

Topics in Stereochemistry, Volume 22. Edited by Scott E. Denmark (University of Illinois). J. Wiley & Sons, Inc.: Hoboken. 1999. xvi + 314 pp. \$110.00. ISBN 0-471-25316-2.

Kurt Mislow jump-starts the first volume in the relaunch of this extraordinarily useful but temporarily dormant series of monographs. Publication of the series was suspended after 21 volumes in 1993 when the devoted co-editors, Eliel and Wilen, finally retired. Fortunately for those of us in the chemistry community, Denmark has stepped forward to take on the editorial duties, and he has done a splendid job of assembling an all-star lineup of authors to write about topics of great current interest. The subject matter ranges from mainstream organic chemistry to biochemistry to main group organometallic chemistry to mathematics and includes valuable information for any chemist interested in synthesis, catalysis, structure and bonding, or reaction mechanisms. It is great to see this series resuming at the same high level to which we had grown accustomed during its first 27 years of publication! In these volumes, college and university professors will find especially convenient one-stop shopping for source material on subjects that belong in advanced level courses for today's students.

Mislow's chapter on "Molecular Chirality" is a classic 82 page "state-of-the-union address" that gives the rest of us a glimpse of what this guru of modern stereochemistry has been pondering lately. Rooted in a field that attracts more than its share of adroit intellectuals, Mislow stands out as one of the supreme thinkers in chemistry today. His own scientific career already passed the half century mark some years ago, but his passion for pushing beyond yesterday's frontiers keeps him in the vanguard. Equally obsessed with the history and development of science, Mislow enriches his chapter with numerous quotes from the early literature, in their original language, accompanied by Mislow's own translations and commentary, for example, Kant, Lord Kelvin, Pasteur, Möbius, and Prelog. Forgive me for gushing, but we are blessed to count as one of us a scientist whose devotion to rigor and truth is coupled with such a love for the beauty in chemistry and a scientific perspective that spans more decades than most of the rest of us will ever have the stamina to match. As the co-author of a chapter in Volume 1 of "Topics in Stereochemistry", Mislow is the perfect choice for the lead chapter in this rejuvenated series.

Mislow begins with an authoritative account of the historical foundations of molecular chirality, showing us who deserves credit for which insights and why. He then addresses the problem of choosing appropriate models for chiral and achiral molecules. From there, he dives into topological chirality, beginning with brief discussions of rubber sheet geometry and molecular graphs and culminating with a thorough examination of molecular knots and links (catenanes). This section of the chapter is bountifully illustrated with molecular structures synthesized by others that illustrate various aspects of topological stereochemistry. A discussion of the left-right dichotomy

that is common to all chiral objects then follows, and a concluding section deals critically with the principles that underlie various measures of chirality. This chapter could stand on its own as an important monograph in modern chemistry.

Hilvert's chapter on "Stereoselective Reactions with Catalytic Antibodies" is a wonderful primer on a topic that has received intensive scrutiny by many laboratories in the short time since its emergence 15 years ago at the dissolving interface between organic and biochemistry. Well over 90% of the references cited in this chapter were published in the 1990s. Readers will find a well-balanced survey of the impressive range of asymmetric organic reactions for which catalytic antibodies have now been developed: acyl, glycosyl, and phosphoryl transfer reactions; addition, elimination, and substitution reactions; aldol reactions; pericyclic reactions; oxidation and reduction reactions; and various cofactor dependent processes. In a field noted for extraordinary hype, it is especially gratifying to see the author's honest appraisal of the limitations and failures in this competitive arena. The narrow substrate specificity customarily observed in reactions governed by catalytic antibodies has its good points and its drawbacks, and catalytic efficiencies have not (yet) reached levels worthy of the hype. Rather than criticisms, however, Hilvert uses these shortcomings to highlight the challenges that lie ahead as this field charges into the 21st century. Creative solutions to the universal problem of product inhibition would dramatically elevate catalytic efficiencies, and more thorough screening of the immune response to individual haptens will be essential to the identification of more active catalysts.

"Asymmetric Catalysis with Chiral Lanthanoid Complexes", the chapter contributed by Shibasaki and Sasai, is tightly focused on one well-defined slice of a much larger field (asymmetric catalysis) and makes no attempt to present a broad perspective of the entire area. More so than the other chapters, this one deals largely with discoveries and advances emanating from the authors' own laboratories, many of which are quite impressive. Deprotonated BINOL and derivatives thereof create chiral environments around cations of the lanthanides, and the resulting complexes catalyze a range of nucleophilic 1,2- and 1,4-addition reactions. The oxophilic metals serve as Lewis acids, while the BINOL anions function as Brønsted bases. In some cases, heterobimetallic complexes are formed that contain alkali metal ions as well, for example, $\text{Li}_3\text{Ln}(\text{BINOL})_3$. X-ray crystallography reveals quite elaborate structures for some of these complexes, and this feature has made it difficult to formulate unambiguous pictures of the transition states for those reaction steps that control the stereochemistry. Nevertheless, progress is being made, and new generations of catalysts are continually being added to the list. The chapter concludes with several pages that summarize previous examples of other asymmetric reactions catalyzed by chiral lanthanoid complexes.

The chapter on "Stereochemical Effects of the Group 4 Metal Substituents in Organic Chemistry" by White and Clark contains a wealth of information on the usefulness of Si, Sn, Ge, and Pb

as control agents in organic reactions. Best known among these is the silicon “ β effect”, wherein the electron-donating C–Si bond stabilizes adjacent carbocations by hyperconjugation. As the heavier group 4 metals become progressively more electropositive, their C–M bonds become increasingly more electron donating, and much is known about their ability to interact not only with adjacent carbocation centers but also with π^* and σ^* orbitals, as well as with heteroatom nonbonding electron pairs and even vicinal C–H bonds. The authors go on to examine systematically what is known about through-space γ -effects of these C–M bonds (“percaudal hyperconjugation”), through-bond δ -effects, and even more remote effects. One sees not only reactivity effects but ground state structural effects as well, all of which show dramatic conformational dependencies, as expected. The entire treatment is beautifully organized and makes the information concerning any specific type of effect of any group 4 metal easily accessible.

Volume 22 concludes with a chapter on the fascinating topic of “Asymmetric Amplification” by Fenwick and Kagan. Since the first report of this remarkable phenomenon in 1986 by Kagan et al., numerous reactions catalyzed by chiral catalysts have been found that give products with an enantiomeric purity that is higher than that of the catalysts used for their preparation. In addition to reviewing the currently accepted mechanistic explanation for these counterintuitive results, the authors provide seven tables documenting the range of asymmetric catalytic reactions that exhibit such a “positive nonlinear effect”. Asymmetric additions of diethyl zinc to benzaldehyde have been studied most extensively; other examples include 1,4-additions of diethyl zinc and organocuprates to conjugated enones, enone epoxidations, the Sharpless epoxidation, allylic oxidations, ene reactions, Diels–Alder and 1,3-dipolar cycloadditions, allylations of aldehydes, inter alia. The most spectacular examples of all are those that exhibit autocatalytic behavior. Chemists unfamiliar with this area will be stunned to learn that products with an enantiomeric purity of >90% ee have been prepared in autocatalytic asymmetric reactions using <1% of nearly racemic catalyst (<0.2% ee). Such processes may well account for the homochiral nature of our present day molecules of life.

This volume belongs in the library of every college and university where organic chemistry is taught beyond the first year course. A personal copy should also be on the shelf of every scientist who is working in one or more of the areas covered and in the personal library of any professor who teaches advanced level courses in organic chemistry.

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Just published, this volume maintains the same high level of excellence that Denmark established in Volume 22 (reviewed above). Five more topics of great current interest are treated in up-to-date chapters written by leading authorities in each field. The subject matter ranges from fullerenes to crystal engineering

to enzyme-catalyzed reactions and deals with stereochemical issues from the time-dependent stereochemistry of ionic intermediates to the topological stereochemistry of mechanically linked systems. There is plenty here for any chemist interested in synthesis, catalysis, structure and bonding, or reaction mechanisms.

Volume 23 begins with a chapter on “Chirality in Fullerene Chemistry” by Thilgen, Gosse, and Diederich. With 449 references, this 124-page chapter covers the greatest amount of material and has the largest bibliography of any chapter in either of the latest two volumes of this series. Some unsubstituted fullerenes comprise inherently chiral arrangements of five- and six-membered rings (e.g., D_2 - C_{76}), whereas any achiral fullerene (e.g., C_{60}) can be made chiral by derivatization. To help systematize the large number of chiral fullerene derivatives, the authors draw a distinction between those derivatives that owe their chirality solely to the presence of chiral elements in the attached addends and those for which the pattern created by multiple addends imparts chirality. In the latter category, a further distinction is drawn between inherently chiral addition patterns and patterns that could be either achiral or chiral, depending on the identity or lack of identity between symmetry-related addends. Dozens of examples from the recent literature are cited to illustrate the various categories. Finally, the authors describe in detail a much needed nomenclature system for the unambiguous “configurational description” of chiral fullerenes and fullerene derivatives.

Molecular dumbbells with rings on the axle constitute the subject of the chapter by Sauvage et al. entitled “Transition-Metal-Templated Synthesis of Rotaxanes”. The authors make no pretense of providing a comprehensive review of the topic. Rather, they focus on highlights that illustrate the many marvelous facets of this intriguing field. Furthermore, despite the narrowness of the title of the chapter, which suggests a coverage limited solely to the authors’ own synthetic strategy, the chapter includes an unbiased review that surveys the most important contributions of early pioneers, as well as those of others who currently synthesize rotaxanes by alternate methods. This introduction of nearly 20 pages also reviews the concepts of threading, slipping, clipping, and stoppering, and delineates the distinctions among the strategies of directed, statistical, and templated synthesis. Overall, the chapter provides a balanced perspective of a fascinating topic that stretches from difficult beginnings to impressive “rotaxanes in action,” which vary from controlled motions of the ring along or around the string to electron transfer between mechanically linked components.

“Memory of Chirality: Asymmetric Induction Based on the Dynamic Chirality of Enolates” draws attention to the surprising result that the stereogenic α -carbon atom in certain ketones and esters of general structure $R_1R_2CH-C(=O)-R_3$ can be deprotonated and then alkylated without racemization, even when R_1 , R_2 , and R_3 are all achiral; for example, α -methylation of *N*-MOM-*N*-Boc-phenylalanine ethyl ester can be carried out with a high degree of retention of configuration (81% ee) in 96% yield. Kawabata and Fuji provide numerous examples of this novel phenomenon and discuss the structural requirements that must be satisfied to trap an enolate, born in a chiral conformation, enantioselectively before it can racemize by bond rotations. The majority of the examples involve the α -meth

ylation of α -amino acid derivatives, but others are cited as well. Scattered examples of related phenomena from the literature are also reviewed.

“Chiral Discrimination during Crystallization” is the phenomenon that makes possible, for example, the selective removal of one enantiomer of a chiral base from a racemic mixture in solution by adding one enantiomer of a chiral acid. Kinbara and Saigo discuss the underlying principles behind this classical method for resolving enantiomers and explain why a successful resolution requires that the mixture of the diastereomeric crystals of the target racemate with the resolving agent constitutes a eutectic mixture, as opposed to a solid solution or a 1:1 addition compound. Aided by extensive X-ray structural data, they go on to describe the rational design of acidic and basic resolving agents. X-ray crystal structures of diastereomeric salts formed with conventional resolving agents (e.g., tartaric acid, brucine, etc.) are also thoroughly examined. These studies teach us many lessons, such as the importance of realizing a supramolecular hydrogen-bond sheet rather than a supramolecular hydrogen-bond column in the less soluble diastereomeric salt. Efficient crystal engineering may still lie in the distant future, but we certainly know more now than we once did.

Wong et al. supply the most biological chapter in this volume with a treatment of “Asymmetric Aldol Reactions Using Aldolases”. The authors’ objective is to convey the power of these particular biocatalytic methods as tools for organic synthesis. Many chemists are already familiar with applications of the oxido-reductase and hydrolase classes of enzymes as gentle, stereoselective synthetic tools; however, the reactions governed by such enzymes are generally restricted to the introduction or interconversion of functional groups (e.g., hydrocarbon hydroxylations, carbonyl reductions, ester cleavages, etc.). By contrast, the aldolases catalyze reactions that result in the formation of a new C–C bond, frequently attended by the production of one or two new stereocenters. The nucleophilic component of the aldol reaction can be glycine, pyruvate, dihydroxyacetone, or derivatives thereof, for example, and many enzymes will accept a wide range of electrophilic partners, such as unhindered aliphatic aldehydes and α -heteroatom-substituted aldehydes, including monosaccharides and their derivatives. Because enzymes catalyze both the forward and the reverse reaction, it is possible in some cases to alter the stereochemical outcome of the reaction by allowing the products to equilibrate under conditions of thermodynamic control. The high-yield kilogram-scale production of L-serine from the enzyme-catalyzed aldol reaction of glycine with formaldehyde attests to the practical quantities of material that one can produce by such methods. Transketolase enzymes are also described that catalyze the equivalent of a stereoselective acyl anion addition to an aldehyde. The range of functionalized carbon chains and chiral building blocks that one can prepare by the methods described in this chapter is truly astounding. The authors conclude with a section on aldolase catalytic antibodies that broadens the range still further.

As with Volume 22, this volume certainly belongs in the library of every college and university that teaches organic chemistry beyond the first year course. Every scientist working in one or more of the areas covered should own a personal copy, and it is highly recommended as an addition to the personal

library of any professor who has an opportunity to introduce one or more of these topics to students in an advanced level course.

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Handbook of Surface and Colloid Chemistry. Second Edition. Edited by K. S. Birdi (Consultant, Charlottenlund, Denmark). CRC Press LLC: Boca Raton. 2003. xiv + 766 pp. \$279.95. ISBN 0-8493-1079-2.

As a collection of contributions from experts, *Handbook of Surface and Colloid Chemistry* represents a well-written and well-organized volume covering a wide range of subjects in the colloidal and interfacial sciences. The second edition is intended to update the reader on the state of the field since the publication of the first edition in 1997. To accomplish this task, Birdi chose to include new contributors in addition to those who contributed to the original text. As a result, the book’s scope is broad, covering important fundamental topics such as hydrogen bonding, solubilization by surfactants, and light scattering theory and practice. Of particular and fundamental interest is an extensive, 209-page chapter entitled “Chemical Physics of Colloid Systems and Interfaces”. More specific topics are also presented, which largely reflect the research focus of the authors, and include discussions of thermally sensitive latex particles, processing of ceramic oxides, the Marangoni effect, template-directed colloidal assembly, and enzymatic reactions in liposomes and vesicles. Regardless of the focus or scope, each chapter effectively presents the fundamental physical chemistry that underlies the topic at hand as well as the current status of research in the area. In this regard, the book could be a valuable resource for researchers in almost any area of colloid and interface science as no other compilation or general textbook contains the wide array of information presented here.

Although this volume contains information that is extremely pertinent to the colloid scientist, the sometimes overly broad scope of the volume makes the goals of the editor somewhat unclear. Some of the chapters almost seem appropriate for a graduate-level textbook on the subject, while others are no more than review articles on the research of a particular group. Because of the time taken to bring such a volume to press, chapters of the latter type are in some cases out-of-date. There are also instances where the contextual overlap is very high, as will happen in a book featuring multiple authors. However, the overlap is perhaps too great in some places. For example, two of the chapters in the book are entitled “Solubilization in Aqueous Surfactant Systems” and “Solubilization in Surfactant Systems”. These chapters reflect the particular vision of the respective authors and are by no means identical in content, but it seems odd to have nearly identical topics presented twice in the same book. In fact, both of these topics are also discussed more briefly in the large chapter on “Chemical Physics of Colloid Systems and Interfaces”. This degree of redundancy somewhat detracts from the impact of the book. The quality of the book is also a little uneven, reflecting the styles of the individual authors. While the writing is excellent throughout and the illustrations and graphs are in most cases very good,

the artwork and graphical data representations can be of varying quality. In a few chapters, the reproduction of the graphics from the original work is poor, and, in others, the original graphics are oversimplistic and not truly representative of the physical system being described. For the most part, the references are current, although some chapters are lacking in this regard, with literature citations no more current than the early to mid 1990s.

In summary, this compilation presents accounts of research across the broad range of colloidal and interfacial phenomena.

As a whole, the volume may not be the best choice as a source book on the subject. However, many of the chapters are of extremely high quality and by themselves offer excellent reference material for the established researcher or the beginning graduate student.

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