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BOOK REVIEWS

Alternative Solvents for Green Chemistry. By Francesca M. Kerton (Memorial University of Newfoundland, St. John's, Canada). From the RSC Green Chemistry Series. Edited by J. H. Clark (University of York, U.K.) and G. A. Kraus (Iowa State University, USA). Royal Society of Chemistry: Cambridge. 2009. xii + 226 pp. $179. ISBN 978-0-85404-163-3.

This book provides an overview of the most frequently studied solvents used in green processes. Each chapter begins with a brief introduction to the physical and chemical properties of a class of solvents. This is followed by numerous examples of processes utilizing the particular solvent for the synthesis, separation, isolation, or purification of various compounds. Many relevant and up-to-date references are provided for further reading.

The first chapter gives an excellent introduction to the evaluation of solvents based on their environmental effects, health and safety concerns, and chemical properties. The complexities and multiple methods for assessing the overall "greenness" of a solvent are explained very well, and the readers are reminded that the best choice of solvent is dependent on its application. Furthermore, the methods for assessing the character and power of a solvent are succinctly discussed, even though an entire book could be written on the subject. This chapter is a must read for any scientist (or concerned citizen!) interested in improving the environmental quality of the chemical industry.

The summaries of reaction or extraction media based on water (Chapter 3), supercritical fluids (Chapter 4), bioderived solvents (Chapter 5), fluorous solvents (Chapter 7), liquid polymers (Chapter 8), and tunable multicomponent systems (Chapter 9) are all very good. The discussions on solvent properties are generally very informative, although there are a few overgeneralizations. For instance, not all fluorous solvent systems are nontoxic, as trifluoroacetic acid and perfluorosulfonates exhibit severe health hazards. The applications included illustrate the general lack of data for these solvents and stimulate curiosity and further research ideas. For example, the author includes a number of less intuitive applications of water as a solvent, such as on-water reactions, reactive emulsions, and carbon dioxide fixation. In addition, the chapters on bioderived solvents and tunable solvent systems are particularly good at illustrating the unique and process-specific applications that green alternative solvents can offer.

On the other hand, the chapter on "solvent-free" systems is one of the weakest in the book. The author begins with a good discussion of the misuse of the term "solvent-free" but, apart from solid-phase reactions by mechanical grinding, fails to provide the many examples of truly solvent-free systems, including gas-phase reactions, reactive extruder processes, and the synthesis of haloaluminate molten salts. Instead, the chapter is focused on reactions using excess reactant as a solvent or the limited use of solvent. Finally, its organization does not provide a clear progression of thought, thereby leading to abrupt changes in topic, repetitive statements, the masking of excellent cautionary statements, and a general confusion of ideas.

The author's decision to discuss only room temperature ionic liquids in Chapter 6 and focus on their use in organic synthesis is disappointing. The omission of early molten salt systems, such as halometalate melts or inorganic salt eutectics, misserves the reader, as these systems provide important information on the behaviors of all-ion systems and also illustrate some promising environmental applications, such as phase-change energy storage and nuclear reactor systems. Furthermore, the limited discussion of electrochemical systems omits the application of ionic liquids for nonaqueous battery systems. However, the discussion of toxicity issues, the importance of hydrophilic character and ionic liquid choice in various applications, and the inclusion of many references for further background should aid any reader interested in pursuing research in this area.

The final chapter, which provides industrial examples of green alternative solvents, is not as illustrative as it could be. The examples of the use of supercritical fluid carbon dioxide are excellent, but the discussion of other solvents is extremely brief. The mass-transfer concerns, e.g., viscosity, that are prevalent in industry are briefly mentioned, but not to the extent warranted by their importance.

Overall, the book provides a very good introduction to potentially green alternative solvents for researchers new to the field. Numerous synthesis and extraction examples are provided, as well as some important basic properties of each solvent. The warnings of system complexities, discussion of chemical behaviors, and the stimulation of ideas that this book provides are particularly impressive. However, readers are cautioned that there are a number of overgeneralizations and omissions that may mislead the inexperienced. In addition, there are a number of grammatical errors and awkwardly worded passages that impede reading. Despite these shortcomings, the advantages this book offers readers make it an excellent starting point for those interested in working with green alternative solvents.

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JA9058469

10.1021/ja9058469

Metal Ions in Life Sciences, Volume 6. Metal−Carbon Bonds in Enzymes and Cofactors. Edited by Astrid Sigel, Helmut Sigel (University of Basel, Switzerland), and Roland K. O. Sigel (University of Zürich, Switzerland). Royal Society of Chemistry: Cambridge. 2009. xxviii + 510 pp. $299. ISBN978-1-84755-915-9.

Metal−carbon bonds have been an important aspect of biochemistry ever since the role of cobalt−carbon bonds in the action of coenzyme B_{12} was recognized about 50 years ago. With the discovery of other metal−carbon bonds in enzymatic systems, the field of bioorganometallic chemistry has grown substantially in the intervening years, most notably with the more recent identification of iron-carbonyl and -cyanide units in hydrogenases. The exploration of the biological chemistry of metal−carbon bonds has been boosted dramatically by the

10.1021/ja9058469 CCC: $40.75

advent of powerful techniques in protein X-ray crystallography, gene expression, and computational modeling, and the current state of this fascinating field is summarized in this book, which contains 12 succinct contributions by leading authors and over 1600 references.

Chapters 1 and 2 cover cobalt−carbon bonds. In the first chapter, Kräutler summarizes naturally occurring and artificial cobalt corrinoids, surveys the structural and spectroscopic properties of B_{12} derivatives, and evaluates the thermodynamics and kinetics of cobalt-centered redox processes. He concludes with a discussion of the organometallic chemistry of B_{12} derivatives as artificial systems and as cofactors in enzymes. In the second chapter, Matthews reviews cobalamin- and corrinoid-dependent enzymes. Two major sections focus on corrinoid-dependent methyltransferases and adenosylcobalamin-dependent rearrangements and eliminations. A host of structural and mechanistic information is given from the atomic to the multienzymatic level.

In the following chapter, Jaun and Thauer review the formation of nickel−carbon bonds in free coenzyme F430 and illuminate the evidence for and against the involvement of nickel−carbon bonds in the formation or activation of methane by methyl-coenzyme M reductase. Lindahl discusses acetyl-coenzyme A synthases and carbon monoxide dehydrogenases in Chapter 4. These enzymes are bifunctional with two physically separate active sites, both containing iron−nickel units, that catalyze the reversible reduction of carbon dioxide to carbon monoxide and the consumption of carbon monoxide in the formation of acetyl-coenzyme A. Evidence for the involvement of nickel−carbon bonds in these two intriguing transformations is laid out in detail.

Chapters 5−8 focus on iron−carbon bonds. In Chapter 5, Fontecilla-Camps provides an account of the elucidation of the structure of [NiFe]-hydrogenases by X-ray crystallography and spectroscopic studies. It is now firmly established that these enzymes contain a thiolate-bridged nickel−iron pair that has carbonyl and cyanide ligands coordinated to the iron center. The intricate pathway of biosynthesis of the active site, which requires the action of at least seven proteins, is outlined. In the topically related Chapter 6, Peters discusses [FeFe]-hydrogenases, which feature two carbonyl- and cyanide-bearing iron atoms at the active site. In both [NiFe]- and [FeFe]-hydrogenases, thiolate groups connect the metal centers. The bridges are formed by cystein thiolates in the [NiFe]-hydrogenases, but by a unique dithiolate ligand with a triatomic connecting unit—whose exact nature is still the subject of discussion—in the [FeFe]-hydrogenases. The 2Fe subcluster of [FeFe]-hydrogenases is connected to a tetranuclear iron thiolate cluster by means of a cystein thiolate bridge. It is the iron center distal to this cluster that is the likely location of hydrogen activation. The chapter is completed by an evaluation of model complexes for the 2Fe subcluster and a discussion of the genetic and biochemical information relevant to the synthesis of the active site.

In the following chapter, Shima et al. discuss hydrogenases featuring only a single iron atom at the active site. These enzymes catalyze the reduction of methenyltetrahydromethanopterin by H_2. The dihydrogen is most likely activated by simultaneous interaction with the cationic carbon center of that substrate and the iron center. A cystein sulfide bond anchors the iron center to the protein. The iron atom bears two carbonyl ligands and one *N*-bonded guanylylpyridinol ligand. The latter has been suggested to have electronic properties similar to those of a cyanide ligand. Thus a remarkable electronic relationship may exist between the iron centers in [NiFe]-, [FeFe]-, and [Fe]-hydrogenases. In Chapter 8, Rivera and Rodríguez outline the role of hemes in the biosynthesis of carbon monoxide. The authors begin with a general discussion of the physiological properties of carbon monoxide and then provide a detailed account of the extensive structural, spectroscopic, and kinetic studies that led to the current understanding of the complex biochemistry of heme oxygenases. An interesting feature of these enzymes is their relative immunity toward inhibition by carbon monoxide.

A common theme of Chapters 9 and 10 is interaction of cyanide with a wide range of metalloproteins. Lucas and Karlin illuminate some of the rich and diverse biochemistry of copper-containing proteins. The primary processes mediated by such metalloproteins do not involve copper−carbon bonds, but their interactions with carbon monoxide, cyanide, and isocyanides have been used to elucidate many mechanistic details, often in conjunction with the study of cleverly designed model complexes. The chapter concludes with an account of biologically intrinsic copper−carbon bonds, such as the weak interaction of the π-system of a tryptophan residue with a copper atom in a copper chaperone protein; the evidence for the role of copper in ethylene sensing by plants; the proposed presence of copper ions in olfactory receptor sites; and the possible formation of copper−alkyl complexes from free carbon-centered radicals. In Chapter 10, Sosa-Torres and Kroneck first provide a general introduction to the role of cyanide in biology and then discuss a range of metalloproteins including vanadium haloperoxidase, vanadium nitrogenase, manganese superoxide dismutase, manganese catalase, protocatechuate 3,4-dioxygenase, and zinc carbonic anhydrase.

In the next chapter, Hille traces the accumulation of experimental data concerning the mechanistic action of molybdenum hydroxylase xanthine oxidoreductase that led to a gradual shift in interpretation from a proposal involving a fully developed molybdenum−carbon bond to a model with at most a very weak interaction of that kind. In the concluding chapter, Liptak et al. give an overview of the current status of computational methods for bioorganometallic enzymes and cofactors and then discuss some of the major theoretical efforts to model the spectroscopic, structural, and magnetic properties of enzyme systems involving metal−carbon bonds.

As a whole, this volume provides an overview of the field that will be useful to experts and, perhaps more importantly, to readers wanting to acquaint themselves with the topic. It should also be particularly valuable as a reference book for bioorganometallic modules in courses on organometallic or bioinorganic chemistry. The editors and authors are to be congratulated for producing an informative and enjoyable guide to the field of bioorganometallic chemistry.

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JA9059766

10.1021/ja9059766

Aptamers in Bioanalysis. Edited by Marco Mascini (University of Florence, Italy). John Wiley & Sons, Inc.: Hoboken, NJ. 2009. xviii + 314 pp. $125. ISBN 978-0-470-14830-3.

This book covers various applications of aptamers as biosensors. The chapters are organized in three major groups: (1) general aspects of aptamers and their selection, (2) aptamers as biosensors, and (3) applications of aptamer biosensors. It is clear even from the Table of Contents that aptamers have been utilized in many types of analytical techniques, including electrochemical, atomic force microscopy, capillary electrophoresis, spectrophotometric, and fluorometric. These applications are well described. However, the chapters tend to be repetitive, often reviewing the same applications and published works several times with little or no discussion of other approaches, such as the applications of aptamer biosensors in microcantilevers, photoinduced electron transfer, aptamer-coated SAW sensors, and evanescent-coupled field-guide wave sensors.

The book focuses on a relatively small number of aptamers that have been adapted as biosensors. Although it is true that the thrombin, IgE, and ATP aptamers have been used frequently for such applications, these are not the only ones utilized for this purpose. It would have been useful if other examples, such as the interferon gamma, guanine, neomycin, HCV, and some viral protein aptamers, had also been discussed to give a broader view of the general applicability of aptamers in measuring analyte concentrations.

A disappointment is the lack of critical analysis of the analytical methods used. For example, no mention is made of inter- or intra-assay variations for any of the assays described. Despite bioanalysis being a quantitative science, there is little discussion of quantification or of the statistical analysis of the results from any of the methods. Parameters and conditions that influence the output, such as the densities of surface-attached aptamer biosensors, the temperature at which the analysis was performed, or the magnitude and variation of the background activity of the sensor in the absence of analyte, are generally not discussed. In almost all cases, the most information given is the lower limit of detection and perhaps the effective concentration range of the analyte for the assay. Even when the opportunity arises to discuss an important complication in aptamer-based assays, the topic is not addressed rigorously. For example, in Chapter 4, a section is devoted to the interaction between cytochrome c and a DNA aptamer that is shown to be nonspecific rather than specific recognition of a protein topology by an aptamer. Although nonspecific interactions are very important to understand and control when developing an aptamer-based biosensor, the discussion is not of this nature; instead it is merely a report on the interaction and a reflection of its being nonspecific. Another important aspect of aptamers as biosensors, their ability to be regenerated, is touched on in several chapters but is not discussed thoroughly or quantitatively. Thus, in general, these aptamer-based sensors and the assays to which they have been applied are not evaluated for their robustness or promise for regular application in a bioanalytical laboratory.

Despite its limitations, the book is very informative, particularly Chapters 6−12, in its discussions of a variety of applications of aptamers as biosensors, including showing primary data from experiments in which their applicability was tested. Chapter 12 is probably the most comprehensive, covering more applications than most and also touching on analytes other than proteins and ATP, such as DNA and cations. The diagrams throughout the book are very useful for illustrating the principles behind the analytical methods described and the role of aptamers as biosensors.

In summary, this book provides descriptions of many applications of aptamers for biosensing, and for this reason, it is very useful and an interesting read. However, it is not comprehensive and the content is sometimes repetitive between chapters. Many procedures are well described, sometimes in great detail, but they are not critically evaluated as analytical methods. This lack of rigor limits the benefit of the book for those who wish to develop new aptamer-based biosensors or to improve those that exist. However, as a means of gaining insight into the many possibilities for aptamers and their applications as biosensors, this book is a good choice.

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JA906077X

10.1021/ja906077x

Nano and Microsensors for Chemical and Biological Terrorism Surveillance. Edited by Jeffrey B.-H. Tok (Lawrence Livermore National Laboratory, USA). Royal Society of Chemistry: Cambridge. 2008. xii + 208 pp. $189. ISBN 978-0-85404-140-4.

The eight chapters in this book are written by worldwide experts in the field and cover a selection of topics that give a flavor of both the well-established and next-generation micro- and nanoscale sensors and platforms. No real attempt is made to cover the field comprehensively, and no significant integration of the topics is attempted. Thus, the book naturally reads as a collection of eight independent review articles that all fit into the same research space. Furthermore, although all of these sensors are applicable to the surveillance of chemical and biological terrorism, there is little to no discussion in the book that is specific to this application. In all cases the chapters are detailed and insightful, the references are up-to-date, and a comprehensive table of contents and index allow easy access to the information in the book.

The first two chapters, “Carbon-Nanotube-Network Sensors” by Snow and “Chemical and Biological Sensing Using Gold Nanoparticles” by You et al. are brief but excellent critical reviews of highly promising next-generation nanoscale sensors. The authors cover the basics of designing sensors using these two novel and adaptable nanoscale systems and discuss the multiple sensing modalities of each. Given the broad potential of these early stage technologies, it is no surprise that the chapters are overviews. Fortunately, the references are detailed and extensive, making these chapters excellent springboards for anyone entering the field.

The next chapter, “Resistive-pulse Sensing and On-chip Artificial Pores for Biological Sensing” by Saleh and Sohn, contrasts sharply with the first two in that it is a review of a very specific sensing system that was designed, implemented, and refined by the authors themselves. This is certainly a useful review for anyone who is interested in their device, but the chapter does not serve the same function that the first two chapters do. I would have been happier to see a broader review of artificial pore-based sensors and/or resistive pulse sensing for a book of this type.

Chapters 4 and 5, “Micro- and Nanocantilever Systems for Molecular Analysis” by Biswal and “Fiber-optic Sensors for Biological and Chemical Agent Detection,” by Aernecke and Walt, fortunately return the book to the type of broad introductory reviews that made the first two chapters so useful. In both cases, these reviews cover slightly more mature sensor technologies that have been developed to the point of signal multiplexing.

Moving squarely into the realm of existing commercial technologies, Rasooly and Herold's chapter, "Application of DNA Microarray Technologies for Microbial Analysis", is a detailed and well-referenced step-by-step discussion of the technology, experimental procedures, and its applications. This chapter may well be the highlight of the book.

The next chapter, "Whole-cell Sensing Systems in Chemical and Biological Surveillance" by Michelini et al., is a very brief but seemingly comprehensive review of the reported whole-cell sensing systems in the literature. What is lacking, however, is a critical contextualization of these systems, allowing the reader to discern the typical strategies used, the range of applicability of each, and the state of development of the field as a whole.

The final chapter is "Conducting Polymer Transistors for Sensing Applications" by Cicoira et al. It is not a literature review, but rather an exploration of the specific mechanism of action of an organic electrochemical transistor and an analysis of the connection of this mechanism to its performance as a sensor. As I felt about Chapter 3, I would have been happier with a broader review of a larger class of sensors, perhaps organic electronic sensors, for a book of this type. Nonetheless, the authors accomplish what they set out to do very well: detailing the chemical and electronic factors that govern the behavior of the device and its applicability as a sensor.

As a whole, *Nano and Microsensors for Chemical and Biological Terrorism Surveillance* is a useful book for anyone seeking an introduction to chemical and biological sensors. It is not comprehensive, but it should give the reader a flavor of the field. As stated above, the chapters on nanotube networks, gold nanoparticles, cantilever systems, fiber-optic systems, and DNA microarray technologies provide excellent overviews and detailed references sufficient to launch a more in-depth literature review for anyone entering the field. The remaining chapters provide useful information, but their narrow focus seems out of place in this book.

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JA906082X

10.1021/ja906082x

Flash Chemistry: Fast Organic Chemistry in Microsystems. By Jun-Ichi Yoshida (Kyoto University, Japan). John Wiley & Sons, Ltd.: Chichester. 2008. xii + 234 pp. $150. ISBN 978-0-470-03586-3.

Organic synthesis in continuous flow systems is a rapidly expanding area with potential advantages in handling highly reactive systems resulting from increased heat and mass transfer. This book is a useful addition to the growing number of reviews on flow chemistry and chemical reactions in microfluidic systems. The author has chosen the title *Flash Chemistry* to emphasize that continuous flow chemistry in microsystems typically involves fast reactions with reaction times ranging from milliseconds to seconds. The book provides a nice, self-consistent overview of the motivation for flow chemistry, the basic principles of chemical reactions and organic synthesis, and an examination of the concepts of fluid flow, heat and mass transfer, and devices. The emphasis, as indicated by the book's title, is on continuous flow chemistry of fast reactions to produce products with high selectivity in a controlled manner. Moreover, sufficient detail is included in the treatment of flow concepts and technologies to make it a useful reference for a chemist embarking on synthesis via continuous flow technology.

The selection of examples nicely illustrates the advantages and capabilities of flow chemistry. Many of the examples derive from the work of the author and collaborators in successive NEDO (New Energy and Industrial Technology Development Organization, Japan) projects on reactions in microsystems, and as such they do not give a comprehensive picture of the many reaction systems already explored in continuous flow. They do, however, provide an informative set of examples to demonstrate the various advantages of using flow chemistry to control reaction exotherms and selectivity.

The early chapters cover the motivation, definition, and background for "flash chemistry". Fundamental concepts of chemical reactions in Chapter 2 set the stage and are familiar to chemists but will be useful to readers from related engineering fields. Chapter 4 motivates the reader to consider the use of microflow systems for controlled synthesis with three illustrative examples: (1) construction of chemical libraries; (2) synthesis of positron emission tomography (PET) probes; and (3) on-demand synthesis in industry. Chapter 5 is a compilation of thermal, photochemical, electrochemical, and chemical methods for activating substrates to generate highly reactive species, a key element in flow chemistry. The focus of Chapters 6 and 7 is on the engineering aspects of flow chemistry, starting with techniques to control fast reactions, mixing (and implicitly mass transfer), heat transfer, and residence time. The basic concepts are introduced, and their implications for controlling fast reactions are demonstrated with illustrative chemical examples. Chapter 7 is a presentation of microfluidic and microflow devices, with an emphasis on mixers and simple tube/channel flow geometries.

The succeeding three chapters focus on the applications of flash chemistry, starting with organic transformations and proceeding through polymerization to a summary of industrial applications. Chapter 8 is a systematic overview of organic reactions for which flow chemistry will have advantages, including highly exothermic reactions, reactions with reactive and unstable intermediates, reactions with selectivity challenges in batch systems, and reactions accelerated by using microflow systems. The content of Chapter 9 is unique in the literature of flow chemistry in that it is an overview of polymerization in microflow systems. Emphasis is placed on cationic and free-radical polymerization. Finally, examples of industrial applications, a topic rarely covered in other literature reviews, are provided in the penultimate chapter. The concluding chapter concerns the future of flash chemistry.

Overall, the systematic introduction of concepts combined with the illustrative examples of applications should make this book useful to chemists and chemical engineers already engaged in or considering starting research in flow chemistry.

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JA906118K

10.1021/ja906118k

Superacid Chemistry, 2nd ed. By George A. Olah (University of Southern California, USA), G. K. Surya

Prakash (University of Southern California, USA), Árpád Molnár (University of Szeged, Hungary), and Jean Sommer (University of Louis Pasteur, France). J. Wiley & Sons, Inc.: Hoboken, NJ. 2009. xx + 850 pp. $150. ISBN 978-0-471-59668-4.

This new edition of the now out-of-print 1985 book *Superacids* now includes a fourth coauthor, Árpád Molnár. As one might expect, there have been many significant developments in the field of superacid chemistry in the intervening years, but the overall organization of this new material is substantially the same as that in the original edition, with the titles of the chapters remaining virtually unchanged: 1. General Aspects; 2. Superacid Systems; 3. Carbocations in Superacid Systems; 4. Heterocations in Superacid Systems; and 5. Superacid-Catalyzed Reactions. The number of citations has more than doubled to 3600, so that 117 pages of this 850-page treatise are used for references, which are collected as a separate group at the end of each chapter and thus may account for a few duplications. In addition, there is a well-organized Table of Contents and a 60-page Index.

The first two chapters cover material that is not greatly expanded from that in the first edition, although, in Chapter 2, carborane superacids and the corresponding low-nucleophilic carborane anionic counterions are now also included. The subsection "Methods and Techniques in the Study of Carbocations" of Chapter 3 has similar or identical text to that in the older edition but now includes two new topics, X-ray diffraction and quantum mechanical calculations, two methods that have actually become more important than many of the older procedures characterizing superacids. The following subsections, "Trivalent Carbocations" and "Equilibrating (Degenerate) and Higher (Five or Six) Coordinate (Nonclassical) Carbocations", include a good deal of the same material and figures as in the first edition. There are many new citations to more recent work, however, including references to the pioneering X-ray crystallography results of Laube and the more recent work of Reed et al., whose notable accomplishments include the determination of the structure of the $C_{60}H^+$ cation.

Of the five chapters in this new edition, Chapter 4, "Heterocations in Superacid Systems", has clearly seen the most spectacular growth with the addition of numerous X-ray structures, improved computational methods, and other modern techniques. The main content of this chapter is divided into three broad areas: "Onium Ions" (bonding to a lone pair or pairs), "Enium Ions" (ostensibly related to carbenium ions), and "Homo- and Heteropolyatomic Cations". In the latter category, the preparation and X-ray structure of N_5^+, a V-shaped structure, is noteworthy (Criste et al.).

The concluding chapter of this book, "Superacid-Catalyzed Reactions," is also greatly expanded from the earlier edition. The term "superacid" in the title allows the authors to focus on reactions that *only* occur with the aid of very strong acids. This chemistry includes the use of a wide range of superacids, including a number of solid-supported systems, the use of which could in principle lead to useful industrial processes. In contrast, there are also many solution-phase reactions described, involving the use of corrosive liquids as the reactant solvent and often resulting in the formation of mixed products. The great breadth of topics discussed makes this material difficult to organize.

In summary, *Superacid Chemistry* is a tightly worded description of the present state of the field, and as an inclusive reference book for this area of chemistry, I believe most active researchers will want access to it.

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JA906130F

10.1021/ja906130f