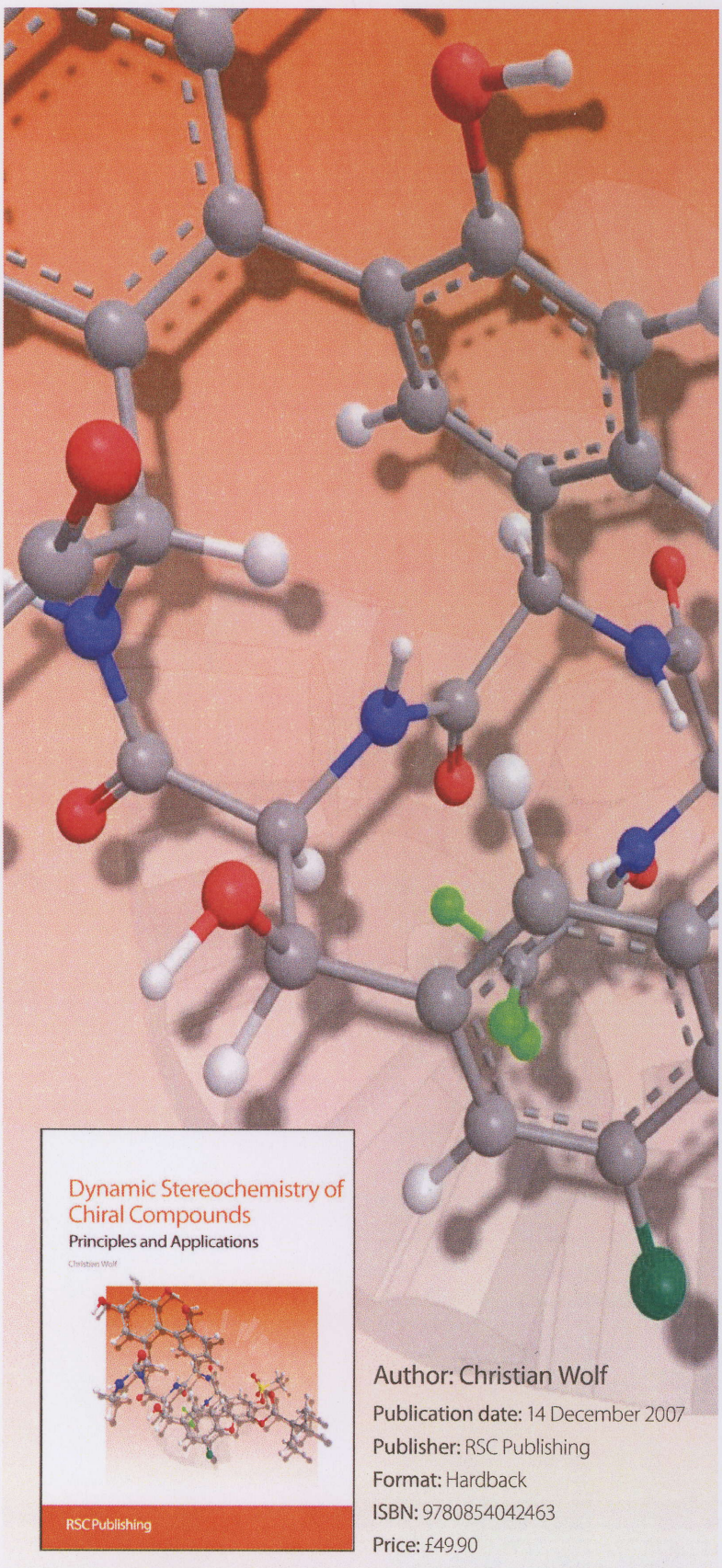

Dynamic Stereochemistry of Chiral Compounds

This book provides an overview of fundamental concepts of asymmetric synthesis highlighting the significance of stereochemical and stereodynamic reaction control. Topics include kinetic resolution (KR), dynamic kinetic resolution (DKR), dynamic kinetic asymmetric transformation (DYKAT), and dynamic thermodynamic resolution (DTR). In-depth discussions of asymmetric synthesis with chiral organolithium compounds, atropisomeric biaryl synthesis, self-regeneration of stereogenicity (SRS), chiral amplification with chiral relays and other commonly used strategies are also provided. Particular emphasis is given to selective introduction, interconversion and translocation of central, axial, planar, and helical chirality.

A systematic coverage of stereochemical principles and stereodynamic properties of chiral compounds guides the reader through the book and establishes a conceptual linkage to asymmetric synthesis, interconversion of stereoisomers, molecular devices that resemble the structure and stereomutations of propellers, bevel gears, switches and motors, and topologically chiral assemblies such as catenanes and rotaxanes. Racemization and diastereomerization reactions of numerous chiral compounds are discussed as well as the principles, scope and compatibility of commonly used analytical techniques.

- More than 550 figures, schemes and tables illustrating mechanisms of numerous asymmetric reactions and stereomutations of chiral compounds
- Technical drawings illustrating the conceptual linkage between macroscopic devices such as turnstiles, ratchets, brakes, bevel gears, propellers or knots and molecular analogs
- More than 3000 references to encourage further reading and facilitate additional literature research
- A comprehensive glossary with stereochemical definitions and terms which facilitate understanding and reinforce learning

This book will be of particular interest to advanced undergraduates, graduates and professionals working and researching in the fields of synthetic organic chemistry and stereochemistry.

Author: Christian Wolf
Publication date: 14 December 2007
Publisher: RSC Publishing
Format: Hardback
ISBN: 9780854042463
Price: £49.90

030804

RSC Publishing

www.rsc.org/books

Registered Charity Number 207890

cable methodology for the chemical construction of oligosaccharides eventually prevail, as we have seen occurring in the realm of automatic peptide syntheses?

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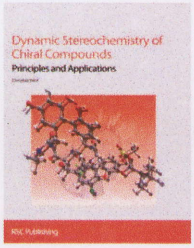
Dynamic Stereochemistry of Chiral Compounds



Principles and Applications. By *Christian Wolf*. Royal Society of Chemistry, Cambridge 2007. 512 pp., hardcover £49.95.—ISBN 978-0-85404-246-3

Chirality is a key feature of natural compounds and plays an essential role in amino acids (and hence in peptides and proteins), sugars, and numerous bioactive substances. Consequently, organic chemists have developed a plethora of methods for the synthesis of chiral compounds starting from the chiral pool, by separation of racemic mixtures, or by performing asymmetric syntheses from achiral precursors. For the latter, a broad variety of concepts have been developed, with homogeneous and heterogeneous catalysis as the most important current methods, but biocatalysis is also used to obtain optically pure chemicals. Furthermore, a wide range of analytical tools for the determination of the optical purity and absolute configurations of chiral compounds have been established in the past. More recently, stereochemistry has also turned out to play an important role in nanomaterials and in the development of molecular chiral devices.

The book by Christian Wolf is organized in three parts and contains nine chapters. The first chapter gives an introduction to the topic. Chapter 2 describes the basic principles, terminology, and nomenclature of stereochemistry. This part is very useful, as it provides practical guidelines, not only to understand the rest of the book but also to determine, for example, the *R* or *S* configuration of complex or rather unusual compounds. Racemization, enantiomerization, and conformational isomers are covered in the third chapter, together with mathematical treatments and mechanistic insights. The next chapter is devoted to analytical methods, with special emphasis on chirooptical methods, NMR spectroscopy, dynamic chromatography, and stopped-flow analysis. Thanks to Wolf's recommendation, one can now freely use the term "chiral chromatography" to describe GC or HPLC methods using chiral phases.

The second part of the book focuses on asymmetric synthesis as the most important synthetic method to create chiral compounds. First, the principles of asymmetric synthesis are introduced, and that is followed by numerous practical examples using a broad range of catalysts, both chiral and nonchiral. In the following chapter, kinetic resolution, dynamic kinetic resolution, and related strategies are treated in depth. Many examples are also explained in detail from a mechanistic standpoint, so that the reader can get a clear understanding of the basic principles behind a given stereoselective reaction.

The third and last part of the book deals with a rather new and—in my view—somewhat esoteric research field: stereodynamic devices and manipulation of molecular motion, where topological chirality plays a crucial role in the design of molecular propellers, bevel gears, brakes, switches, motors, etc. This section also includes the synthesis, chirality, and stereodynamics of catenanes, rotaxanes, and related compounds. The book ends with an extensive and very useful glossary of stereochemical definitions and terms, followed by an index.

Biocatalytic methods are adequately covered in the chapter about (dynamic) kinetic resolution. However, I was disappointed to find that the use of enzymes in asymmetric synthesis, where they indeed play an important role and are applied in many industrial processes, is not covered. Examples such as the use of ketoreductases to prepare chiral alcohols, and of hydroxynitrile lyases or aldolases to perform C–C coupling reactions, should at least have been mentioned briefly.

The only error I found was in the equation for measuring optical rotation by polarimetry, where the concentration *c* of a compound was given in g/ml, whereas it should read g/100 ml.

Overall, I was highly impressed by the excellent scientific level of the book, the language style, which made it a pleasure to read it (if reading a chemistry book can be pleasurable at all), and especially the care taken to illustrate the examples with numerous (often highly complicated) chemical structures, reaction schemes, and mechanisms.

Without any doubt, I strongly recommend this book to advanced students and experienced chemists, as it is a very rich source of information on all aspects of stereochemistry.

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DOI: 10.1002/anie.200785592

Book Reviews

Dynamic Stereochemistry of Chiral Compounds - Principles and Applications. Edited by Christian Wolf. RSC Publishing: Cambridge, U.K. 2008. 512 + xx pp. £49.95. ISBN 9780854042463.

The author of this monograph indicates in the preface that it took 2 and 1/2 years to write this book—I can well believe it. It would be interesting to measure the effort in man hours!

Well, I think it was worth it. This is a fresh approach which will be of some interest to process chemists and engineers who are not only interested in synthesis but also in kinetics and rates of processes. Process chemists will enjoy Chapter 7 in particular, entitled "Asymmetric Resolution and Transformation of Chiral Compounds Under Thermodynamic and Kinetic Control"; this 57-page chapter has several industrial examples of dynamic kinetic resolution as well as numerous academic ones, along with discussion to assist the reader to understand the mechanistic rationale.

An earlier chapter on "Racemisation, Enantiomerisation and Diastereomerisation" is over 100 pages long and has 850 references, almost a monograph in itself. This chapter is an excellent discussion of the physicochemical principles involved in isomerisation and is unlikely to be found in other books on asymmetric processes.

The rest of the book continues in the same excellent style, with a 100-page chapter on "Asymmetric Synthesis" and a short but necessary chapter on "Analytical Methods".

The last 100 or so pages, on Chiral Propellers, Gears, Brakes, Scissors, Catenanes, Rotaxanes, etc. will not interest the process chemist, but the book is worth the price for what goes before.

The downside? I could not find any reference after 2005. In this fast-moving area this is a serious drawback, and students and industrial researchers will feel short-changed by this defect. Whether this is the fault of the author or the publisher, we shall never know. Hopefully, an updated edition will appear in the future.

Trevor Laird

Editor

OP9002856

10.1021/op9002856

Published on Web 11/17/2009

media. Not surprisingly, the citations in this section, albeit relevant, are somewhat dated. This section establishes the language and foundation of many of the guiding principles and objectives of nonaqueous enzymology that are discussed throughout the remaining chapters, including enantioselectivity, kinetics and thermodynamics of biocatalysts in the absence of bulk water, the effect of organic solvents on substrate specificity, and activating enzymes under nonaqueous conditions. Although not intended to be a stand-alone textbook, if supplemented with an additional discussion on protein structure−function relationships or an overview of biocatalysis, the first part of this book could function as the text for a graduate-level half-semester course for students interested in special topics in synthetic organic chemistry.

The second part focuses on the more established and well-studied areas of nonaqueous enzymology, such as enantioselectivity in hydrolase chemistry, chemoenzymatic deracemization for the synthesis of enantiomerically pure chiral molecules, exploiting the specificity of enzyme active sites for chemo- and regioselectivity, and the use of biocatalysts in industrial scale applications. Despite this focus on the more mature areas in the field, the citations are surprisingly current in this section, with most chapters containing 30−40% of their references to literature since 2004.

Although the second section undoubtedly represents the heart of nonaqueous enzymology, it is the final part of the book that sets it apart from any other text on the subject. Within these last five chapters are detailed overviews of the emerging areas in biocatalysis, such as the use of biphasic systems or ionic liquids as the transformation media in enzymatic reactions, solid-phase biocatalysts acting on gas-phase substrates, and biocatalysis with undissolved solid substrates and products. These promising and unusual areas of nonaqueous enzymology are covered in significant detail in the present book and are not found in the previous Klibanov and Koskinen text. The only weakness that detracts from the efficacy of this section in conveying the importance of these rising areas is that the timeliness of the references is highly variable from chapter to chapter, particularly in the last two, in what should have been the most current section.

In summary, *Organic Synthesis with Enzymes in Non-Aqueous Media* provides an excellent overview of the fundamental principles and utility of biocatalysts in organic transformations and represents a comprehensive reference guide for both organic chemists and enzymologists interested in the field. Unfortunately, the moderately high list price of this hardback precludes its use as a graduate-level textbook and may limit its distribution to the shelves of institutional rather than personal or even departmental libraries, particularly when one considers several other titles with somewhat overlapping subject material available from Wiley-VCH.

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JA807826G

10.1021/ja807826g

Organocatalysis: Symposium Proceedings 07.2. Edited by Manfred T. Reetz, Benjamin List (Max-Planck-Institut für Kohlenforschung, Mülheim an der Ruhr, Germany), Stefan Jaroch, and Hilmar Weinmann (Bayer Schering Pharma AG, Berlin, Germany). Springer: Berlin, Heidelberg, New York. 2008. xiv + 340 pp. $119. ISBN 978-3-540-73494-9.

This book was developed from a symposium on the titled subject organized by the Ernst Schering Foundation which took place in Berlin in April 2007. The goals of the symposium and workshop was to give an overview of organocatalytic processes, mechanisms, and applications and to discuss future directions in the field. There are 11 chapters, a sampling of which includes "Biomimetic Organocatalytic C−C Bond Formations" by Enders et al., "Nucleophilic Carbenes as Organocatalysts" by Glorius and Hirano, and "Recoverable, Soluble Polymer-Supported Organic Catalysts" by Benaglia. There is no subject index.

JA8078797

10.1021/ja8078797

Dynamic Stereochemistry of Chiral Compounds: Principles and Applications. By Christian Wolf (Georgetown University, Washington, DC). Royal Society of Chemistry: Cambridge. 2008. xx + 512 pp. $99.00. ISBN 978-0-85404-246-3.

This book provides a feast of fascinating chemistry involving wide-ranging stereochemical studies. The author presents a unique perspective of phenomena involving the intersection of molecular chirality and stereodynamics. Topics include asymmetric synthesis, racemization/diastereomerization, kinetic resolution, molecular devices, topologically chiral assemblies, and other phenomena in which dynamic molecular phenomena are involved. With such an angle, the book transcends traditional divisions of organic chemistry and draws together themes common to diverse chemical phenomena. It is a useful entry into the literature, with over 3000 references. These include a number of papers from 2005 and a couple as recent as 2006.

Such a discussion of stereochemistry and asymmetric synthesis requires the use of accurate terminology and nomenclature. The book provides reasonably comprehensive overviews of the pertinent concepts and terms in a very succinct manner, targeting an audience that has some prior exposure with the material. Many fundamental principles of synthetic and physical organic chemistry are reviewed, including inversion of amino and other heteroatom moieties, hindered bond rotation, reactions giving racemization via achiral intermediates, mechanisms of epimerization of spiro-compounds, enantiomeric integrity of chiral Grignard, organolithium, and other organometallic reagents, conformational analysis, and atropisomerism. Discussion of these foundational topics generally focuses on the phenomena without going into extensive detail and is accompanied by thermodynamic or kinetic data in many cases, although detailed physical rationale is beyond the scope of the volume.

A limited discussion of analytical methods is presented, with a glimpse into chiroptical methods and a bit more detail on the use of NMR—especially dynamic NMR methods—and stopped-flow chromatographic and electrophoretic analysis, including a thorough discussion of dynamic chromatography.

After an introduction to the terms and principles of asymmetric synthesis with broad applicability, the discussion focuses on chemistry in which dynamic behavior plays a role, such as atroposelective synthesis of axially chiral molecules, chirality transfer, and interconversion of chiral elements such as in S_N2' reactions or sigmatropic rearrangements. Transfer of chirality

from one molecule to another is discussed, as is self-generation of stereogenicity and chiral relays. The very interesting topics of asymmetric resolution, dynamic kinetic resolution, and related chemistry are examined. Reactions are typically presented with a mechanistic rationale.

The text also covers stereodynamic phenomena including molecular gears, propellers, switches, sensors, and motors. Topological chirality and isomerism are discussed, with a smattering of studies involving chiral rotaxanes and catenanes. The major missing area is the rich chemistry of dynamic chiral polymers, gels, and liquid crystals, which had to be excluded due to space and time. However, the book contains more than enough organic chemistry to satisfy most readers.

This is a book that people will love to read. The topics are well chosen and interesting, and the writing is succinct and accurate. It could be used as a textbook for an advanced undergraduate or graduate special topics course and will serve as a valuable source of stimulating supplementary material for many courses.

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JA8074055

10.1021/ja8074055