charides. According to the dust-jacket, the book is suitable for reading by everyone with an interest in the chemistry of carbohydrates, and especially for advanced students.

All important aspects of carbohydrate chemistry are treated in a clear and understandable way. After a nice introduction on the historical development of the subject and an account of Emil Fischer's remarkable contributions, the author gives a clear explanation of important concepts such as conformation and anomeric effects. This is followed by an excellent chapter on the role of protecting groups in carbohydrate chemistry, which gives the reader a good overview of the special problems of using protecting group techniques for sugars. The next two chapters deal with the reactions of monosaccharides (44 pp.) and with glycosylation reactions, including the structure of the *o*-glycosidic bond (64 pp.), both essentially following the usual pattern found in previous monographs. The latter chapter is really excellent, and gives a very good account of all the most recent developments. The last four chapters of the book, dealing with the synthesis of oligosaccharides (including new types of solid phases and enzymatic methods), with disaccharides, with oligo- and polysaccharides, and with glycoconjugates and carbohydrate vaccines are rather brief, and here the reader will need to refer to other books to gain a full understanding. In particular the biological aspects of carbohydrates are treated very superficially here, and it would have been desirable to have more factual information. Each chapter of the book ends with a short bibliography listing the most important relevant publications. At the end of the book is an appendix on the nomenclature of sugars, referring the reader to the literature on the subject, and a bibliography of the most important journals and monographs devoted to carbohydrates. The subject index is very thorough and comprehensive, enabling one to quickly find a topic of interest. The formula schemes are excellent and all have been drawn with great care.

The literature list at the end of the book contains 205 references and seems to be adequate. A slight criticism is that for some topics the list gives only textbooks and no original papers. The book is suitable for all researchers who seek a fast and convenient source of information about the most important aspects and modern developments in the rapidly advancing area of carbohydrates. However, the book does not seem very suitable as a textbook for advanced students.

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Green Chemical Syntheses and Processes. (ACS Symposium Series, Vol. 767.) By *Paul T. Anastas, Lauren G. Heine* and *Tracy C. Williamson.* Oxford University Press, Oxford 2000. x + 353 pp., hardcover £ 79.50.—ISBN 0-8412-3678-X

The editors have grouped the papers under five subject areas. After an introductory chapter written by the editors, the first main section has the title "Designing Safer Chemicals". It begins by reporting on measures to control caterpillars of the genus *Lepidoptera.* Tebufenozide gives improved selectivity in insect control by acting as a mimic of 20-hydroxyecdysone: the Rohm and Haas company received the Presidential Green Chemistry Award for it. The control of similar insects using pheromones, which can now be manufactured more cheaply from precursors made by an in vivo synthesis using yeasts, is hampered by too high species specificities.

Another article reports on attempts to make certain metal-complex dyes more environmentally acceptable by substituting Fe in place of Cr, Co, or Cu. The use of these new products for the dyeing of polyamide is restricted to a few special cases (patents are cited). Applying a permanent protective layer to metals using paints or polymers usually involves dipping them in a chromate bath. An alternative is treatment with phosphoric acid, although even then one obtains better adhesion if it is followed by chromate treatment.

The section on "Green Chemical Syntheses" consists of four chapters. The topics include the substitution of dimethyl carbonate in place of phosgene, dimethyl sulfate, and methyl halides, and the use of water or mixtures of water with organic solvents in organic syntheses. It is noticeable that there is no mention of the versatile solid-state reactions that give 100% yields without solvents, without generating wastes, and without the need for product workup. That is all the more surprising since none of the examples described approaches a yield of 100%, and all involve a workup stage to give a pure product. The achievable yields from the (usually incomplete) reactions are at best described as "good", and the subsequent workup is not mentioned. Strategies for avoiding waste generation are seldom discussed.

Nevertheless, some of the reactions described are interesting from a synthesis viewpoint. Thus, dimethyl carbonate (b.p. 90 °C) can be used for the monomethylation of active methylene compounds at 180–220 °C, for splitting ketones to give two methyl esters, and for converting oximes with active methylene groups into *N*-methyloxazolinones. The monoalkylation of aniline derivatives can be carried out at 120–150 °C in the presence of zeolites. However, the claim on page 98 that there are no wastes to be disposed of is incorrect. The discrepancy is especially striking in Table 5 on page 96, which cites 100 % conversion and only 22% yield.

Syntheses carried out in water have long been known. However, the optimism about environmental benefits expressed here is immediately dampened when it turns out that one adds compounds such as pyridine, triethylamine, acetonitrile, tetrahydrofuran, or heavy metals or their complexes, or when the workup (chromatographic in some cases) requires the use of organic solvents. The articles devote particular attention to allylations and propargylations (aldehydes, cycloketones) and ethynylations using the metals Sn, Zn, In, Bi, Mn, Pd, and Ru or their complexes. The usefulness of such reactions is demonstrated in carbohydrate syntheses without the need for protecting groups. No direct comparisons with extensively researched synthetic methods using other reaction media are given. The net gain to the environment is especially questionable in cases where an intensive workup procedure is needed, and where one has to dispose of the aqueous phase as a waste product (however, indium can be recovered electrolytically). In any case, it is always beneficial where one can reduce the number of stages in the synthesis. Reactions of allylindium with carbonyl compounds in aqueous media (usually with tetrahydrofuran as cosolvent) are discussed from a mechanistic standpoint. The diastereoselectivities and yields achieved vary greatly. The allylation products are useful as intermediates for further synthetic reactions.

In the section on "Biocatalysis and Biosynthesis", some fundamental enzymatic processes are treated in four chapters. The addition of water to adiponitrile gives 5-cyanovaleramide. The process, which uses *Pseudomonas chloraphis* B23 cells in calcium alginate beads, is in commercial operation. In another reaction toluene is converted into *p*-cresol and thence into *p*-hydroxybenzoic acid using recombinant *Pseudomonas putida*-EM-2878 with over 99% selectivity. This method offers a great advance compared with the energy-consuming synthesis from potassium phenolate by the Kolbe–Schmitt process, which gives only a 48% yield with 60% conversion. Similarly, toluene derivatives with various substituents in the *para* position or 4-methylphenols can be converted into the corresponding *p*-hydroxybenzoic acids. Further research along these lines may prove worthwhile.

It is reported that cellulosic biomasses can be converted into ethanol using genetically modified recombinant *Saccharomyces* yeasts, which ferment both glucose and xylose. The genetic integration techniques needed for this are described. Pilot plants have operated successfully over hundreds of generations of the yeasts. The authors envisage a cost-efficient conversion of cellulose wastes into ethanol as a motor fuel.

Alcohol production in Brazil apparently generates over 10^{11} liters of toxic sugar cane vinasse per year, and various approaches to finding a use for this have been investigated. A suggested environmentally friendly route is conversion into a microbial biomass which could be treated by recombinant strains of *Aspergillus nidulans.*

The section entitled "Environmentally Benign Catalysis" consists of five chapters that differ greatly in character. The first is concerned with the separation of catalysts from reaction mixtures, which often presents difficult problems. One approach being investigated is to attach a perfluoroalkyl chain to a homogeneous catalyst to make it soluble in a fluorinated hydrocarbon; by using two-phase reaction technology it should then be possible to extract the catalyst from the reaction solution. Perfluorinated compounds are regarded as environmentally acceptable and industry is being recommended to use them in future processes. Metal salt catalysts soluble in perfluoroheptane can be used in the oxidation of cyclooctane by $t\mathrm{BuO_2H/O_2}$ to give cyclooctanol and cyclooctanone in 80% yield (alkane turnover: 1% in 24h). Similarly cyclohexene is converted first into cyclohexenyl hydroperoxide and thence into cyclohexen-3-ol and cyclohexen-3-one. By using fluorinated ruthenium or nickel acetylacetonates and chiral SALEN-manganese complexes it is possible to perform epoxidations (yields: 77–85% and 70% respectively; 0–90% *ee*).

Homogeneous catalysts can also be recovered from reaction solutions using soluble polymers, a method based on the fact that the solubilities in the different phases are strongly temperature-dependent. Polymers with "smart" ligands are used for the purpose. Hydrotalcides (magnesium-aluminum hydroxides) containing noble metals mediate the liquid-phase condensation of acetone to give mesityl oxide, which is then immediately hydrogenated in 20-g batches by H_2 to give methyl isobutyl ketone (up to 82% selectivity with 38% conversion). The catalyst is multifunctional. No patents are cited.

Photochemical oxidation of toluene in a zeolite with O_2 gives benzaldehyde, but the absorption conditions specified here ($\lambda > 400$, >455, >495 nm) and the discussion are unclear, and there are no obvious environmental advantages.

The photocatalysis of auto-oxidation using TiO_2 and UV light is very energy-consuming, and the method is unlikely to be developed for industrial use, as had been hoped. A proposal to set up a process for the auto-oxidation of alkanes or cycloalkanes in the gas phase is ruled out because of the work involved in preparing the catalyst films, the low rate of material conversion, and the formation of absorbent product mixtures with a risk of explosion. The method is certainly not suitable for producing bulk chemicals such as cyclohexanone. However, TiO_2 may have a role in processes to make wastes nontoxic to the environment using sunlight (M. Anpo's work; not cited).

The separate treatment of "Green Solvent Systems" in the last section, rather than incorporating its six articles into "Green Chemical Synthesis", seems rather arbitrary. As an aid to finding alternative environmentally friendly solvents (or solvent mixtures), a solvent design software package PARIS II has been developed and will soon be commercially available. The aim is to reduce toxicity and improve the environmental acceptability indexes without sacrificing effectiveness. For this purpose a number of different databases are searched. For example, the calculations indicate that methyl ethyl ketone can be replaced by a 90:10 mixture of ethyl acetate and ethanol which has very similar physical properties and activity coefficients.

An alternative approach to choosing "green" solvents, which is unfortunately separated from the above by several intervening chapters, does not use the PARIS II program, but instead relies on general principles of "green chemistry". The idea of avoiding the use of solvents altogether is quickly dismissed, even though the authors could instead have mentioned more than a thousand successful examples from solid-state chemistry which also avoid the need for workup of the product. A table is provided listing many requirements that a "green" solvent should meet, and guidelines for the choice are given.

Independently of these considerations, linear methylsiloxanes are proposed as environmentally friendly solvents—for example, in coating applications and for degreasing sensitive surfaces. There is already much published work on supercritical carbon dioxide, but essentially only the American literature is covered here; two articles discuss well-known free-radical reactions, as well as Diels–Alder reactions, substitution reactions, and polymerizations. The call for scaling-up to real processes is not particularly new.

The title of Chapter 23, "Expeditious Solvent-Free Organic Syntheses using Microwave Irradiation", is misleading. The description of a synthesis should include the isolation of the product, and processes that involve finely divided supports (clays, silica gel, aluminum oxide) are likely to use excessive amounts of solvents for extraction, filtration, centrifuging, purification, etc. The use of microwave radiation and of supports is elevated to the status of a fetish here. However, the authors fail to check if their reactions may give a higher or even quantitative yield at a lower temperature without a support and without uncontrolled overheating of the pretreated support material. One has to question whether the laborious techniques described are necessary for reactions such as deprotecting, condensations, cyclizations, rearrangements, oxidations, or reductions, as the reactions are then never quantitative, and separating the product from a large quantity of ballast involves procedures that are not environmentally friendly. It is regrettable that ballast-free techniques giving a 100% yield without the need for workup are not mentioned. To take an example, one has to mix 106 mg of benzaldehyde and 93 mg of aniline with 20 mg of montmorillonite K10, then irradiate for 3 minutes with 800–900 W microwave power in a bath that heats up to 110 °C, followed by extraction with a large quantity of dichloromethane, giving only 98% of impure benzylidene-aniline; the montmorillonite must then be cleaned and reactivated for re-use. Instead, as shown by this reviewer's results, one can simply mix 848 g of benzaldehyde with 744 g of aniline (both 99.5% pure) in a $31 \times 44\,\mathrm{cm}^2$ flat steel vessel. The temperature does not rise above 35 °C. The water of reaction is then evaporated under vacuum from the crystalline product. One obtains 1.436 kg of pure crystalline benzylidene-aniline (100% yield).

In the interest of the subject, the reviewer bears a duty to counteract the dogmatic tendency that appears again and again in this book. It probably arises from the pressure to demonstrate rapid progress in environmentally friendly methods of synthesis, even though the results are unsatisfactory. The potential for a proper balanced evaluation is easily lost when flawed "general principles", for which there is no rational justification, lead to the rejection of good or even better alternatives. The absence of an international input to the US symposium (e.g., by the OECD) also leads to imbalance. This can easily lead to an exclusive circle which attempts to reserve activities in "green" (or "sustainable") chemistry for its members, ignoring the many innovations generated by synthetic chemists in almost all universities and industrial research laboratories throughout the world without any special sponsorship. An example of this damaging dogmatism is the authoritative call in this report for efforts to replace all existing stoichiometric processes by catalytic processes, supported by frequent references to statements by P. T. Anastas (The White House) and T. C. Williamson (Environmental Protection Agency); on page 4 these two refer to "stoichiometric reagents" and "catalytic reagents". Work towards truly environmentally friendly processes should actually emphasize the opposite of that, seeking wherever possible to get away from catalysis towards stoichiometric syntheses that require no workup of the product. The justification for that is provided by over a thousand solid-state reactions, and a few stoichiometric liquid-state reactions in which the product crystallizes during the reaction; these reactions, giving yields of 100%, are not mentioned anywhere in the book. It would be a shame if "green syntheses" became a synonym for complicated and laborious syntheses.

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Computational Organometallic Chemisty. Edited by *Thomas R. Cundari.* Marcel Dekker Inc., New York 2001. 428 pp., hardcover $ 185.00.—ISBN 0-8247-0478-9

To anticipate the verdict at the outset: this collection of articles about the use of computers in organometallic chemistry by various well-respected research groups is well written. I agree with Thomas Cundari's view, stated in his introduction, that "the time was ripe for a book on computational organometallic chemistry". The volume gives a good overview of the many different methods and their particular advantages, as well as identifying problems that still remain to be solved.

The use of computer methods in organometallic chemistry has become more and more important in recent years. One reason for that is, of course, the enormous increase in computational power. One can now perform even the most demanding calculations using a PC, and the relationship of computing power to cost is very good. A second reason is that many research groups throughout the world have demonstrated that theory can make important contributions to the understanding of experimental results. In the area of organometallic chemistry, density-functional theory naturally deserves to be mentioned. Its significance was recognized in the award of the Nobel Prize for Chemistry in 1998: "… to Walter Kohn for his development of the density-functional theory and to John Pople for his development of computational methods in quantum chemistry".

The chemist working in the field of organometallic chemistry nowadays has access to many different ways of using calculations to yield additional information for his or her research, as can be seen in the 15 chapters of this book, which deal with a wide variety of topics. All the chapters are accompanied by numerous literature references including recent review articles.

In the first chapter Per-Ola Norrby describes his "recipe for an organometallic force field", which he has already used many times with great success. He explains the basic structures of different force fields, the differences between them, and methods for determining their parameters. The discussion covers the automatic generation of force fields, optimization methods such as the Simplex and Newton–Raphson techniques, validation methods, and some commonly encountered problems. Three examples of the application of the "recipe" concept are described.

In the second chapter David White describes methods for the quantitative determination of steric effects, both by the use of molecular mechanics programs (Allinger: MM2, MM3, MM4) and by means of mathematical decriptions (cone angles and solid angles). The most well known among chemists is undoubtedly Tolman's cone angle, which