

Science of Synthesis, Stereoselective Synthesis 1: Stereoselective Reactions of Carbon–Carbon Double Bonds; edited by Johannes G. de Vries; Georg Thieme Verlag: Stuttgart, 2011, hardcover, 1072 pp., €2590, ISBN: 978-3-13-154111-6; softcover, 1072 pp., €249, ISBN: 978-3-13-165161-7

As part of the *Science of Synthesis* Reference Library, *Stereoselective Synthesis* is a state-of-the-art reference work, written by experts in the field. Rather than being comprehensive, the work focusses on the topics that have seen considerable progress and are most relevant for synthesis. Part 1 of Stereoselective Synthesis treats the literature on Stereoselective Reactions of Carbon–Carbon Double Bonds. The work critically evaluates the literature and, hallmark of the *Science of Synthesis* series, provides selected general experimental procedures and extensive tables.

The work commences with a chapter on dihydroxylation, aminohydroxylation and related reactions. These 1,2-difunctionalization reactions have seen a rapid development and are treated together with their less-known relatives diamination and dibromination. The closely related epoxidation reactions are discussed in chapter 1.2, with a nice combination of transition-metal catalysis, organocatalysis and enzymatic catalysis. Even for the experts in this field, an overview of this reaction, with its vast amount of literature and bewildering variety of methods and substrates, is more than welcome.

The epoxidation of enones is mechanistically different from the epoxidation of isolated alkenes; in the former the alkene is the electrophile, whereas in the latter it acts as the nucleophile. Therefore the epoxidation of electron-poor alkenes is discussed separately. Especially the progress in enantioselective nucleophilic epoxidation has been tremendous and this is very relevant for synthesis. A chapter on aziridination completes the part of 1,2-difunctionalization reactions and is focussed on stereoselective aziridination. Both stoichiometric and catalytic methods are discussed.

For years, literature on ‘stereoselective reactions of carbon–carbon double bonds’ was dominated by hydrogenation. It must have been an endeavour to compose a chapter on this topic, with enough literature available to fill a fist-thick book. Nevertheless, a very readable chapter has resulted, going criss-cross from catalyst systems, metals and substrates to lab scale and industrial applications. The length of several tables is impressive – and extremely useful for the non-specialist that considers using this methodology in synthesis. A separate chapter has been devoted to the hydrogenation of arenes and hetarenes, rightly so because this field is much younger and requires different catalysts. It is striking to see that, whereas in the preceding chapter on the hydrogenation of (isolated) double bonds, organocatalysis is absent, in this chapter it plays an important role and keeps pace with hydrogenation and transfer hydrogenation.

The chapter on stereoselective hydroboration and diboration reads very well and is perfectly documented. In particular diboration has evolved in recent years from a reaction-under-study to a valuable tool in synthesis and a decent competitor for asymmetric dihydroxylation.

Chapter 1.8 on carbometalation describes the bisalkylation of nonactivated alkenes and clearly shows how rapidly this field has been evolving in the last years. More and more, this kind of reaction comes within the realm of organic synthesis and once the right reaction conditions are found, it provides extremely useful tools in the construction of the carbon skeleton of more complex molecules. This line is basically continued in the chapter on hydroformylation, hydrocarbonylation, hydrocyanation and hydroacylation and in the subsequent chapter on hydrovinylation and hydroarylation of carbon–carbon double bonds. This plethora of reactions has traditionally been difficult to access by organic chemists not specialized in those fields because of the bewildering variety of catalysts, reaction conditions and safety precautions. Thanks to overviews like these, supplied with established procedures, barriers are levelled and the reader is invited to use these methods.

Chapter 1.11 on reductive coupling and cyclization of carbon–carbon multiple bonds in a way completes this part of the volume. Covering a broad variety of reactions, it is shown that these kinds of reactions are able to prepare functional groups and complex carbon skeletons from often simple and readily available starting materials. The subsequent chapter on conjugate addition reactions is, together with the chapter on epoxidation, the chapter in which enzymes play an important role. It is very insightful to see an overview with homogeneous and biocatalysis next to each other. In addition, the chapter contains a wealth of tables and procedures.

Chapter 1.14 discusses the recent development in cyclopropanation reactions. Once the realm of the Simmons–Smith reaction and halocarbenes, this field has seen stunning progress in (stereo)selectivity and catalysis. The presence of decent procedures is extremely important here as well, especially for the non-specialist. The chapter on enantioselective and diastereoselective alkene methathesis was logically completely absent in the previous edition of *Science of Synthesis*. This chapter is welcomed because in the bewildering variety of procedures and methods in the field of metathesis, it is difficult to obtain the overall picture. In the current chapter the achievements but also the challenges are clearly described.

The chapter on the addition of free radicals to carbon–carbon multiple bonds depicts the growing possibilities in this field and it is very insightful to compare this strategy with those described in the chapters on conjugate addition and carbometalation. There is considerable complementarity. The presence of well established procedures is again very important.

Finally, the chapter on asymmetric hydrosilylation of carbon–carbon double bonds gives an insightful overview on the progress in this field using palladium catalysis. Considering the fact that trichlorosilane is inexpensive and procedures are improved continuously, it is an important strategy in synthesis.

Overall, the volume *Stereoselective Reactions of Carbon–Carbon Double Bonds* is a milestone reflecting the progress in the field, a pleasure to read or just browse, either on paper or on screen.

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