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Book Reviews *

Fine Chemicals Through Heterogeneous Catalysis. Edited by Roger Arthur Sheldon and Hermann van Bekkum. Wiley-VCH: Weinheim, New York. 2001. 611 pp. DM 298. ISBN 3-527-29951-3.

Summary. This is an excellent and comprehensive review of an area of chemistry(and technology) that offers great potential for Fine Chemical synthesis. The up-to-date bibliography and well-written text (by a multitude of contributors) should be of interest to academics and industrialists alike.

Chapter 1. An interesting general introduction with sufficient emphasis on environmental benefits versus the constraints stemming from the nature of fine chemicals, notably their lack of thermal stability and volatility. Additional reference Professor Clark's work at York University is relevant (Clark, J. H.; Macquarrie, D. J. *Chem. Commun.* **1998**, 853).

Chapter 2. A concise description of the importance of catalyst design, both chemical and physical (mechanical strength, structure, stability, pore size, and mass-transport limitations). The influence of methods of preparation on catalyst activity is more than adequately described. Linkage to reactor design is done smoothly and completes this Chapter in an interesting and satisfactory manner.

Chapter 3. Emphasis is given to the structure of acidic clays, zeolites, and sulfonated resins. The relationship of catalyst structure and acidity to catalytic activity and selectivity is well-described. The supporting bibliography is comprehensive for those readers wishing to follow-up further. The whole Chapter rounds off an excellent introduction in Chapters 1−3 to the science behind catalyst structures and design and the commercial potential of heterogeneous catalysts.

Chapter 4. The concise literature review of nitration clearly illustrates the difficulty of replacing the classic homogeneous catalyst, sulphuric acid, with a heterogeneous substitute in commercial nitration processes. In contrast, significant progress in halogenation is described, where homogeneous catalysts such as $AlCl_3$ and $FeCl_3$ have been replaced by a variety of solid catalysts in both liquid and vapour-phase reactions. The application of solid catalysts to the commercially significant area of Friedel−Crafts alkylation of aromatics is also well-reviewed. In addition to environmental advantage, shape selectivity, stemming from the geometric structure of zeloite catalysts, is also well-highlighted. Shape selectivity is emphasised even more in the review of heterogeneously catalysed acylation of activated aromatic/hetroaromatic substrates and the Fischer−Indole synthesis.

Chapter 5. Starts off well with a detailed review of so far unsuccessful attempts to replace oleum with heterogeneous catalysts in the Beckmann rearrangement of cyclohexanone oxime to the commercially significant ϵ-caprolactam. The unusual and interesting zeolite-catalysed benzamine rearrangement (anilines to picolines) is also adequately described, along with the intra- and intermolecular Fries rearrangement of phenylacetate in the gas- or liquid phase. The significant potential of zeolites in the shape-selective synthesis of higher added-value products is further highlighted in the review of rearrangement of epoxides, diols, and terpenes. The review points out that the significant environmental benefits will only be achieved when problems of reaction selectivity and rapid catalyst deactivation are solved.

Chapter 6. The use of solid acid catalysts in amination/dehydration of alcohols, heterocyclic ring synthesis, Diels Alder reactions, and alkylation of carbohydrates is well covered. One particular highlight is the description of continuous vapour-phase manufacture of the commercially significant pyridines/alkylpyridines and thiophene/3-methylthiophene.

Chapter 7. This is a good review of the less well developed solid base catalysis of reactions such as aldol, Michael addition, and Knoevenagel. Varying catalyst structures, design, preparation, and basicities are described.

Chapter 8. This is a large Chapter covering the well-established and commercially important area of hydrogenation and dehydrogenation. The use of a variety of supported precious metal catalysts and promoted metal oxides to effect a number of important functional group transformations is described. (One notable omission: Laporte's patented, EP 0 178718 B2, and commercialised vapour-phase transformation of pivalic acid to pivaldehyde, a precusor to *tert*-leucine). Hydrogenolysis and the potential of heterogeneous enantioselective hydrogenation catalysts to displace homogeneous transition metal variants are well-reviewed sections.

Chapter 9. Environmental advantages arising from heterogeneous catalysis of oxidation have yet to be realised over a large area of Fine Chemical manufacture. This review contains comprehensive bibliography and highlights the current limitations compared to homogeneous catalysis in epoxidation, in selective oxidation of alcohols/aldehydes, and in enzymatic oxidation of carbohydrates. The review also points out that commercial exploitation of aromatic ring hydroxylation and ammoxidation is similarly limited. The latter is only applied largely to synthesis of cyanopyridine(s) from the corresponding methylpyridine(s).

Chapter 10. Catalysts promoting alkane/alkene metathesis are succinctly described together with the application of heterogeneously catalysed cross metathesis(mainly ethenolysis of alkenes), which affords many different products useful in synthetic musk, pheromone, and perfume manufacture. Application of the Pd-on-C-catalysed arylation of olefins

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*Unsigned book reviews are by the Editor.

(Heck reaction) to the synthesis of sunscreen intermediates, APIs, and polymer (PEEK) intermediates is reviewed.

Erratum on Page 583: the first structure on the second line of Scheme 9 should be the octyl ester not the Na salt.

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Modern Amination Methods. By A. Ricci. Wiley-VCH: Weinheim. 2000. 286 pp. £75.00. ISBN 3-527-29976-9.

Virtually all synthetic chemists will need to make organonitrogen compounds at some time in their career. Often, these are prepared by manipulation of naturally occurring nitrogen-containing starting materials (e.g., amino acids), particularly when enantiomerically pure materials are required. Receiving increasing attention, though, is the alternative strategy of introducing C−N bonds as required. This book aims to serve as an overview of some of the most active areas of such amination chemistry, with an emphasis on asymmetric synthesis.

Prevalent among the methods covered are those involving alkenes as starting materials. Thus, Jørgensen describes allylic amination, including substitution of exisiting allylic functionality as well as direct introduction of nitrogen. A Chapter by Brown and Fernandez discusses electrophilic amination of alkenes, with the amination of organoboranes being of prime concern. Komatsu reviews the use of nitridomanganese complexes for alkene aziridination, while a chapter from the Carreira group covers the synthesis of transition metal nitride complexes in general. A contribution from Genet, Greck, and Lavergne highlights the use of sulfonyloxycarbamates and azodicarboxylates, principally for the α-amination of enolate derivatives. Kunz and co-workers review many highly useful stereoselective reactions involving glycosylamines as chiral auxiliaries. Indeed, an overall impression from the book is that catalytic asymmetric amination methods still lag behind the use of auxiliaries or stoichiometric reagents.

The final Chapter covers a relatively new area of amination chemistry that has already had an enormous impact—the palladium-catalysed coupling of aromatic halides or sulfonates with amines in the presence of base. Written by Hartwig, one of the pioneers of the field, this chapter shows clearly how mechanistic studies can lead to improved reagent systems, allowing the synthesis of many highly useful aromatic amines. The author points out that this methodology now allows a single substrate class (aromatic halides) to be used as a starting point for formation of carbon−heteroatom as well as carbon−carbon bonds, a particularly interesting feature, given the current popularity of library synthesis.

Clearly a book covering such a rapidly developing area cannot keep pace with all of the developments in the field, which means that, for example, the recent palladium-catalyzed intermolecular hydroamination of vinylarenes by Hartwig is not included. Nevertheless, the reviews are of a uniformly high standard and the book amply succeeds in its aim of providing a valuable overview of the field that can be recommended to all synthetic chemists.

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From Bench to Market: The Evolution of Chemical Synthesis. By Walter Cabri and Romano Di Fabio. Oxford University Press: New York. 2000. 266 pp. £19.99. ISBN 0-19-850383-0.

The synthesis of a new chemical entity often goes through many stages of evolution. The starting point is the original discovery synthesis of the product (or of an analogue) through lead optimisation programme(s) and then through process R&D, to provide larger quantities, leading to a manufacturing route and finally, after patent expiry, alternative routes devised by generic manufacturers.

At the core of this book are nine case studies, each of which describes the research and development carried out on a particular pharmaceutical product. This starts with the various research/discovery routes, moving through the routes investigated in process development to, in most cases, the manufacturing route and in some cases the generic manufacturing routes. Each chapter includes useful introductory information detailing which company discovered the compound and when, how long it took to get to market, the therapeutic area, and some discussion on the mode of action. The chemistry itself starts with a retrosynthetic analysis and some comments on the main challenges that the molecule presents as a synthetic target. The various synthetic strategies from the initial research synthesis through improved research syntheses, the various process development routes, and finally the manufacturing route (where applicable) are described, compared, and where appropriate, criticised.

In most examples the authors have had to rely on what has been published, both in the open literature and in the patent literature, and on their own considerable experience of process development. The authors have personal experience of working on at least one or two of these compounds, and probably in reviewing the feasibility of generic manufacture of some of the others. The subject matter is well-organised and will make interesting reading for anyone involved in pharmaceutical research and development, particularly if they are starting out in the generic side of the industry. In more general terms this book is a useful addition to the large amount of information already available on the subject of total synthesis and synthetic strategy. As such the book will be of interest to anyone working in this area and could be used as the basis of a university course on industrial organic synthesis.

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Fluorine Chemistry for Organic Chemists. By M. Hudlicky. Oxford University Press: New York. 2000. 130 pp. £60. ISBN 0-19-513156-8.

This is an unusual book; essentially it is a set of problems (which Hudlicky terms surprises—and they usually are!) with a subsequent set of solutions. So it is not useful for those wishing to get a comprehensive knowledge of basic organofluorine chemistry, but it is useful as an additional text to assist with understanding of critical issues and to demonstrate how different organofluorine chemistry can be from traditional organic reactions. Unfortunately, the references used are mostly before 1990. The slim volume will be useful in tutorials and in problem classes, but not for general reading.

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Oxidation and Reduction in Organic Synthesis. By T. J. Donohue. Oxford Science: New York. 2000. 90 pp. £7.00. ISBN 0-19-855-6640.

This slim volume forming part of the Oxford Chemistry Primer Series seems intended for undergraduates, but nevertheless these useful—and cheap—books are useful as refreshers for industrial chemists. Tim Donohue has been presented with a difficult task in trying to cover oxidation and reduction in under 100 pages. The question is “what to leave out?” The subject is almost too important for one volume, and the series editors should, maybe, have devoted one volume to oxidation and a second to reduction.

The book is written in a clear, easy-to-read style ideal for undergraduate and postgraduate use. I liked the use of mechanisms to explain issues such as selectivity and reactivity. The chapters are arranged by synthetic transformation (e.g., oxidation of carbon−carbon double and triple bonds) with the selection of reagents discussed in as much detail as is feasible. In the limited space it is not possible to discuss all reagents. However, I would have liked more emphasis on catalytic oxidation methods using hydrogen peroxide (e.g., Noyori’s new methodology), and it would have been useful to educate students in “atom economy” when dealing with oxidation methods. After all, most students will end up in industry, so why not get them thinking industrially at the start?

In the reduction chapters the impression is given (by omission) that catalytic hydrogenation cannot be used for C═O, C═N, and C═C bonds adjacent to a carbonyl group, whereas this method is used industrially. I was also disappointed to find no mention of transfer reduction as an alternative to catalytic hydrogenation, since this is often a simpler practical procedure for undergraduates to perform.

The references for further reading could have been more comprehensive (e.g., Augustine’s excellent text on catalysis in organic chemistry—mostly catalytic hydrogenation—has been omitted). The index also is patchy—although lithium aluminium hydride and Red-Al are mentioned many times, they do not appear in the index. DIBAL-H is only recorded on one page, yet it appears on many pages. Why cannot the publishers provide better indices?

But these are minor quibbles. The book is a useful addition to any library and, as with all volumes in this excellent series, is at a price so that anyone can afford a personal copy.

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Chiral Separations by Chromatography. By S. Ahuja. Oxford University Press: Oxford, New York/American Chemical Society: Washington, DC. 2000. 244 pp. £50.50. ISBN 0-8412-3631-3.

This book is based on an ACS short course taught by the author with Professor W. Pirkle and Dr. C. Welch. Chromatography is now seen as a technically feasible and sometimes economically attractive method for preparation of high-value compounds, and already kilogram to tonne quantities are being produced using this technology. The book is therefore very timely. It focuses on the pharmaceutical industry, whereas other industries (e.g., flavour and fragrance) may also be of interest in the future. After an initial overview and review of stereochemistry, separation and detection methods are covered in two chapters. Desirable features of chiral stationary phases are discussed followed by a chapter on understanding chiral chromatography, which is most useful. Method development and preparative separations followed by method selection and applications complete the work.

This is a highly recommended volume for those wishing to learn about chiral chromatography from a practical viewpoint. The text is enhanced by lots of useful tables and many references, although the latest seem to be 1997 or before. Thus, Simulated Moving Bed methods, which have come to the fore in industry over the past few years, are given little attention. However, this is a minor criticism—the book should be in every library. It nicely complements Stig Allenmark’s *Chromatographic Enantioseparation* (Ellis Horwood: New York, 1991).

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