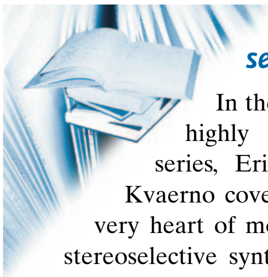

Classics in Stereoselective Synthesis

In the latest installment of the highly successful "Classics" series, Erick Carreira and Lisbet Kvaerno cover a topic that lies at the very heart of modern organic chemistry: stereoselective synthesis. Indeed, selectivity issues pervade organic chemistry, and despite a recent emphasis on chemoselectivity (i.e., "protecting-group-free synthesis"), stereoselectivity has remained one of the most vibrant and intellectually rewarding research areas.

The book starts out, somewhat unusually, with a chapter on stereocontrol in macrocycles, which could have benefited from demonstrating the predictive power of computational methods. The next three chapters are concerned with topics that include many of the true classics of stereoselective synthesis: additions to carbonyls, α-functionalizations, and finally aldol reactions. These sections contain clear discussions of the Felkin–Anh model, chelate-controlled reactions, remote stereocontrol, open vs. closed transitions states, and the Zimmerman–Traxler transition state in all its variations. Catalytic asymmetric synthesis is covered here for the first time, and a concise discussion of non-linear effects is provided. As a counterpart to aldol reactions, allylations of C=O bonds are discussed in a separate chapter.

The text then turns to chiral acetals, including glycosides and spiroketals. This useful intermezzo is followed by three chapters on hydrometalations (in particular hydroborations), reductions, and oxidations of olefins, which feature all the requisite classics but also cover the most recent literature. Important concepts, such as 1,3-allylic strain, and methods, such as catalytic asymmetric hydrogenations, epoxidations, and dihydroxylations are covered here. A nice subchapter then highlights the usefulness of iodolactonizations and related reactions induced by electrophiles in natural product total synthesis. Throughout the book, the methods discussed are interwoven with case studies in natural product synthesis, an area where stereoselective reactions have found some of their most elegant applications.

A short chapter on the asymmetric synthesis of amino acids then provides a segueway to stereoselective additions to C=N bonds. This is followed by a comprehensive chapter on additions to electrophilic C=C bonds, in other words stereoselective conjugate additions, where much of the recent progress in stereoselective synthesis has occurred. Another intermezzo on chiral carbanions is followed by a chapter on metal-catalyzed allylations, where many classic concepts in catalytic asymmetric synthesis have first emerged. The text then turns to cycloadditions, firstly in a chapter on stereoselective cyclopropanations. The mechanistically related C−H insertion is also covered at this point. Pericyclic reactions are covered in the final three chapters, which deal with sigmatropic rearrangements, ene reactions, electrocyclizations, Diels–Alder reactions, and [2+2] as well as [3+2] cycloadditions.

Although the "Classics" format would have allowed the authors to make a highly personal selection, the book is quite comprehensive and covers most of the important concepts and trends of the field. As such, it almost reads like a textbook on modern organic synthesis. The most regrettable omission are stereoselective olefinations, that is, methods for the stereoselective formation of C=C bonds. This includes stereoselective formation of enolates (cf. Ireland model), which would have been a nice prelude to the discussion of the Zimmerman–Traxler transition state. The stereoselective attack of nucleophiles to cyclic ketones, an important topic that has been well studied, is also neglected. Electrocyclic reactions, where the predictive power of the Woodward–Hoffmann rules has been most elegantly demonstrated also receive less attention than they deserve. Perhaps, in a future edition or an expanded textbook version of this book, an introductory chapter with a systematic discussion and classification of stereoselective reactions could be added. Although they are occasionally mentioned, basic concepts, such as simple, induced, and double diastereoselection, substrate-directed vs. reagent/catalyst-directed reactions etc. could be highlighted more clearly. However, addition of these topics might exceed the space limitation of the book, which already comprises more than 600 pages.

Overall, Carreira and Kvaerno have provided a magnificent book that will be useful to students, instructors, and practicing chemists in industry and academia alike. It lays out the canon of stereoselective synthesis while pointing out important new trends in the field. Whether some of the methods discussed will stand the test of time to grow into true classics of stereoselective synthesis remains to be seen. Many of them are taken from the most recent literature, which does convey a sense for the vibrancy and importance of the field. In any case, this timely book is an excellent source of teaching material, a useful handbook, and enjoyable bedtime reading for synthetic chemists.

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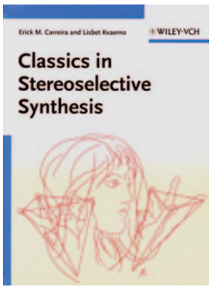

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