis*-glycosidic linkages, while the 1,2-*trans*-glycosidic bonds can be reliably constructed via the participation of neighboring groups. Chapter 4 describes current techniques to control the 1,2-*cis*-glycosylation in the context of complex glycan syntheses and, most importantly, presents the evidence for and rationale of those stereoelectronic effects that regulate the otherwise erratic intermediates in the glycosylation reactions. Chapter 5 summarizes experimental data on the remote participation of protecting groups that are scattered throughout the literature. Although the stereoselectivity in numerous glycosylation reactions could be, and always is, attributed to the participation of a remote group, there is little direct experimental evidence to support this assumption.

Chapter 6 introduces the chemical derivatization of aminoglycosides, in efforts to overcome the drug resistance and nephrotoxicity of these antibacterial agents that have long been in clinical use. Selective modifications of these complex glycans, each containing a characteristic pseudo-sugar aminocyclitol unit, rely on differentiation of the many hydroxy and amino groups. A topic that has attracted wide attention in the medicinal chemistry of carbohydrates is the heparins, which bind to numerous proteins so as to regulate various physiological processes. In targeting the ternary structure formed by the heparin/fibroblast growth factor 2/tyrosine kinase receptor, Chapter 7 describes syntheses to construct a library of heparin fragments relevant to the binding motif. The success of current work on the synthesis of glycans as complex as the densely sulfated heparin octasaccharides is an impressive achievement in the context of the medicinal chemistry research programs of the pharmaceutical industry.

Chapter 8 interrupts the flow of the book by describing the brave attempts in "Light Fluorous-Tag-Assisted Synthesis of Oligosaccharides". Chapter 9 returns to the main theme by describing recent advances in cyclodextrin chemistry. One would not expect that the highly symmetrical cyclodextrins are able to be modified at each of the hydroxy groups or at nearly any combination of them, thus leading to tremendous opportunities for developing new molecular architectures, supramolecular tectons, and materials.

The last three chapters are devoted to two important glycoconjugates present in cell membranes, which are glycosphingolipids and glycosylphosphatidylinositol (GPI) anchors. Chapter 10 presents a case study on the design and synthesis of mimetics of the glycosphingolipids GM1 as cholera toxin ligands. Chapter 11 describes approaches to the synthesis of native glycosphingolipids, highlighting the current methods for introduction of the sialic acid and ceramide units into these complex glycolipids. The book ends strongly with Chapter 12, summarizing the advances from the pioneering efforts in the early 1990s to the recent development of general strategies towards GPIs and GPI-anchored proteins.

Each chapter, which can be explored independently, provides up-to-date references and a few representative experimental procedures. Combined together in this book, the chapters allow one to gain an appreciation of the frontiers of current research on synthetic carbohydrate chemistry. The problems that are described and the state-of-the-art solutions, many developed by the authors, will inspire everybody interested in the chemistry, biology, and medicine relevant to carbohydrates. I enjoyed reading this timely book.

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