Book Reviews

Stereoselective Synthesis, Volume E21d. Edited by Gunter Helmchen (Heidelberg), Reinhard W. Hoffman (Marburg), Johann Mulzer (Berlin), and Ernst Schaumann (Clausthal). Georg Thieme Verlag: Stuttgart, Germany. 1995. xxi + 1195 pp. DM2360. ISBN 3-13-100114-3.

Carbon−carbon bond formation by sigmatropic rearrangements and electrocyclic reactions begins the fourth volume in the Houben-Weyl set for *Stereoselective Synthesis*. However, the formation of carbon−hydrogen bonds by stereoselective protonation, radical reactions, reduction of carbonyl and imino groups, hydrogenation, and [1,*n*] sigmatropic hydrogen shifts provides the largest contribution of chemical transformations. The final section of this volume is devoted to the formation of carbon−halogen bonds. In all, 26 internationally renowned authors contributed to this volume.

The 530-page treatment of sigmatropic reactions includes the Claisen and Cope rearrangements, including hetero- and polyhetero-Claisen reactions, tandem sigmatropic rearrangements, [2,3] sigmatropic rearrangements and [1,2] alkyl shifts. Asymmetric catalysis and chirality transfer are thoroughly discussed as are the factors that influence the rate and selectivity of these reactions. Reaction variants, including those of Ireland, Reformatsky, Meerwein and Eschenmoser, Carroll, and Johnson are separately identified and described in a useful historical perspective. Claisen and Cope rearrangements with allenes and acetylenes are reviewed. [2,3]-Sigmatropic rearrangements involving carbanions derived from allylic ethers, the [2,3] Wittig rearrangement, amines, and sulfides are thoroughly described; ylide-derived [2,3] sigmatropic rearrangements receive considerably less attention. The treatment of [1,2] alkyl shifts and of electrocyclic reactions provides useful examples of stereocontrolled reactions, but these sections are accorded less than 20 pages each. References into 1993 are used, but except for the section on electrocyclic reactions, the vast majority of the investigations reported are pre-1985.

The section on formation of C−H bonds by protonation of carbanions and polar double bonds is the most comprehensive treatment of this topic currently available. Although enolate protonation is the major focus, significant attention is given to stabilized carbanions, enamines, enols, and ketenes. Enantioselective and diastereoselective protonation are thoroughly reported from literature extending into 1994.

The remainder of the section on the formation of C−H bonds consists of individual expertly written subsections on specific methodologies beginning with radical reactions, organized in part according to acyclic and cyclic radicals. The reduction of carbonyl groups by catalytic hydrogenation is a thorough and practical survey of optimum methodologies and catalysts for enantioselective reduction. Dissolving metal reductions portray diastereoselection with an accumulation of examples appropriate for evaluation of their synthetic utility, and hydride reductions give a thoroughly modern treatment of stereocontrol with aluminum hydrides and borohydrides. Enantioselective reductions of ketones with chiral boron hydrides and modified aluminum hydrides are the capstone for synthetic applications of hydride reagents. Hydrosilylation is treated in sections on acid- or fluoride-catalyzed reactions and on transition metal catalyzed reactions. Other reagents, including organoboranes, metal alkoxides, and enzymatic reductions, are presented, and their applications are described. Extensive tables and diverse examples characterize the section on enzyme-catalyzed and biomimetic reductions of carbonyl groups. The reduction of imino groups is treated separately.

The reduction of olefinic double bonds provides a 180-page survey of catalytic hydrogenation, dissolving metal reductions, diimide reductions, ionic hydrogenation, and enzyme-catalyzed hydrogenation, as well as hydroboration and hydroalumination. Enantioselective hydrogenations and isomerizations include a thorough description of optimum chiral phosphine ligands and numerous examples of the preparation of ruthenium phosphane complexes. The section on enzyme-catalyzed hydrogenations contains numerous experimental procedures and comparative results with different enzymes.

The final sections of this volume are devoted to [1,*n*] sigmatropic hydrogen shifts and the formation of carbon−halogen bonds. They, like others, contain experimental procedures and sufficient examples to serve as a useful laboratory guide. However, the greatest strength of this volume is a comprehensive reference for modern organic chemistry in which stereocontrolled reactions form the basis of practical methodologies.

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Stereoselective Synthesis, Volume E21e. Edited by Gunter Helmchen (Heidelberg), Reinhard W. Hoffman (Marburg), Johann Mulzer (Berlin), and Ernst Schaumann (Clausthal). Georg Thieme Verlag: Stuttgart, Germany. 1995. xxi + 1261 pp. DM2682. ISBN 3-13-100124-0.

The fifth volume in the Houben-Weyl set for *Stereoselective Syntheses* covers the formation of carbon−oxygen, carbon−sulfur (selenium and tellurium), carbon−nitrogen, carbon−phosphorus, carbon−silicon, and carbon−tin bonds with 28 authors contributing their expertise and authority. By far, the sections on the carbon−oxygen bond (520 pages) and the carbon−nitrogen bond (568 pages) enlist the greatest number of authors and the largest outlay of pages. Although one can find individual reactions that are not included in this volume, the composite provides a comprehensive array of transformations and processes appropriate to the superb reference that this set has become.

Treatment of carbon−oxygen bond formation is devoted primarily to oxidations. Major subsections cover dihydroxylation and epoxidation with thorough treatment of methodology, synthetic applications, and mechanisms of reaction. Extensive tabular listings provide a valuable resource for the evaluation of results. References extend into 1994. Additional sections include hydroboration−oxidation, hydrosilylation−oxidation, microbial oxidations, and allylic oxidations with singlet oxygen and selenium dioxide. Sigmatropic rearrangements and intramolecular addition of alcohols and acids to olefinic double bonds comprise some of the nonoxidative methodologies that are surveyed.

The treatment given to carbon−nitrogen bond formation is even more diverse than that given to carbon−oxygen bond formation. Included in this section are electrophilic amination that includes azidation with organic azides and amination with reagents that include azodicarboxylates and benzenediazonium salts. Addition of electrophilic nitrogen reagents to olefinic double bonds and of nucleophilic nitrogen reagents to conjugated substrates are given comprehensive coverage. Palladium-catalyzed allylic substitution, sigmatropic rearrangements, and ene reactions that establish a C−N bond are also included.

Other sections in this volume are appropriately representative of the heteroatom being described. For sulfur, sulfenyl−, sulfinyl−, and sulfonyl−carbon bonds are separately covered. With phosphorus, treatment is of P(III) primarily. Hydrosilylation is covered only marginally, but earlier treatment in Volume E21d complements this section and, overall, gives a complete survey of the field.

As in prior volumes, a copious number of experimental procedures gives this series the practical flavor of an experimental reference set. The comprehensive critical treatment given to the subject matter, however, provides its unique advantage. This is the primary resource for anyone wishing to learn about stereoselective syntheses.

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Photochemistry and Photophysics of Metal Complexes. By D. M. Roundhill (Tulane University). Plenum Press: New York and London. 1994. xii + 356 pp. ISBN 0-306-44694-4.

In his introduction, Prof. Roundhill states that this book is intended to serve as “both a reference source and as a teaching text” with an emphasis on the photochemical aspects of the field of transition metal photochemistry. To its great credit, the book seeks to provide a balanced treatment of the major topics in contemporary photochemical studies and is, in large measure, successful. The literature is well covered up to 1992 with a handful of references from 1993. The major literature reviews are cited separately in the chapters allowing the reader to easily locate additional resources. While one might quibble that the occasional relevant reference has been omitted, the coverage is sufficiently complete that the reader may easily use the cited references as a bridge to the broader literature.

After an introductory chapter reviewing the major points of the photochemistry of metal complexes, the book proceeds with discussions of the photochemistry of monomeric complexes of the first row, monomeric complexes of the second row, dimeric and multimetallic complexes of the second and third rows, photochemistry of $Ru(bpy)_3^{2+}$ and related complexes, metal carbonyl and isocyanide complexes, metal alkene, arene, alkyl, hydride and carbene complexes, and finally lanthanide and actinide complexes. Discussions of the more mature fields such as the first-row complexes and the photochemistry of $Ru(bpy)_3^{2+}$ and related complexes do an excellent job of relating the observed photochemistry of the photophysics of the various compounds. A discussion of the photochemistry of dipalladium and diplatinum complexes is hampered by the murky quality of the bonding diagram accompanying the text and by an error in the electronic distributions in this figure.

Much of the discussion is in the style of a lengthy review with bulleted summaries of the literature. This approach does not lend itself to reflection or analysis of the broad aspects of the photophysics and photochemistry of these compounds; thus, the reader is frequently left with great quantities of information with little sense of how it fits together. As the emphasis is on the chemistry, there was no attempt to describe how the experiments are carried out, nor to describe techniques such as stopped flow, matrix photochemistry or the modern time-resolved techniques.

Perhaps the most serious drawback in using the book as a text is the number of typographical errors in the text, figures, and particularly the equations. While many of these errors involve failure to follow the usual conventions for nested parentheses, i.e. {[( )]}, there are enough errors of fact to confuse a student who might attempt to use this book as a text. The applicability of this book for use as a text is further hampered by the lack of structural diagrams for compounds, particularly those for which the molecular structures are not obvious.

In general, the book presents a good summary of the literature and will be invaluable to those actively engaged in this field and to those who seek an entre to the critical literature. It is unlikely that this edition will see significant application as a textbook.

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Biomolecular NMR Spectroscopy. By Jeremy N. S. Evans (Washington State University). Oxford University Press: Oxford and New York. 1995. xvi + 444 pp. $85.00 ISBM 0-19-85467-6.

With the advent of powerful new pulse techniques available on commercial instruments and the (almost) routine acquisition of protein structures it might be imagined that NMR spectroscopy has reached a plateau similar to that of IR spectroscopy 30 years ago. I regard this refreshing book by Jeremy Evans as a harbinger of the future of NMR which, far from remaining static, is reaching out in may directions and dimensions at the chemistry−biology interface. Evans is really addressing the working scientist who is looking for spectroscopic solutions to problems not only in structural biology but also in the dynamics of protein folding, drug receptor interaction, and stereochemistry of enzymatic reactions and, most pertinently, in the application of *both* solid and solution spectroscopy to the study of enzyme mechanism in real time.

No other text of which I am aware attempts to cover these exciting developments while including the strong mathematical component necessary for understanding the physical basis of each NMR experiment. There has been no compromise in the theoretical treatment which occupies first third of the book, and this approach, although heavy going at times, is entirely appropriate where the text is to be used in an advanced graduate course and also for those who are seriously interested in designing NMR experiments to solve both structural and mechanistic problems. I found the examples, although selective, very rewarding reading and the perspective just right—at least for a bioorganic chemist. The section on membranes is particularly stimulating and gave this reviewer some useful ideas for future experiments. The wide range of topics (proteins, DNA, RNA, enzyme mechanism), while spread thin at times, provides an excellent overview of the field.

No book is perfect, and one might carp at the superficial treatment of heteronuclear coupling constraints in conformational analysis, the omission of discussions on pulsed field gradients for solvent suppression and spin selection, and the lack of detail regarding sample size, acquisition times, and the actual cost of performing sophisticated multidimensional experiments (which includes the necessary molecular biology to obtain $^{13}C/^{15}N$ enriched specimens).

These are minor criticisms which can be corrected in a second edition which I am already anticipating. I found Evans' book not only timely and useful but above all successful in hitting just the right level by explaining not only what is possible today but where the future of the field lies. I can recommend the book wholeheartedly to novice and seasoned practitioner alike—and the price is right!

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Stereoselective Synthesis. By Robert S. Atkinson (University of Leicester, U.K.). Wiley: New York. 1995. xii + 529 pp. $59.95. ISBN 0-471-95419-5.

This 16-chapter book is devoted to a rapidly evolving field, presenting an overview of the best methods used in modern stereoselective synthesis. The reader will find several ways in which factors such as ring effects, strain effects, steric and stereoelectronic effects, and orbital symmetry may mediate the synthesis pathway. The realistic 3-D representations of transition states for stereochemical reactions are very helpful. Critical assessment allows the reader to select methods most appropriate for their needs. In addition, the aim of this book is to describe a new unique simplified classification of stereoselective reactions as type 0, I, II, or III based on the number of chiral centres created. This choice results in four very knowledgeable and clear treatments of the material, providing a consistent notation, extensive cross-referencing between chapters, and complete literature citation up to 1992.

The most basic concepts of selectivity in organic synthesis and the classification of stereochemical reactions are introduced in Chapters 1 and 2. Chapter 3 describes type 0 reactions, in which no new chiral center is created. As the application of this type of reaction is limited to the use of starting materials and blocks, a large selection of commercially available enantiopure compounds and building blocks are described.

Chapters 4 and 5 contain an elegant discussion of type I reactions. These are reactions proceeding with inversion or retention of configuration at a single chiral center as well as simple chirality transfer reactions.

Chapters 6, 7, and 8 cover type II reactions and focus on simple diastereoselectivity in 1,2-additions to alkenes, Diels−Alder, and 1,3-dipolar cycloadditions. The ene reaction as well as occasional diastereoselectivity and simple diastereoselectivity in the aldol and related reactions are also described with a detailed analysis of factors which bring about asymmetric induction.

The major part of this book is dedicated to type III reactions. Type III reactions involving asymmetric induction are presented in Chapter 9 focusing on preferred conformation and conformational freedom. Chapters 10 and 11 deal with the familiar substrate-controlled $\mathrm{III}_{\mathrm{s.c.}}$ diastereoselective reactions mediated by factors such as torsional strain, $\sigma-\pi$ interactions, and ring formation. In Chapter 12, there follows a discussion of reagent-controlled reactions (type $\mathrm{III}_{\mathrm{r.c.}}$) with an emphasis on the difference between type $\mathrm{III}_{\mathrm{s.c.}}$ and type $\mathrm{III}_{\mathrm{r.c.}}$ reactions. The author presents, in a more traditional survey, numerous figures and schemes explaining transition-state preferred reacting conformations for type $\mathrm{III}_{\mathrm{rc}}$ reactions.

Chapter 13 describes type II/III reactions and reactions involving chirality transfer. Illustrations of the stereochemistry of type II/III reactions and Diels−Alder reaction containing a chiral substituent on the dienophile, as well as [3,3]sigmatropic (Cope) rearrangement and aldol reactions, are given using 38 schemes.

Chapter 14 presents 59 schemes, and 3-D representations of transition states, in which stereoselectivity is created in catalytic enantioselective reactions, the advantages of which are also discussed. Finally, Chapter 16 completes type III reactions by discussing the use of enzymes particularly for reactions where chemical methods lack efficiency.

The book ends with a subject index which with the stereochemical vocabulary, in accordance with IUPAC rules, provides a good overview of stereoselective synthesis. It is a pleasure to recommend this book to students and to anyone actively engaged in the syntheses of target molecules as single stereoisomers.

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Analytical Techniques for Foods and Agricultural Products. Edited by G. Linden (University of Nancy). VCH: New York. 1996. xxi + 578 pp. $145.00. ISBN 1-56081-687-2.

The text contains four major sections. The first and largest section is a concise discussion of numerous instrumental methods for the analysis of food and agricultural products. The second section covers biochemical techniques, the third covers sensory analysis, and the fourth discusses nutritional and toxicological analysis.

Nearly all of the subject areas or methods in the first part include a brief discussion of the theory behind each analysis. Most of the discussion in the instrumental section (unlike the other four parts) is not specific enough to allow one to do an analysis based just on the information provided in the text. One will have to refer to the original reference for sufficient information to do an analysis. This is not a criticism, just an observation. A choice had to be made by the authors between experimental detail and brevity, and the decision made appears appropriate.

With the rapid development in analytical instrumentation, computers, and instrumental methods, this text is likely to be out of date (as are nearly all texts on instrumental analysis) within 8−10 years. However, the text is an excellent summary of many of the techniques in wide use today. The text would be a good addition to the reference library of any food or agricultural scientist. The text could also be used as a text for an advanced food analysis course for graduate students. It would also be an excellent starting point for those interested in extending their analytical expertise. Each chapter provides an introduction to the technique, the theory behind the technique, and several practical examples of the technique.

There are some minor flaws. It is a second edition, and the references are somewhat dated. A few chapters have more pre-1980 references than current references (e.g., chromatography). On the positive side, it gives one a good historical perspective of many of these analytical techniques. In addition, the chapter on chromatography overlooked an important and recent detector advance, the evaporative light scattering, which is really the first sensitive and generic detector available for HPLC. There are additional analytical techniques that show great promise but have not yet received widespread use in the food and agricultural analysis. For example, the subchapter on electron microscopy has overlooked an important recent addition to that area, the atomic force microscope, which enables direct observation of the topological properties of nonconductive material at the molecular level. However, it is probably unrealistic to expect that all of the relatively new techniques could be discussed in a single text.

The section on biochemical techniques provides limited information on enzymatic analysis and immunochemical analysis and a few applications for the microbial analysis of antimicrobials and vitamins. The discipline of immunochemistry has progressed rapidly in the past 10 years. This section provides a good introduction to the subject and to the numerous types of immunochemical analyses in use in the food industry.

A 90-page section on sensory analysis provides a wealth of information for the sensory analyst in terms of selecting and training a taste panel, selecting the appropriate sensory test (with numerous case studies as examples to assist in the selection process), overall experimental design, and analysis of the taste panel data. Several different techniques and procedural formats are presented and discussed to help the sensory analyst ensure that the data collected will accurately portray the sample characteristics. Sensory analysis provides critical data and information on a product or sample that is complementary to instrumental analysis. From a commercial perspective, accurate sensory data can generally provide a better indication of consumer acceptance and eventual success relative to instrumental analysis. The combination of sensory analysis and instrumental analysis provides an interesting combination that makes the text particularly useful for flavor chemists.

In light of the recent change in nutritional labeling required in the U.S., the last section on nutritional and toxicological analysis is very timely. The nutritional analysis techniques' chapter provides information on the use of animals for nutritional analysis, effectively extending the range of techniques beyond instrumental analysis and *in vitro* biochemical analysis. The chapter on food toxin analysis provides additional applications for the techniques discussed in earlier chapters (enzymatic analyses, chromatographic analyses, etc.). The chapter on mutagen analysis provides detailed information on several tests used for the detection of mutagens, including the principle of the assay and important details on procedure specifics and data analysis. The text is well worth the money as a reference text for food and agricultural scientists, although it is relatively expensive for use as a textbook.

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Modern Acetylene Chemistry. Edited by Peter J. Stang (University of Utah) and Francois Diederich (ETH-Zentrum Lab, Zurich). VCH: New York. 1995. xxi + 506 pp. $105.00. ISBN 3-527-29084-2.

Acetylene chemistry directed at novel materials and biologically active molecules has undergone noteworthy advances in recent years. This book has assembled leading investigators to review important developments in acetylene chemistry. As discussed in the forward, this book is distinctly different than previous acetylene monographs and provides an update to, rather than a replacement for, previus treatises (e.g., books by Patai, Houben-Weyl-Müller, and Brandsma).

The format is a compilation of contributed reviews which focus on specific interests and/or the research of each author. As a result of this format the book doesn't cover all recent developments in acetylene chemistry. The editors have taken the liberty to include contributions which are not explicitly focused on acetylenes. Chapter 6 describes the chemistry of the phosphorous−carbon triple bond, and Chapter 10 reviews synthetic routes to polyacetylene, the majority of which do not involve the polymerization of acetylenes. Nevertheless, a very credible group of authors have been assembled which address most of the important developments in acetylene chemistry through 1994. Chapter 1 describes theoretical aspects of acetylene chemistry with an emphasis on reaction transition states and on cyclic C_n compounds. A useful summary of the reaction chemistry of 1-cyanoacetylenes and 1-haloacetylenes is described in Chapter 2. Chapter 3 is more specialized and focuses on the chemistry and properties of iodonium salts of acetylenes. The unsaturation of the acetylene group has recognized utility in organometallic chemistry which is addressed in Chapters 4 and 5. Chapter 4 provides a general overview of organometallic acetylene chemistry, while Chapter 5 describes acetylene reactions with Fischer carbenes and acetylene $Co_2(CO)_6$ chemistry. Biochemical aspects of acetylenes are covered in Chapter 7 with a review of cyclic enediyne antibiotics. This is followed by contributions (Chapter 8 and 9) on the synthesis and properties of cyclic alkynes. The remainder of the book (Chapters 10−13) is principally directed at supermolecular and materials aspects of acetylenes. Chapter 11 deals with the esoteric area of high-spin molecules based upon acetylene compounds. Acetylene-based nanostructures such as dendrimers and three-dimensional scaffolds are discussed in Chapter 12. Acetylene chemistry as it pertains to novel carbon allotropes is covered in Chapter 13.

Overall, the book presents a good resource for chemists interested in contemporary acetylene chemistry. The organization of the book was strategically planned, and by in large, the different chapters support and complement each other. In this regard it is better than most edited books with many contributors. There is some duplication of recent reviews written by two of the authors (i.e., cyclic enediynes and carbon allotropes). However, I still believe that the book will serve as a good reference since it has a 27-page subject index, an author index, and a procedure index. The book is not comprehensive. However, considering the rapid ongoing progress in the area, an attempt to be comprehensive would be of dubious utility. Indeed there have been noteworthy advances even prior to publication. *Modern Acetylene Chemistry* presents a good summary of recent acetylene chemistry which will be useful to a broad spectrum of chemists.

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