Book Reviews

Stereoselective Synthesis. Houben-Weyl, Methods of Organic Chemistry, Volume E21c. Edited by G. Helmchen, R. W. Hoffmann, J. Mulzer, E. Schaumann. Thieme: Stuttgart, 1995, 1096 pp., hardback. DM 2550 (Subscription price DM 2295). ISBN 3-13-798004-6.

Volume E21c, the third volume in the series "Stereoselective Synthesis" continues the high standards set by the first two volumes. This volume treats, in detail, the synthesis of chiral compounds by the formation of carbon–carbon bonds, and covers free radical addition, carbenium ion addition and transition metal catalyzed additions to olefinic double bonds, as well as hydroboration, cycloadditions and ene reactions. As is typical for this series, the discussions are very brief, with most of the extensive data being presented in tables and figures, interspersed with specific, detailed experimental procedures, each section ending with an extensive list of literature citations. These, in most cases, are current through 1994, and in many cases, even important references from 1995 are included, making this volume extraordinarily up to date.

The volume begins with a treatment of stereocontrol in the addition of free radicals to alkenes (85 pp) both in an inter- and an intramolecular sense, and presents a "state-of-the-art" treatment of asymmetric induction via chiral radicals, chiral alkenes, and chiral auxiliaries, as well as control of relative stereochemistry in achiral systems. The following section (of about equal length) deals with addition of carbenium ions to olefins and allylic systems, inlcuding inter-, intra-, and transannular additions. Of particular interest here are the factors effecting stereocontrol in cationic polycyclizations.

Palladium-catalyzed allyic alkylation has been the subject of extensive studies and is given a thorough treatment in the following section of this volume. Since both the oxidative addition step and the alkylation step of the transformation are highly stereoselective (inversion) in this process, high overall stereoselectivity is expected and observed. The very wide range of allylic substrates amenable to this process is thoroughly treated in this section as is, to a lesser degree, the use of optically active ligands to induce asymmetry into palladium-catalyzed allylic alkylations. This section can serve as an excellent entry into the field for those unfamiliar with this chemistry.

After a very brief (14 p) section on the very limited number of examples of hydroboration processes in alkylation of olefins, a very large (250 pp) section on transition metal catalyzed formation of C–C bonds by addition to olefins is presented. The bulk of this material deals with the very active and important areas of asymmetric hydroformylation and hydrocarboxylation, and extensive tabulated data is presented. This is important since it is difficult to predict what ligand systems and conditions will be most effective in any given case. In addition to these two topics transition metal catalyzed hydrocyannation, hydroalkylation, oligomerization, carboacylation, dialkylation, cyclopropanation, and cycloaddition are covered thoroughly but concisely.

The remainder of this volume covers asymmetric induction into pericyclic reactions. This is a huge area under active investigation, and the coverage presented is thorough and for the most part up to date. As might be expected, the bulk of the discussion deals with [4+2] cycloaddition chemistry, and the myriad of ways to control stereochemistry in this synthetic process of paramount importance. Intermolecular, intramolecular, and hetero [4+2] cycloadditions are presented in depth, again with extensive tabulated data.

Stereocontrol in 1,3-dipolar cycloadditions is covered in a relatively brief (35 pp) exhaustively referenced (432) section that is invaluable to anybody engaged in this area of reasearch. Diradical cyloaddition (11 pp) and organometallic [3+2] cycloadditions (mainly trimethylene methane type reactions) are also presented. Since most of the latter cases involve the combination of two achiral precursors to form two stereogenic centers, the processes are nonasymmetric, and *diastereo*selectivity as opposed to *enantio*selectivity is the issue here.

Both thermal [2+2] cycloaddition (e.g. ketene–imine, ketene-alkene) and photochemical [2+2] cycloadditions are presented, the latter in great detail, with many tables and references. The influence of the various partners on the stereoselectivity of the process is systematically considered.

The final section on cylcoaddition chemistry treats asymmetric cyclopropanation reactions in all their variations including Simmons–Smith reactions, dihalocarbene reactions, metal-catalyzed diazo decomposition reactions, and thermal reactions of Fischer-type carbene complexes. This section is organized according to the carbene substituents rather than reaction type, so it is sometimes a little hard to follow. However, it is clearly written, and

This document was downloaded for personal use only. Unauthorized distribution is strictly prohibited.

thoroughly documented, and the very many ways for controlling stereochemistry for each carbene type are discussed.

The volume ends with a discussion of stereocontrol in the formation of C–C bonds via the ene reaction, beginning with simple diastereoselection, through asymmetric induction by chirality resident elsewhere in the substrate, by chiral auxiliaries, and finally by external species.

In summary, this is a valuable addition to the reference literature on stereoselective synthesis, and is certainly the best starting point for information on the span of reactions treated in this volume. It, along with the rest of the series, is likely to become and remain the definitive resource on stereoselective synthesis.

L. S. Hegedus,. Colorado State University, USA.

Stereodirected Synthesis with Organoboranes. By D. S. Matteson. Springer: Heidelberg, 1995, 405 pp., hardback. DM 198. ISBN 3-540-59182-6.

This is a splendid book. It provides a nearly comprehensive coverage organic synthesis via compounds/reagents with C–B bonds organized in a logical way, and discussed at an appropriate level of detail.

The introductory chapter forms an sound basis for the rest of the book, without being superficial. Useful thermodynamic and physical parameters are tabulated, and there are guidelines on safety and laboratory procedures.

Routes to organoboron compounds are covered in the second chapter. Inevitably, there must be some overlap with this and some of the material that appears later, but the author has pitched the focus well and provided adequate cross referencing where necessary. Most of the very latest material on catalyzed additions of diboron compounds to unsaturated compounds, and on zirconium-mediated hydroboration, could not be included since it is too new. Otherwise, the important syntheses of organoboron compounds are discussed.

Chapter 3 shows the authors impressive depth of knowledge in this area. It is difficult to write on the "general reactions of organoboranes" since there are so many, but here it is done very thoroughly. Frankly, I encountered several transformations that I had not seen before (most of them originally reported in the Russian literature) and there appeared to be no notable omissions.

The remainder of the book concentrates on the areas in which organoboron chemistry has had the most impact on organic syntheses. Specifically (with some major original contributors in parentheses): alkenylboranes for alkene synthesis (Zwiefel, Brown, Soderquist); a-haloboronic esters (Matteson, Hoffmann); asymmetric hydroborations (Brown, Masamune); allylboron and boron enolates (Brown, Hoffmann, Roush, Corey, Evans); Diels–Alder reactions with organoboron dienes or dienophiles (Singleton, Valtier) or organoboron Lewis acids (Yamamoto); and, asymmetric reductions (Midland, Brown, Itsuno, Corey). Overall the reader is left with an impression of depth and *balance*. Matteson has not yielded to the temptation that everyone writing on their own area must experience: to emphasize ones own research and economize on the attention given to that of others.

Throughout this book, the diagrams and the text are clear and well presented. There is a subject and an author index at the end, while references are listed the end of each chapter.

There are errors in this book, but I did not spot many. Those that I did find were minor mistakes in diagrams, incorrect stereoselectivities, or misquoted references. Most of these would only be noticed by researchers intimately involved in the field. Weaknesses in the book are few, but perhaps include the following. First, notes on nomenclature probably would be better placed in a preface, than in the fifth chapter. In that same section there is a curious analogy between wedged bonds and "railway tracks on LSD"; I could imagine some readers for whom English is a second language wondering what railway tracks, LSD, and wedge bonds have in common. Some of the representations of pinene are not clear. For some of the more obscure references it is helpful to have the reference and the *Chemical Abstract* citation, but this is only done in a few cases. Similarly, it would be helpful to have reference titles, not just the authors, journal, volume, and year. Finally, Patterson's work on chiral *B*-enolates could have been included in preference to some of the less important enolate material that was discussed. Overall, however, these minor negatives should not detract from the overwhelming positive feature: this is the type of book that could only be written by a scholar who has devoted many years to organoboron chemistry. Matteson has done it, and done it well.

K. Burgess, Texas A & M University, USA.

Book reviews are generally by invitation. Publishers should send books to Dr Ray J. Boucher, Book Review Editor, Synthesis Editorial Office, Georg Thieme Verlag, Rüdigerstrasse 14, D-70469 Stuttgart, Germany.

This document was downloaded for personal use only. Unauthorized distribution is strictly prohibited.