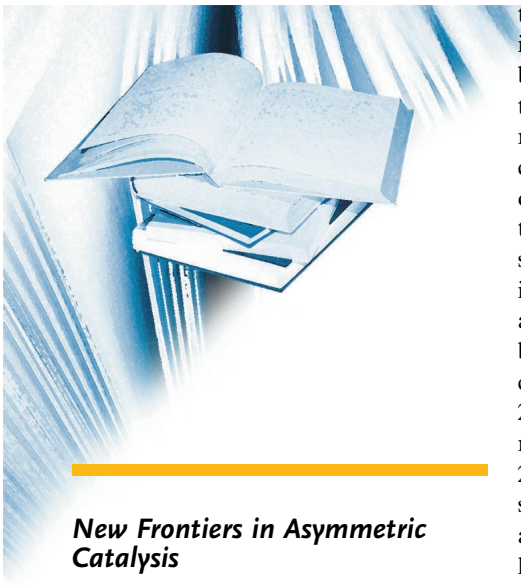

New Frontiers in Asymmetric Catalysis

Edited by *Koichi Mikami* and *Mark Lautens*. John Wiley & Sons, Hoboken 2007. 418 pp., hardcover € 96.90.—ISBN 978-0-471-68026-0

Catalytic reactions for asymmetric hydrogenation of dehydroamino acids and for asymmetric epoxidation of allylic alcohols developed in the 1970s and 1980s have had a tremendous impact in synthetic organic chemistry. Since then, the field of asymmetric synthesis has shifted gradually from the auxiliary-based diastereoselective synthesis of enantiopure compounds towards catalytic and enantioselective variants. Indeed, the development of catalytic asymmetric processes has been one of the major research activities of the past quarter-century, and nowadays remains in the mainstream of chemical technology. New concepts and even new fields are currently being pursued, as witnessed by the recent boom in organocatalysts. The book edited by K. Mikami and M. Lautens is thus a timely publication, despite the availability of a number of excellent treatises dealing with the same subject.

The title implies that the book is focused on the recent conceptual development of the field rather than on a comprehensive description of all important reaction types, which is in any case impossible to do in a monograph. The book comprises 13 independent chapters written by leading experts in the respective areas. While most of the chapters provide an in-depth overview of the subject, some authors highlight their own seminal contributions to a few specific reactions, and therefore the title is a bit too general with regard to the actual contents of some chapters. The book is up-to-date, as the literature coverage extends to the beginning of 2006. It contains in total more than 1500 references, most of them dating after 2000. The fact that some novel concepts, such as a chiral counterion strategy for asymmetric transition-metal catalysis, have emerged since the publication of the book is evidence of the rapid pace of developments in this ever-growing area. Publication of the present book, which is intended to be thought-provoking, is thus fully justified.

Chapters 1 to 3 deal with ligand design for catalytic asymmetric reduction, for oxidation, and for C–C bond formation, respectively. They emphasize the importance of rational catalyst design in the development of novel enantioselective processes, fully illustrating the spirit of the book. It is fair to say that most of the catalytic processes have been developed by trial and error. However, the authors advocate that, with an in-depth understanding of the catalytic mechanism, one can indeed discover new catalytic asymmetric transformations by design. In Chapter 1, T. Ohkuma, M. Kitamura, and R. Noyori discuss the enantioselective reduction of olefins (enamides and simple nonfunctionalized double bonds), ketones, and imines by catalysts in which phosphorus-containing ligands are associated with transition metals such as rhodium, ruthenium, and iridium. The often predictable stereoselectivity is clearly illustrated by a schematic presentation of the stereochemical models using binap as supporting ligand. Besides hydrogenation and transfer hydrogenation, hydroboration of ketones by chiral oxazoborolidine (CBS method) and reduction of imines using the Brintzinger-type C2-chiral titanocene catalysts are also briefly discussed.

Chapter 2, by T. Yamada, is concerned with the design of ligands for oxidation, and begins with a brief introduction to the Katsuki–Sharpless epoxidation of allylic alcohols and the Sharpless dihydroxylation of alkenes. This is followed by a detailed description of the (salen)-Mn^{III}-catalyzed enantioselective epoxidation of unfunctionalized olefins. The author then describes recent progress in enantioselective Baeyer–Villiger oxidation, and catalytic oxidative kinetic resolution of secondary alcohols using molecular oxygen as terminal oxidant. A separate section is devoted to the synthesis of optically active 1,1′-bi-2-naphthol (binol), an important ligand for asymmetric synthesis, by catalytic enantioselective oxidative coupling of 2-naphthols.

In Chapter 3, R. Shintani and T. Hayashi select asymmetric 1,4-additions and asymmetric cross-coupling reactions as examples to illustrate the recent development of ligand design for enantioselective C–C bond formation. They describe copper-catalyzed enantioselective conjugate additions of dialkylzinc or (less usually) Grignard reagents to cyclic as well as acyclic enones, nitroalkenes, lactones, and lactams. This is followed by rhodium-catalyzed 1,4-addition of organoboronic acids and organosiloxanes. The last part is devoted to Ni-catalyzed enantioselective Kumada cross-coupling and palladium-catalyzed Suzuki–Miyaura reactions, a field that is still very much in its infancy.

Chapter 4, by K. Nozaki, deals with asymmetric processes involving small molecules such as CO, CO_2, HCN, and RNC. The first part discusses the metal-catalyzed enantioselective hydroformylation, hydrocarboxylation, and hydrocyanation of olefins, including comments about mechanisms and about applications in natural product synthesis. There are descriptions of copolymerization of olefins with CO, and polymerization of isocyanides leading to chiral helical structures. The chapter continues with discussions of the asymmetric Strecker reaction, recent advances in the enantioselective addition of isocyanides to aldehydes (Passerini reaction), and the kinetic resolution of racemic propylene oxide by copolymerization with CO_2.

In Chapter 5, C.-J. Li outlines recent achievements in the activation of C–H

and C–C bonds for the enantioselective formation of C–C, C–O, and C–N bonds. The chapter begins with the copper-catalyzed enantioselective addition of terminal alkynes to polarized double bonds. This is followed by a brief description of transition-metal-catalyzed activation of aromatic C–H bonds and metal-carbenoid-induced C–H insertion. New reactivity patterns of 1,3-dicarbonyl compounds in ruthenium-catalyzed conjugate additions are presented. Asymmetric hydroxylation of alkanes for the formation of C–O and C–N bonds is also described. The last section is devoted to the enantioselective Lewis acid catalyzed Strecker reaction using acetyl cyanide as the cyanide donor. This emerging field will certainly attract more and more attention from synthetic chemists, and one can expect that the concept will eventually lead to the development of highly efficient asymmetric synthetic methodologies.

The following chapter is concerned with the metathesis reaction. In this longest contribution to the book, M. Mori distils the enormous subject of this powerful reaction into a systematic, concise, and clearly written description, focusing on catalyst development, mechanistic issues, and applications in organic synthesis. After a short introduction, the chapter is divided into three subsections, dealing with olefin metathesis, enyne metathesis, and alkyne metathesis. Under each reaction category are presented ring-closing metathesis, cross-metathesis, and (where available) the catalytic enantioselective version.

Chapter 7, by H. Kagan, is devoted to nonlinear effects (NLE) in asymmetric catalysis. The author, who discovered this phenomenon in the mid-1980s, briefly discusses the physical and chemical properties of nonracemic mixtures of enantiomers, as well as mathematical models that account for the origin of NLE. This is followed by a summary, in table form, of examples of organometallic catalysis and organocatalysis that display nonlinear effects. The importance of asymmetric amplification in catalysis development and in prebiotic chemistry is discussed in the last part of the chapter.

In Chapter 8, K. Mikami and K. Aikawa give a comprehensive review of asymmetric activation and deactivation of racemic catalysts. The principle of this concept is based on the activation or deactivation of one of the enantiomers of the racemic catalyst by a compound that is chiral, readily available, and cheap, thereby generating in situ an otherwise expensive chiral catalyst for the desired chemical reaction. A number of examples are given illustrating the validity of such a strategy. At the present stage of development, a stoichiometric amount of chiral activator (or deactivator) is nevertheless required in order to maximize the enantioselectivity of the given transformation. The authors conclude that the possibility of using a catalytic amount of chiral activator to resolve the racemic catalyst in situ will be a major challenge in this exciting area of research.

Chapter 9, by K. Soai and T. Kawasaki, discusses asymmetric autocatalysis with amplification of chirality, and the origin of chiral homogeneity of biomolecules. The probability of finding a perfect asymmetric autocatalytic reaction that provides a product without erosion of enantioselectivity as the reaction proceeds is extremely low, unless it displays positive NLE. Addition of diisopropylzinc to 2-alkynyl-pyrimidine-5-carbaldehyde is one such reaction that has been discovered in the authors' laboratory. They describe how, using this reaction as a tool, they have achieved asymmetric autocatalysis triggered by circularly polarized light (CPL), by chiral inorganic crystals, or by chiral organic crystals composed of achiral compounds. The chapter ends with a description of spontaneous absolute asymmetric synthesis.

In Chapter 10, T. Rovis gives a well-structured description of catalytic asymmetric desymmetrization reactions. The discussion is focused on methodological issues rather than applications in synthesis. Transition-metal-catalyzed allylation, ring opening of bridged-ring systems, cross-coupling reactions, Lewis acid catalyzed ring opening of epoxides, azirines, and cyclic anhydrides, olefin metathesis, acylation, deprotonation, oxidation, reduction, and C–H insertion are some of subjects that are treated in this chapter.

Chapter 11, by G. Lelais and D. W. C. MacMillan, is entitled "History and Perspective of Chiral Organic Catalysts". Since 2000, the field of organocatalysis has developed in such a way that it has quickly become the third fundamental branch of asymmetric catalysis, providing a valuable complement to enzymatic and organometallic catalysis for the synthesis of enantiomer-enriched compounds. After an informative historical survey of the development of organocatalysis, the authors discuss four major subfields encompassing iminium, enamine, Brønsted acid, and phase-transfer catalysis. The conceptual development and representative examples of enantioselective transformations in these four areas are presented. This chapter with 514 references ends with an insightful perspective.

Chapter 12, by K. Ishihara and H. Yamamoto, is concerned with chiral Brønsted/Lewis acid catalysts. The section dealing with Brønsted acid catalysis contains, inevitably, some information that overlaps with that discussed by Lelais and MacMillan. But they are analyzed from different angles and are thus complementary. Selected examples of enantioselective reactions catalyzed by Lewis acids, especially those derived from B^{III}, Al^{III}, and Ti^{IV}, are presented. The concept of Lewis acid assisted chiral Brønsted acid catalyzed transformations is discussed in the last section of the chapter.

The last chapter, by M. Shibasaki and M. Kanai, discusses enantioselective reactions using a chiral base catalytic method. The authors define chiral base catalysis as catalytic enantioselective reactions using chirally modified nucleophiles as asymmetric catalysts. Using recent examples, most of them published after 2000, they discuss five types of chiral base catalysis: a) Brønsted base, b) Brønsted base–Lewis acid bifunctional, c) Brønsted base–Brønsted acid bifunctional, d) Lewis base, and e) Lewis base–Lewis acid bifunctional. Purely organo-bifunctional catalysts are not included.

The book is not comprehensive in its coverage of reaction types. However, this is understandable, since its aims are to show where the frontiers of asymmetric catalysis actually are, to identify the limitations of the present method-

ologies, and to predict future research directions. One regret is that the schemes and figures are often not on the same page as the corresponding text. Also, the index is not as precise as one would like.

In conclusion, this book has definite value and is strongly recommended for inclusion in both academic and industrial research libraries. It will be very useful to every chemist working in the field of organic synthesis.

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