Additions and Corrections

2,6,10-Tris(dialkylamino)trioxatriangulenium Ions. Synthesis, Structure, and Properties of Exceptionally Stable Carbenium Ions [*J. Am. Chem. Soc.* **1998**, *120*, 12255−12263]. BO W. LAURSEN,* FREDERIK C. KREBS, MERETE F. NIELSEN, KLAUS BECHGAARD, JØRN B. CHRISTENSEN, AND NIELS HARRIT

In this paper, we claim that crystal violet shows the highest pK_{R^+} value reported prior to our work. Recently, however, our attention has been turned to investigations which disprove this statement. A pK_{R^+} value of 13.0 was reported for a stabilized tropylium ion (Komatsu, K.; Akamatsu, H.; Jinbu, Y.; Okamoto, K. *J. Am. Chem. Soc.* **1988**, *110*, 633−634), and pK_{R^+} values in the range of 14 (and even beyond, but not quantified) were also reported for a series of substituted triazulenyl carbenium ions (Ito, S.; Morita, N.; Asao, T. *Tetrahedron Lett.* **1994**, *35*, 751−754. Ito, S.; Kikuchi, S.; Morita, N.; Asao, T. *Chem. Lett.* **1996**, 175−176).

Unfortunately, these references were not included in our publication, and we are grateful to professor Roger Alder for pointing out this negligence.

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Enzyme-Amplified Amperometric Detection of Hybridization and of a Single Base Pair Mutation in an 18-Base Oligonucleotide on a 7-μm-Diameter Microelectrode [*J. Am. Chem. Soc.* **1999**, *121*, 769−774]. DAREN J. CARUANA† AND ADAM HELLER*

The direction of some of the arrows in Figure 5B was incorrect. The corrected figure is shown below.

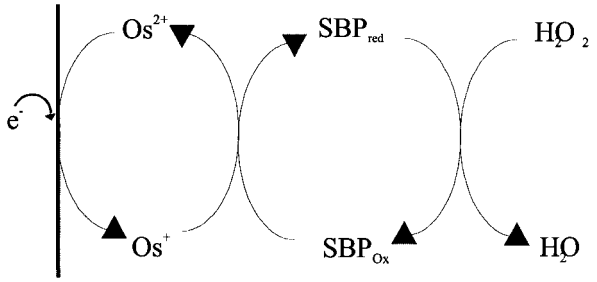

Figure 5. (B) The enzyme-amplified signaling process. When soybean peroxidase (SBP) is bound by hybridization to the electron-conducting redox polymer on the microelectrode, electrons flow from the electrode, via the $Os^{2+/3+}$ complex based redox centers of the polymer, to the SBP heme centers, which reduce H_2O_2 to water. The current of H_2O_2 electroreduction to water is monitored.

The authors also wish to acknowledge the contributions of Dr. Thierry de Lumley-Woodyear, who performed the preliminary experiments and, in particular, suggested the DNA spacer arm chemistry.

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Book Reviews

Microwave-Enhanced Chemistry. Fundamentals, Sample Preparation and Applications. Edited by H. M. Kingston (Duquesne University) and Stephen J. Haswell (University of Hull). American Chemical Society: Washington, D.C. 1997. xxviii + 772 pp. $109.95. ISBN 0-8412-3375-6.

This book is multi-authored and consists of 16 chapters. After an initial chapter on the theory of microwave heating and an overview of its application to chemical synthesis, the remaining chapters are focused on sample preparation and applications in analytical chemistry, organic chemistry, inorganic chemistry, and biochemistry. Although a previous book, *Introduction to Microwave Sample Preparation: Theory and Practice*, edited by H. M. Kingston and L. B. Jassie, was published in 1988, there have been considerable advances in chemical applications of microwaves in the last 10 years and there has been a definite need for an updated and more comprehensive book on the subject. This book has largely fulfilled this need.

The first chapter gives a very useful and informative overview of the theory of microwave dielectric heating and an excellent introduction to the application of microwaves in chemical synthesis. The reasons for the rate enhancement of reactions by microwaves are also discussed in some detail.

Chapters 2 and 3 give a detailed overview of microwave assisted sample preparation and environmental microwave sample preparation, respectively. The importance of well-defined and controlled methods is emphasized and some of these methods are described in detail. Coverage of the literature is fairly comprehensive and a large number of references are quoted. These chapters should prove to be a very useful resource for chemists who would benefit from faster and more controlled methods of sample preparation prior to analysis.

Chapters 4−7 describe some of the alternative instrumentation that is being used in microwave sample digestion including flow methodology, which can be used to advantage in carrying out rapid organic synthesis. There have been considerable advances in microwave technology and instrumentation during the past few years. It is to be noted, however, that there are no references later than 1995 in three of these chapters.

Chapter 8 gives a reasonably comprehensive survey on applications of microwaves to organic synthesis and is an update of previous reviews in this field published in 1989 and 1991. It is disappointing, however, that this new review only covers work published prior to the spring of 1993. Research and publication in this field has expanded dramatically since then and so this review is already dated. Nevertheless, this chapter should be useful in describing the types of reaction for which microwave heating can be used to advantage, i.e., by reducing considerably the time required for normally slow reactions. It may also convince some synthetic chemists that microwave heating should be seriously considered as an alternative method of carrying out these reactions. As pointed out in this chapter, microwave heating sometimes results not only in shortening reaction time but also in giving cleaner products, for example, reducing polymer formation in a Diels−Alder reaction (p 460).

Chapter 9 discusses the use of microwave heating in undergraduate laboratories and makes the point that considerable time savings can be achieved allowing the student time to do additional experiments. Although the equipment is relatively expensive, incurring a large initial cost, this may be partially offset in the long run since some of the conventional apparatus may no longer be required.

Further chemical applications of microwaves are discussed in Chapters 10−12. Chapter 10 gives an up-to-date review of microwave-assisted inorganic reactions, which have until recently received comparatively little attention. There is no doubt after reading this chapter that there is tremendous potential for these applications. The authors also discuss the possibility of specific (nonthermal) effects in solid-state reactions, indicating that more research is required before this concept can be accepted or rejected. However, it is clear that dramatic rate enhancements can be achieved by microwave heating of a wide range of inorganic reactions. The following two chapters show that microwave heating can also speed up considerably catalytic reactions and solvent extractions. The latter procedures have now been well established and are used routinely in some laboratories, showing considerable improvements in efficiency as well as speed over traditional extractive methods.

Biochemistry applications are described in Chapters 13 and 14. These are limited, however, to microwave hydrolysis of proteins and peptides and to sample preparation in pathology. The hydrolysis of proteins is important in amino acid analysis and microwaves enhance the rate of this process. The author clearly establishes the advantage of the microwave method over conventional techniques.

A very useful feature of the book is found in Chapter 15, which introduces the Internet as a resource for analytical sample preparation and microwave-enhanced chemistry. This access to electronic media will allow readers to keep up-to-date in this rapidly expanding field. Finally, there is an informative chapter on microwave laboratory safety that is strongly recommended reading for chemists about to use this alternative technology for analytical or synthetic work.

Overall the book should be of considerable interest to chemists, particularly those currently using microwave heating, or contemplating using it soon to enhance reaction rates in a convenient and controlled manner. Although the book is generally well written, there are a number of typographical errors, including an incorrect eq 9 on p 288 where one the products should be xCO_2 and not xCH_2, and the wrong diagram, Figure 1, p 524 that is actually identical with Figure 2, p 525. The headings at the top of the odd-numbered pages in Chapter 13 should read “Microwave Hydrolysis of Proteins” and not “Microwave Hydrolysis of Amino Acids”. Another reservation, mentioned earlier, is the lack of up-to-date references (e.g. in 1995 and 1996) in some chapters.

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Natural Products Isolation. Edited by Richard J. P. Cannell (Glaxo-Wellcome). Humana Press: Totowa, NJ. 1998. x + 473 pp. $89.50. ISBN 0-86903-362-7

Natural Products Isolation is the fourth volume in the Methods in Biotechnology Series (Series Editor: John M. Walker). The book is both an introduction and a practical guide to the theory and techniques of natural products isolation and purification. Researchers who are starting natural products laboratories or projects as well as experienced investigators who are seeking alternative methods will benefit from this informative text. Ideally, for the beginner who is faced with the task of extracting, isolating and purifying a compound or group of compounds from a biomass, this volume will be indispensable. The book is composed of 15 chapters which are written by contributors from both industrial and academic settings. Chapter 1, written by Richard Cannell, comprises an introduction to approaches involving natural product isolation from start to finish. These involve the usual sequence of extraction, purification and characterization interspersed with general information on separation and detection methods and bioassays. Several schemes which detail the stepwise sequence in the isolation of an actual natural product are shown along with structures of the isolated compounds. Chapter 2, written by F. Patrick Gaillot, deals with initial extraction methods and product isolation prior to the final purification steps. The central theme is workup of the desired compound or compounds from fermentation broths. The discussion of product capture techniques from the biomass ranges from centrifugation and filtration to various extraction and adsorption protocols. Chapter 3, written by Ed Venkat and Srinivas Kothandaraman, addresses the theory and practical application of supercritical fluid extraction (SFE) technology in natural product isolation. Schematics and descriptions of supercritical fluid extraction setups are described along with the determining factors in supercritical methods development. The chapter is well-referenced and the use of SFE technology as applied to active compounds such as taxol and cyclosporin are discussed. The majority of the references in Chapter 3 are within the last 15−20 years which gives clue to the relative newness of SFE technology as compared to the classical isolation methods. Chapter 4, written by Gino M. Salituro and Claude Dufresne, discusses the applications of low-pressure column chromatography when employed for natural products isolation. General

information on stationary phases, column setup and operation, and detection is included. While the chapter offers much guidance for the beginner in column chromatography, more information on the nature of the solvents, or perhaps the eulotropic series, would be an added benefit. A few practical examples of column chromatographic separation of compounds such as rachelomycin and (+)-aphyllidine are detailed. Chapter 5, written by Claude Dufresne, outlines the use of ion exchange methods for natural products isolation. Although a few pages are devoted to the theory of ion exchange chromatography, the major emphasis is on practical applications. Tables of cation and anion exchangers, buffers, resin selection experiments and cartridge column data are included. Practical separations of compounds such as paromomycin, Paluamine, gualamycin and cephamycin using ion exchange chromatography are also detailed in stepwise sequence. Isolation of natural products by preparative high-pressure liquid chromatography (HPLC), written by Paul Stead, constitutes Chapter 6. This chapter focuses on the practical aspects of HPLC with minimal attention to theory. After the chapter is introduced, separation types such as normal, reverse-phase and gel permeation are addressed along with tables which detail stationary phase types and solvent properties. The chapter continues with topics such as HPLC hardware, modes of detection, methods development in isocratic, gradient, reverse-phase HPLC and ion-pair techniques. Scale-up in HPLC separations is given a great deal of attention in Chapter 6 as well as special methods and concerns such as recycling, fractionation and chiral separations. Chapter 7, coauthored by Simon Gibbons and Alexander Gray, renders an account of the many variations of planar chromatography in natural product isolation. The main emphasis of the chapter is on thin-layer chromatography (TLC) and the associated methods and techniques. Variations of the TLC theme include preparative TLC and centrifugal TLC. Detection methods are discussed including staining, bioautographic overlay assay/desorption and compound recovery. An informative table which outlines TLC separations of representative compounds by name, structure and method is included. Natural products separation by high-speed countercurrent chromatography (HSCC) is reviewed by Jim McAlpine in Chapter 8. The principles and equipment design surrounding HSCC is discussed although some type of schematic or sketch of an HCSS instrument would have been helpful to those unfamiliar with the technique. Examples of HSCC separations of compounds such as pristinamycin, taxol and the niddamycins are described which include structures and conditions. A table of HSCC systems employed for the isolation and separation of 30 natural products is presented along with the associated references. Crystallization and the final stages of purification are topics which comprise Chapter 9, contributed by Norman Shankland, Alastair Florence and Richard Cannell. This chapter focuses on the final stages of sample preparation prior to spectral or X-ray crystallographic analysis. Chapter 10, written by Frank VanMiddlesworth and Richard Cannell, covers dereplication and partial identification of natural products during the isolation process. Isolation, separation and extraction techniques are discussed in Chapter 10 within the context of dereplication. Special topics covered include mass spectrometric techniques, bioassays and natural product databases. Yuzuru Simizu discusses the purification of water-soluble natural products in Chapter 11. General extraction procedures dealing with heavy metal contamination and choice of chromatographic supports are the general topics along with methods used for the isolation of tetrodotoxin and domoic acid. Chapter 12, written by Gloria Silva, Ik-Soo Lee and A. Douglas Kinghorn, addresses special considerations with natural products isolation from plants. Topics such as treatment of fresh plant material, extraction processes, detannification, alkaloid isolation, glycoside and carbohydrate isolation are discussed. Flowcharts which outline alkaloid and saponin isolation are included. Chapter 13 focuses on the isolation of marine natural products. Authored by Amy Wright, the chapter discusses collection, storage, and extraction of marine organisms. Isolation methods with flowcharts describing the step-by-step isolation of compounds from marine sponges such as *Ptilocaulis* and *Cinachyra* are included. Isolation of compounds from ascidians is detailed as well as extraction and detection methods for compounds derived from deepwater sponges, echinoderms and cyanobacteria. The chapter is well-illustrated with structures which are representative examples of marine-derived compounds. Chapter 14, contributed by Michael Verrall and Stephen Warr, discusses the scale-up of natural products isolation mainly from the standpoint of fermentation. The chapter involves process improvement as applied to fermentation and covers medium development, optimization of fermenter conditions and removal of intra- and extracellular byproducts. Chapter 15, entitled "Follow-Up of Natural Products Isolation" concludes the volume. In this chapter Richard Cannell identifies several topics of investigation which may be stimulated by a newly identified natural product or its source. The topics encompass further extraction and isolation of minor components or analogues, maximizing gene expression, biosynthetic mutants, directed biosynthesis, biotransformations and combinatorial biosynthesis. Overall, *Natural Products Isolation* is well-written, practical and interesting. The book is highly recommended as a reference for the natural products library and would nicely complement the library of the organic chemist engaged in natural products synthesis.

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Advances in Molecular Vibrations and Collision Dynamics, Vol. 3: Molecular Clusters. Series edited by Joel M. Bowman (Emory University). Volume Edited by Joel M. Bowman and Zlatko Bačić (New York University). JAI Press: Stamford, CT. 1998. ix + 460 pp. $109.50. ISBN 1-55938-790-4.

The excellent original volume of this series, published in 1991, was subtitled "A Research Annual", yet the second volume did not appear until 1994, and now four years later we have volume 3. Nevertheless, the subsequent volumes have been well worth the wait. Volume 1 treated molecular vibrations, and volume 2, reactive scattering. The subject of this new volume is molecular clusters, the floppy noncovalently bound groupings of atoms and molecules that are readily formed in low-temperature supersonic jets. These clusters are well-defined isolated systems, which makes them well suited for detailed theoretical and experimental study. Furthermore, the changes in properties with cluster size in principle allow one to follow the gradual evolution from gas to condensed phase. The book consists of 12 chapters by different specialists. Each chapter is focused on the authors' own work, but the editors have made a sufficiently wide-ranging choice of topics that this volume, taken as a whole, gives a representative overview of contemporary work in the field. In the first chapter, Syage and Zewail describe their real-time measurements of reaction dynamics, including photodissociation, electron transfer, proton transfer, isomerization, and aligned bimolecular reactions, where the reactants are in clusters of solvent molecules. Next, Christoffel and Bowman discuss molecular dynamics simulations of the effect of a solvent Ar atom on the photodissociation of H_2O. Then Heaven, Chen, and Lawrence present spectra of CN in rare-gas clusters (and rare-gas solid matrixes), as a prototypical study of a solvated radical. Buck presents results from IR spectroscopy of small clusters that have been size selected by deflection with a beam of He atoms. Dykstra describes the use of the quantum Monte Carlo (QMC) method to compute the vibrational ground-state energy of weakly bound clusters, and Whaley describes QMC results for doped He clusters, which are interesting on account of very large quantum effects. The remaining chapters deal with hydrogen bonding. Bačić and Qiu develop optimized basis sets that make it feasible for them to carry out variational calculations of vibration−rotation energies for $(HF)_2$ and $(HCl)_2$. There follows a treatment of HF clusters by Quack and Suhm that contains a nice summary of theoretical techniques and discusses spectroscopic results for the full range from dimer to bulk. Then Zwier describes his use of resonant ion-dip spectroscopy to obtain IR spectra of H-bonded clusters that are selected for size and for configuration. Xantheas and Dunning review the use of ab initio potential energy surfaces to determine minimum-energy configurations of small water clusters, and Gregory and Clary present a detailed QMC study of the vibrations of water clusters with emphasis on tunneling dynamics. Wales analyzes the complex patterns of tunneling splittings seen in IR spectra of water clusters. Each chapter contains a good deal of background material, which makes this a good starting point for physical chemists looking for an introduction to this interesting and vibrant subject. The book should also be of use to experts in this field because the narrow focus of each chapter allows for a fair amount of depth, and most of the chapters are quite up-to-date, with references through mid-1998.

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