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Book Reviews *

Handbook of Industrial Mixing. Edited by E. L. Paul, V. A. Atlemo-Obeng, and S. M. Kresta. Wiley Interscience: New Jersey. 2004. 1437 pp. $100. ISBN 0-471-26919-0.

Organic chemists will not be enthused at the title of this formidable treatise, but they should be encouraged to dip into this massive volume. Two chapters in particular should be compulsory reading for all development chemists involved in scaling-up processes (Chapter 13, Mixing and Chemical Reactions, and Chapter 17, Mixing in the Fine Chemical and Pharmaceutical Industries). Engineers will find even more of interest, and the handbook should be on the shelf of every chemical engineer involved in chemical manufacture. The authors are, in part, experienced practitioners in industry and, in part, academics at the forefront of this field. The editors have tried to ensure that most chapters are written by a combination of academic and industrial experts. The result is a very readable work, with the emphasis on using the theory for practical application—I wish there were organic chemistry books in a similar vein.

The encyclopaedic volume begins with a fascinating introduction which includes "conversations" with an industrial person on problems encountered in the plant. The editors use this to point the reader to chapters where the relevant discussion on how to solve the problem occurs. At the end of the introduction, a series of decision trees related to particular problems, usually of scale up, are presented, again pointing the reader to the chapters where useful ideas are discussed.

The editors insist that this is not a book to be read cover-to-cover, but to be dipped into, reading a chapter at a time. Chapter headings include turbulence in mixing applications, laminar mixing, mechanically stirred vessels, mixing in pipelines, blending of miscible liquids, solid—liquid mixing, gas—liquid mixing in turbulent systems, immiscible liquid—liquid systems, heat transfer, mixing of particulate solids, mixing of viscous liquids, mixing on fermentation and cell culture, mechanical design of mixing equipment, and the role of the mixing equipment supplier. Perhaps a surprising omission is a separate chapter on gas—liquid—solid systems. As a result, the important area of heterogeneous catalytic hydrogenation is not given enough prominence. Thus, there is no mention of the use of loop reactors, pioneered by Buss in the 1950s and still in regular use today, particularly for the difficult and very exothermic nitro-group reductions. Of course, many companies these days are also using the special Biazzi reactors for the same purpose, but again, these are not mentioned specifically.

Another surprising omission was the recent trend towards the use of microreactors to improve mixing and to aid the selectivity of chemical processes. Since these reactors are already being used on the tonne scale by Merck (Darmstadt) and Clariant, I would have expected a separate chapter on this topic.

The chapters are, as one would expect, written by chemical engineers, but this means that only the chemical engineering literature is covered. Thus, there are no references to books on chemical development, where examples of mixing-related issues have been discussed (e.g., Anderson; Atherton and Carpenter) nor are there any references to articles in *Organic Process Research & Development* (OPRD). For example, in the discussion of the relevance of the particle size of inorganic reagents such as potassium carbonate to reactivity, and the agitation requirements of the vessel, the case study in OPRD from DSM and the Eindhoven University of Technology (*Org. Process Res. Dev.* **2003**, *7*, 622−640) is not mentioned. Nor is Bourne's OPRD review on Mixing and Selectivity of Chemical Processes (*Org. Process Res. Dev.* **2003**, *7*, 471−508). Perhaps this arises because the work has been a long time in preparation, with many chapters covering literature to only 2001.

Despite these criticisms, this is still an excellent book, which will be used as the reference work on mixing. It represents outstanding value for money at 100 U.S. dollars for over 1400 pages. At the current excellent exchange rate for Europeans, chemists and engineers can afford a personal copy. The library copy is likely to be well used, so a personal copy would be an excellent investment.

OP049955I
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Organic Reactions Mechanisms: 40 Solved Cases. By M. Gomez Gallego and M. A. Sierra. Springer: Heidelberg. 2004. 290 pp. 49.95 Euro, $54.95. ISBN 3-540-00352-5.

A simple, one-sentence review of this book would be—"This is an outstanding book—just buy it". But the authors deserve a bit more detail. They have written a book primarily for an academic audience, to assist in teaching chemists the importance of understanding reaction mechanisms in detail. But it is of immense value in teaching process chemists and engineers how to decide on the mechanism of a reaction. Why should they want to do this? Without understanding, there can be no control, and a key part of scaling-up processes is to appreciate the complexities of the mechanism and decide which factors (concentration, temperature, pressure, order and rate of addition of reagents, etc.) are critical to the success of the process. A knowledge of the mechanism also helps to understand why and how certain impurities are formed, and from this how to prevent their formation—this is much better than having to remove impurities afterwards.

The 40 examples the authors have chosen to examine in detail are all from the literature, mostly from within the last

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[*] Unsigned book reviews are by the Editor.

10.1021/op049955i CCC: $27.50

10 years, and cover a wide variety of reactions encompassing heterocycle formation, organometallic reactions, tandem reactions, cycloadditions and rearrangements, as well as simpler oxidations and reductions, solvolysis, and nucleophilic substitution. They are divided into three sections; level 1 examples are designed to revise fundamental concepts concerning the elucidation of reaction mechanism (crossover experiments, isotopic labeling, kinetics, isotopic effects, activation parameters). Level 2 are regarded as easy to medium-difficult problems by the authors.

For each example, a discussion of several possible mechanisms, which might fit the experimental data, is followed by an analysis of why one mechanism might be the preferred solution. The key references, usually only one or two, are given for each example. Each example has a title (e.g., The Baylis–Hillman Reaction) followed by key points (Catalysis, Volume of Activation), a summary of the experimental data, and then the detailed discussion.

My only criticism is that the work could merit a short introduction, rather than going straight into the problems. This would have the advantage of pointing the reader to important books on the subject of physical organic chemistry (e.g., Isaacs), which the student may need to read in conjunction with the book. It could also have provided the student with a brief summary of key areas such as activation parameters, transition states, etc., and a glossary of terms, so that the book could be more "stand alone".

I thought that giving a couple of references was a little sparse; a reference to a recent review on a key topic (e.g. the Baylis–Hillman Reaction review in *Organic Reactions*) would have been useful.

In summary, this is an excellent, well-produced teaching text which could be used in tutorials and discussion groups in both academic and industrial environments.

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Organosilanes in Radical Chemistry. By Chryssostomos Chatgilialoglu. Wiley: Chichester, UK. 2003. 227 pp. £90, 135 Euros. ISBN: 0-471-49870-X

Over the past 25 years, the stature of radical reactions in organic synthesis research has grown from academic curiosity to wide use as a preparative tool. Central to much of the development has been the emergence of tributyltin hydride as a useful mediator of many radical reactions. It has also been a limiting factor, as the well-documented problems of product purification and organotin toxicity have largely confined such applications to academic laboratories. Chatgilialoglu's book provides a timely reminder that organosilanes, too, can be effective mediators of radical reactions and that through their use the toxicity and purification problems are often overcome.

The book is a delight to read. Its 227 pages are appropriately divided into eight chapters, allowing ready access to the material presented. The book begins by outlining the methods available for generating silyl radicals. There follows a concise summary of a wealth of physical, spectroscopic, and theoretical studies relating to the structure and reactivity of silyl radicals. Important thermochemical data on silanes and other partners in radical reactions follow in Chapter 3, setting the stage for an overview of their use in synthesis.

The bulk of Chapter 4 is devoted to the reductive removal of halogens and chalcogens with silanes. Chapters 5 and 6 review additions of silyl radicals to unsaturated carbon and heteroatom centres in both bimolecular and unimolecular reactions. Topics covered include hydrosilylation, radical Brook rearrangements, aryl migrations, and homolytic substitution reactions. Extensive coverage is then devoted to applications of silyl radical intermediates in carbon-to-carbon bond-forming reactions (Chapter 7). Intermolecular, intramolecular, and cascade radical reactions are presented and discussed in an easily assimilated form. The book concludes with a survey of applications in the polymer and materials chemistry field.

At every stage, material is logically presented and easy to access. The commentary and diagrams are concise and informative, summarising an extensive body of work without ever becoming overbearing. As you read through the book, the case for switching away from tributyltin hydride becomes ever more compelling. Indeed, the author offers the view that "tradition" prevents tris(trimethylsilyl)silane from coming to the fore as the reagent of choice for most radical reactions. That passage was the source of my only gripe as it failed to comment on the respective cost of the two reagents. For those working on large-scale synthesis, or to a tight budget, the appeal of tris(trimethylsilyl)silane is lessened the moment you consult the suppliers catalogue!

Organosilanes in Radical Chemistry is an impressive work that will find favour with experienced users and newcomers alike. It is both informative and stimulating. The way material is presented deserves special praise as the book succeeds as a reference text whilst being an excellent read from cover to cover. It is a timely and most useful addition to the organic chemistry literature.

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Name Reactions: A Collection of Detailed Reaction Mechanisms, 2nd ed. By Jie Jack Li. Springer Verlag: Heidelburg. 2004. 465 pp. $79.95. ISBN 3-540-40203-9

The second edition of Dr. Li's book on Name Reactions has added a further 16 reactions to the previous collection, making a total of 331. I have to confess that some reactions I had not heard of (e.g., Dutt–Wormall reaction) and therefore was enlightened. Each reaction occupies one or two pages and is given a very brief introduction, often only one sentence, before the mechanism is delineated in a scheme. Up-to-date references are given.

I am not sure at whom this book is aimed. If it is undergraduate readers, then this will help them understand the basics. More demanding readers will find the mechanisms not detailed enough, with little attempt made to understand stereo control (e.g. in the aldol reaction). Enantioselectivity is rarely mentioned in reactions which can now be carried out in an asymmetric manner (e.g., the Henry reaction). Some readers may dispute Li's mechanisms; for example, the Hofmann and Curtius rearrangements are shown without a nitrene intermediate. A little more written explanation about the reactions would also have helped the reader (e.g. in the Jacobsen−Katsuki epoxidation).

Overall, this potentially useful collection of named reactions is let down by the lack of detailed discussion and absence of stereochemical insight.

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A Fragrant Introduction to Terpenoid Chemistry. By Charles Sell. Royal Society of Chemistry: Cambridge. 2003. 410 pp. £49.95 (paperback). ISBN 0-85404-681X.

Process chemists might be forgiven for thinking that there is nothing of interest for them in a book on terpene chemistry written by someone from the flavour and fragrance industry. But nothing could be further from the truth. Terpenes provide raw materials for industrial synthesis, often at a low price for a complex molecule. Charles Sell's engaging book teaches chemists about the topic from both an academic view, when he discusses detailed mechanisms of complex chemical transformations, and also from an industrial view, when he compares and contrasts the different ways to make (and that means on large scale) a variety of interesting molecules.

For the synthetic chemist, there is a wealth of useful information, particularly on natural product syntheses, where names such as Corey and Stork are mentioned a number of times.

The most useful chapter for process chemists is on commercial production of terpinoids, where manufacturing cost is a key factor. In the introduction to this chapter, issues such as safety in scale up, environmental issues (e.g. atom economy in synthesis), quality, reproducibility, and capacity are discussed, as well as cost. There is even a short section on experimental design, although this focuses on simplex optimisation, rather than the more widely used factorial designs.

The other chapters (Background; Biosynthesis; Linear and Monocyclic Monoterpenoids; Menthol and Carvone; Bicyclic Monoterpenoids; Precious Woods; Other Woody Odorants; Degradation Products; Discovery and Design of Novel Molecules) are complemented by a bibliography and an interesting set of 33 problems with solutions.

My only criticism is that there are not enough references in each chapter and that the bibliography is not comprehensive. Thus, the section on Chemical Process Design and Optimisation includes mainly chemical engineering books, whereas the chemical development books by Anderson or Lee and Robinson would be much more appropriate citations.

Overall conclusion: excellent value for money!

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Modern Carbonyl Olefination: Methods and Applications. Edited by Takeshi Takeda. Wiley-VCH: Weinheim. 2004. £100. 349 pp. ISBN 3-527-30634-X

This book reviews the most significant methods for olefinating carbonyl compounds, with chapters devoted to the Wittig and related reactions, the Peterson and related reactions, the Julia reaction, utilisation of metal carbene complexes (Tebbe and related reagents), low-valent chromium, zinc, or titanium mediated olefinations, and the McMurry coupling and related reactions.

Although numerous reviews and surveys of each of the reaction classes above have been published over the years (some of which are now a little outdated), this would appear to be the first book to pull them all together in one volume, and it is therefore a useful literature entry point for the synthetic chemist.

The Wittig chapter is the shortest, reflecting not its utility but the fact that much has already been written about this. The Peterson chapter is the longest, primarily due to its detailed exposition of the generation of a wide range of substituted α-silyl carbanions and their Peterson reactions. The Julia reaction is probably the least applied of the methodologies, perhaps owing to the slightly less convenient reagents commonly used (Na/Hg), although a number of alternative reductive elimination reagent systems have been developed in recent years, and these too are reviewed. Recent developments include both sulfoxide- and sulfoximine-based modifications which look to enhance the stereocontrol achievable via the Julia-type process. The Schrock-type metal carbene complexes and related reagents (e.g., Tebbe) are highlighted for their special ability to olefinate esters and amides to enol ethers and enamines, while the short chapter on *gem*-dizinc- and chromyl chloride-based approaches emphasises their advantages in specific situations (particularly resulting from their enhanced nucleophilicity). The McMurry chapter will be a particularly useful source for those contemplating a McMurry reaction, thanks to its extensive use of tabulated data and diagrams, comprehensively cataloguing the literature in this area. The final chapter describes the application of carbonyl olefination in asymmetric synthesis - by differentiation of enantiotopic carbonyls, by desymmetrisation of prochiral carbonyl compounds, or by kinetic resolution of racemic carbonyl compounds.

The chapters are each written by different authors, and the observed stylistic differences are therefore not unexpected. Nevertheless, each chapter is well written and includes mechanistic discussions as well as synthetic applications. The conclusion section at the end of each chapter highlights key points and makes occasional references to the alternative olefination protocols. However, the reader cannot help but feel that the opportunity for a more critical and coherent comparison of all of the olefination methodologies has been missed here.

Overall, this is a good book, which will be of use to practising synthetic chemists.

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