

Book reviews

Transition metal reagents and catalysts: innovations in organic synthesis

Jiro Tsuji

John Wiley & Sons, Ltd, Chichester, 2000

xv + 477 pages. £125

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It is abundantly clear that the modern-day synthetic organic chemist relies, to an ever-increasing extent, on the host of transition-metal-based reactions that can now be selected from his armoury. At the highest level, transition metals that can function as catalysts to achieve crucial carbon–carbon bond-forming reactions and to transform prochiral substrates into enantiomerically pure building blocks have revolutionized the art of organic synthesis, both in important industrial processes and in academia.

As always, however, the most successful practitioners are those who understand the mechanistic subtleties of the reactions that they elect to use, especially in more complex multifunctional environments. In this book, Professor Tsuji not only provides an excellent overview of the current state of the art, but additionally takes time in the opening chapters to illustrate key industrial processes and lay the foundations of mechanism upon which these reactions are based, thus providing a clearer mental picture for those synthetic organic chemists who are less familiar with the processes of counting electrons and considering more ‘unusual’ geometries around a metal centre. Although this chapter is relatively short, it is a vital component of the book.

The following five chapters are organized by substrate, with necessarily artificial divisions being made between the reactions of organic halides and pseudohalides, allylic compounds, conjugated dienes, propargylic compounds, and alkenes and alkynes. The remaining chapters form a miscellany of themes and include areas such as the reactions of transition metal carbene complexes, encompassing both catalytic metathesis and cyclopropanation reactions, as well as a further chapter on reactions involving Fischer carbenoids and the use of stoichiometric metal carbonyls of iron, cobalt and chromium for protection and activation. The important areas of catalytic hydrogenation, transfer hydrogenation and hydrosilylation are also grouped together, as are reactions promoted and catalysed by palladium(II) compounds. In terms of overall organization, chapters can therefore be found that are classified by substrate class, by reaction type, and by the metal itself and, at first sight, this appears to imply that a unifying overall theme is difficult to maintain. Synthetic organic chemists who tend to relate to named reactions, such as Heck, Stille, Suzuki and Pauson–Khand, will find them in the index

more easily than in the chapter sub-headings. Since carbon–carbon bond formation is pre-eminent, this is essentially an organometallic book, and reactions such as asymmetric epoxidation and vicinal dihydroxylation are not covered.

Even though it is almost impossible to organize and provide a comprehensive coverage of this vast area in a single volume, the author has, nevertheless, provided an excellent compilation of those reactions that are currently of wide-ranging synthetic utility to the organic chemist. The emphasis is, of course, correctly placed on carbon–carbon bond formation and catalytic reactions, but all of the important stoichiometric reagents are also there, thus providing inspiration for young researchers to take up the challenge of further development. The book is richly adorned throughout with very recent examples that amply demonstrate the power of transition metals in complex multifunctional organic synthesis, and make browsing a veritable pleasure.

Those of us who were inspired by the author’s seminal book in 1975 can recognize that, once again, his expert knowledge gleaned over many years and his careful selection of topics have combined to create a worthy successor that should be a valuable addition to the library of any modern-day synthetic organic chemist.

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Solid-phase synthesis and combinatorial technologies

Pierfausto Seneci

John Wiley, New York, 2000

xii + 637 pages. £70.95

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The impact of parallel and combinatorial approaches to small-molecule synthesis since the late 1980s has been enormous. Initially, these approaches were largely limited to developments in the pharmaceutical industry,

but other industrial and academic laboratories have followed suit, utilizing existing methods for their own research and developing others. More recently, and perhaps most excitingly, the principles are being applied to wider fields still, from the discovery of new catalysts to polymer and materials science. The challenge of reviewing activity in this now vast field has been taken up by the author, Pierfausto Seneci.

This book begins with a brief discussion of the basics of solid-phase chemistry, introducing some of the key concepts (such as different solid supports and linkers) and differences from traditional solution-phase chemistry. The author then turns his attention to combinatorial chemistry, discussing its historical origins in peptide and oligonucleotide chemistry through to the advent of small-molecule organic synthesis. The process of generating a library based upon a desired target structure is discussed using literature examples that take in solution-phase and solid-phase validation sequences. The importance of quality library design and choosing the correct type of library for the job in hand is emphasized in a separate chapter.

The three subsequent chapters form the core of the book and review in more detail the synthesis of libraries as solid-phase discretely, solid-phase pools, and in the solution phase. The various issues, such as quality control, purification, structure determination and deconvolution, are illustrated in each case through appropriate examples from the literature. Appropriate discussions of the available analytical tools are presented and, helpfully, web addresses of some of the more specialist instrument suppliers are included. Each chapter closes with a section highlighting new trends in the respective areas, such as the exploitation of large-member libraries prepared on a solid phase for the discovery of new biological targets. The disadvantage of including such sections is that in a rapidly moving field they will quickly become outdated, but they do serve to illustrate the scope and boundaries of current techniques.

Though the examples until this point concentrate largely on the chemical synthesis of pharmaceutical-like small organic molecules, the final three chapters of the

book demonstrate the increasingly important application of these techniques to other areas. These vary from more 'organic-based' experiments designed to aid in reaction optimization, catalyst identification and molecular recognition, through to the design and screening of libraries for materials sciences, including polymers and solid-state photoluminescent materials. Again, the need for appropriate analytical tools and high-throughput screens is highlighted. Fittingly, given the bioorganic origins of combinatorial methods, the circle is completed by a review of prospects in the areas of combinatorial biosynthesis and biocatalysis.

Stylistically, the subject matter is presented in a clear and detailed manner, with the liberal use of diagrammatic schemes and real-life examples for clarification and amplification of new ideas and concepts. The challenge in writing a work such as this is to keep the attention of the expert while explaining the basics to the novice. Helpfully, the layout is such that the more experienced readers will be able to skip some or all of the introductory material without losing the overall thread of the book. There are a few minor errors in the schemes and text, and a small but frequently occurring irritation is that the text and diagrams often fall out of step with each other, leaving one to leaf back and forth over several pages to find the correct examples.

At 637 pages, and with more than 1700 references (up to and including early 2000), this is almost certainly the most complete text in the area to date. Although other works may serve better as a primer text in the subject for students, this book will be an invaluable tool for those entering the area, from whatever discipline, seeking to select the most appropriate methods and minimize start-up time in their projects. The remarkably comprehensive and wide-reaching content, on which the author is to be congratulated, will also make this a valuable reference text for the more experienced practitioners to draw upon.

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