

Book Reviews

Oligonucleotides and Analogues. A Practical Approach. Edited by F. Eckstein. IRL Press: Oxford, New York, and Tokyo. 1991. xxiv + 313 pp. \$65.00 (cloth) and \$45.00 (paper). ISBN 0-19-963279-0.

Given the recent advances in biotechnology and particularly the utilization of oligonucleotides and their analogues as potential therapeutics, the publication of this book could not have been more timely.

The first out of the twelve chapters comprising the volume describes in detail "state of the art" automated solid-phase synthesis of oligodeoxyribonucleotides utilizing the efficient phosphoramidite methodology. The second chapter describes the extension of this methodology to the synthesis of oligoribonucleotides. In addition to basic chemistry, purification, and characterization techniques, specific applications of synthetic oligoribonucleotides are explored in this chapter.

The following four chapters are devoted to the synthesis of oligonucleotide analogues which include 2'-*O*-methyloligoribonucleotides, oligonucleoside phosphorothioates/dithioates, and oligodeoxyribonucleoside methylphosphonates. The application of these oligonucleotide analogues as antisense molecules is emphasized.

In an effort to probe protein-nucleic acid interactions, the synthesis of oligodeoxyribonucleotides containing modified nucleobases is reviewed in Chapter 7. The last five chapters pertain to the functionalization of oligonucleotides with linkers and/or reporter groups at the 5'-terminus, the internucleotidic phosphodiester functions, or the nucleobases. Reporter groups were selected from fluorophores, chromophores, spin labels, intercalators, and photoactive functionalities, and cleaving agents. The application of such functionalized oligonucleotides as DNA sequencing primers, diagnostic probes, affinity ligands for the capture of DNA-binding proteins, and research tools for the elucidation of gene structure and function is also reported.

Each of the chapters contains detailed and accurate synthetic protocols with a reference section covering relevant and recent publications. However, the book is somewhat limited by the lack of a chapter entirely dedicated to the purification and analysis of synthetic oligonucleotides and their analogues. The description of various HPLC and electrophoretic techniques regarding the purification of oligonucleotides in addition to protocols for conditioning these oligomers for use in cell cultures would have been informative and useful. This limitation is, nonetheless, partially compensated by the presence of adequate purification and analysis protocols in Chapters 2 and 5.

To summarize, the chapters of this book are authoritatively written and provide valuable experimental information to scientists interested in the synthesis and applications of oligonucleotide analogues. This volume should undoubtedly serve as a reference book in every nucleic acid chemistry laboratory.

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Specialist Periodical Reports. Catalysis. Volume 9. Edited by J. J. Spivey (Center for Process Research, Research Triangle Institute, NC). Royal Society of Chemistry: Cambridge. 1992. xii + 279 pp. £97.50. ISBN 0-85186-604-2.

Although catalyst deactivation is inevitable and in spite of its economic importance, there is relatively little in the catalysis literature devoted to the subject. The most recent of the Catalysis Specialist Periodical Reports from the Royal Society of Chemistry serves to rectify that shortcoming. The volume pays particular attention to catalyst deactivation in that three out of the five review articles, and a significant portion of a fourth, deal with different aspects of the subject. According to J. J. Spivey, who edited this edition, this was not by design. Instead, he feels it reflects more of a growing interest and need for understanding of deactivation processes and routes to regeneration which are especially true with increasing environmental awareness.

In Chapter 1, G. F. Froment, W. J. H. Dehertog, and A. J. Marchi give a thorough review of the conversion of methanol into olefins over zeolites. The authors have divided the subject according to small-pore, medium-pore, and large-pore molecular sieves and included for each class the characteristic reactivity and, following the overall theme of the volume, deactivation by coke formation for individual zeolites. Special emphasis is given to medium-pore materials. In a final section, the reaction mechanism and kinetics are discussed.

The deactivation and regeneration of naphtha reforming catalysis are reviewed by J. M. Parera and N. S. Figoli. These bifunctional (metal/acid) catalysts demonstrate nearly all the known causes of deactivation, and as such, their deactivation is one of the most studied in the literature. The authors focus their chapter on the major causes of deactivation,

namely coking, poisoning, and sintering. In a final section they describe efforts at catalyst regeneration.

J. R. Kittrell, J. W. Eldridge, and W. C. Conner discuss the deactivation of air emission control catalysts for stationary sources including detailed discussions of the deactivation of catalysts for removal of nitrogen oxides as well as volatile organics and halogenated hydrocarbons. The authors have also included a section on characterization methods employed to understand the deactivation processes.

The direct conversion of methane into liquid fuels and chemicals is described in a chapter by R. D. Srivastava, P. Zhou, G. J. Stiegel, V. U. S. Rao, and G. Cinquegrane. The authors review the literature and divide the work into four basic groups: direct partial oxidation to methanol, oxidative coupling to ethylene, oxyhydrochlorination, and other direct conversion processes. They also discuss work in biomimetics, i.e., the duplication in heterogeneous or homogeneous catalysts of the critical enzyme functions of microorganisms known to convert methane into complex compounds. A section is devoted to economic and engineering evaluation of the routes.

The final chapter, written by D. B. Dadyburjor, details the effect of deactivation on catalyst selectivity. Coking, poisoning, and/or sintering can all alter selectivities by suppressing (or in some cases enhancing) certain sites or hindering the transport process. Examples of reactions over zeolites and supported metals are described in some detail.

Although there is some duplication, the authors approach the topic from different viewpoints. The reviews include some literature references through 1990. It is unfortunate that there is no index to the volume; however, the Table of Contents is quite detailed. Overall, the volume is a worthwhile reference to anyone studying catalysts, their characterization, and modes of deactivation.

David R. Corbin, *E. I. du Pont de Nemours and Company*

Advances in Photochemistry. Volume 17. Edited by David H. Volman (University of California, Davis), George S. Hammond (Bowling Green State University), and Douglas C. Neckers (Bowling Green State University). Wiley-Interscience: New York, Chichester, Brisbane, Toronto, and Singapore. 1992. ix + 365 pp. \$95.00. ISBN 0-471-55884-2.

This volume is the latest in a series that has become essential reading for photochemists since the first volume was published in 1963. The contents of the present volume reflect the diversity of modern photochemistry, and the editors have been able to obtain excellent reviews of several highly contemporary topics. The six reviews are Photochemistry and Luminescence of Cyclometallated Complexes by Maestri, Balzani, Deuschel-Cornioley, and von Zelewsky; Photochemistry of Phenyl Azide by Schuster and Platz; The Photochemistry and Photophysics of the Silver Halides by Marchetti and Eachus; The Bimolecular Reactivity of Singlet Oxygen by Gorman; Photochemistry in the Treatment of Cancer by Dougherty; and Photochemistry and Photophysics of the Onium Salts by DeVoe, Olofson, and Sahyun. The quality of the reviews is uniformly excellent, and the topics span the range from organometallic photochemistry through physical organic photochemistry to a potentially important medical application of photochemistry. Two chapters on silver halides and onium salts reflect the technological importance of photochemistry. The review of cyclometallated complexes includes an extensive survey of syntheses and key ground state properties of these materials in addition to a review of their luminescence and photochemistry. The chapter on onium salts has excellent coverage of the patent literature, which befits this industrially important topic. The chapter on cancer phototherapy may stimulate more chemists to get involved in what may become a major method of cancer treatment in the near future. Four of the six reviews include 1991 citations; the other two include 1990 citations, so the coverage is quite up to date. The book itself is well printed with clear text, illustrations, and tables. Almost all the reviewers point out their intention of critically reviewing their particular topic rather than aiming for comprehensive coverage of all publications on a particular topic. They seem to have succeeded admirably in this objective. This book has something of interest for a large fraction of the photochemistry community and belongs on the shelves of every research library. The

price, by contemporary standards, is not too high for individuals to acquire personal copies of reviews of this quality.

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Crystallography in Modern Chemistry: A Resource Book of Crystal Structures. By Thomas C. W. Mak (The Chinese University of Hong Kong) and Gong-Du Zhou (Peking University). John Wiley & Sons, Inc.: New York. 1992. xiii + 1323 pp. \$175.00. ISBN 0-471-54702-6.

This book is a treasure chest: an extensive compilation of crystal structures presenting a broad survey of structural information, organized on the theme that crystallography and modern chemistry have undergone parallel development. A brief introductory essay on the development of X-ray crystallography and its enormous influence on modern science is followed by a series of crystal structure descriptions at increasing levels of complexity, organized into groups as follows: 27 fundamental structures; 43 inorganic compounds of main group elements; 23 transition metal compounds; 23 organic compounds; 16 organometallic compounds; and 9 inclusion compounds.

Each of the 141 sections begins with a clear description of the structure in the section title and then continues with a brief essay on the kinds of chemical information that can be developed from that structure and the related ones discussed and illustrated. Some basic knowledge of crystallography is assumed, but the focus is on the chemical significance of crystallographic results. The discussions are very wide-ranging. Major themes developed and considered throughout include chemical bonding in all its richness and variety, molecular conformations, electron density distributions, atomic and molecular interactions, and the synergy among theoretical chemistry, synthetic chemistry, and crystallography. The book was designed as a systematic overview, and the structures chosen for discussion were selected carefully. Nonetheless even browsing among the little essays is likely to spark interest in material the reader may not be familiar with in detail.

Chapter 2, on fundamental structures, includes discussions of the ccp, hcp, diamond, graphite, NiAs, rutile, spinel, benzene, and urea crystal structures, among others. These are simple structures, but the discussion is quite sophisticated. For example, the authors note that in almost all hcp metals the axial ratio c/a is in fact slightly less than the ideal value. Fullerenes are discussed in the section on graphite. I found two essays particularly nice: one on the flexibility of the NiAs structure type and its relation to the Ni_2In and other structures; another on NaTl and the Zintl phases.

Chapter 3 describes a variety of inorganic compounds of the main groups, including KHF_2 , P_4S_3 , $(SN)_x$, various allotropes and polymorphs of B, P, and S, H_2O_2 , XeF_2 , beryl, and zeolite 4A. Borax, still listed in textbooks, handbooks, and catalogs as $Na_2B_4O_7 \cdot 10H_2O$, is correctly described as $Na_2B_4O_5(OH)_4 \cdot 8H_2O$ in part of the section on structural units in borates. Especially good are the discussions of " $HCl \cdot 2H_2O$ " (really $H_3O_2^+ Cl^-$) and the structural formulas of acid hydrates; a complex containing a cryptated sodium cation and a natride ion, $Na^+(C_{18}H_{36}N_2O_6) \cdot Na^-$; zeolites; and xenon fluorides.

Chapter 4 treats transition metal compounds and complexes, including $VO(acac)_2$, Wilkinson's catalyst, K_2ReH_9 , Fe(II) phthalocyanine, isopolyanions and heteropolyanions, $K_2[Re_2Cl_8] \cdot 2H_2O$, Mo-S clusters, Fe-S clusters, and high T_c superconductors. Particularly noteworthy here are the sections on a cobalt sepulchrate complex, the properties of caged metal ions, and the elegant and complex chemistry of macrocyclic ligands, clathrochelates, catenands, and helicates; Fe-S clusters; metalloporphyrin complexes, which includes two marvelous electron density diagrams; and metal clusters.

Chapter 5 covers selected crystal structures and chemistry of organic compounds, ranging from α -glycine and potassium dihydrogen isocitrate to methyl *p*-bromocinnamate, chosen to illustrate organic solid state reactions, cyclooctatetraene and the interconversions among its valence isomers, polymers, polynuclear aromatic hydrocarbons, organic conductors, sucrose, cholesterol, codeine, penicillin, vitamin B₁₂ coenzyme, and valinomycin. A large number of the major fields in organic structure and reactivity and natural products chemistry are covered using representative examples.

Chapter 6, Organometallic Compounds, includes alkyl lithium and alkyl aluminum compounds, Grignard reagents, Zeise's salt, metallocenes, metal carbonyls, organomercury and organotin compounds, and organocobaloximes. The summaries of the structures and chemistry of alkyne complexes of transition metals and of metal carbonyls are particularly strong.

Chapter 7 discusses different types of inclusion compounds: clathrates formed by water, quinol and phenol, Dianin's compound, and tri-*o*-thymotide; Hofmann-type clathrates; cyclodextrin inclusion compounds;

and inclusion compounds of crown ethers, carcerands, and cryptands. The discussion that accompanies the crystal structure descriptions ranges from the properties of water, which are apparently inexhaustibly complex, to molecular recognition. This chapter has some particularly spectacular stereoviews illustrating these complicated three-dimensional structures.

Noteworthy features of this text include: (1) extensive illustrations of the molecules and crystal structures described, with many stereoscopic figures (these authors evidently share in the esthetic delight most crystallographers derive from crystal structures); (2) many plots of experimentally determined electron density; (3) listings of unit cell parameters and atomic coordinates for the principal structures discussed, so readers can explore structural details and understand the intricacies of three-dimensional structures with the aid of graphics programs; and (4) extensive references, from the historical to the very current (through 1991), at the end of each section.

Biological macromolecules are mentioned only briefly in the introduction; quasiperiodic crystals are touched on very lightly in the essay on gamma brass. A certain number of errors were noticed, many simply typographical, a few, more serious: for example, in the introduction, giving As_2O_3 rather than As_2S_3 as the formula for orpiment (p 2); errors in equations for electron density (p 8), Moseley's law (p 66), fractional volume (p 70), and violation of Friedel's law (p 75); and inconsistent signs for phase angle in equations on p 8 and p 140.

The extensive but unannotated bibliography is a good listing of the most useful books on structural chemistry of solids, chemical bonding and molecular structure, inorganic and organometallic chemistry, crystal structure analysis, general crystallography, and the principal compilations of structural data. Data bases for computer searching of structural data are not mentioned.

This would be an extremely valuable text for a chemical crystallography course and will surely serve as a handy reference work for chemists and graduate and undergraduate students. This book is the best single compendium of the wide variety of information derived from crystal structure analysis and should certainly be in every chemistry library, even though the price may deter some individuals from buying it.

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Synthetic Fluorine Chemistry. Edited by George A. Olah, G. K. Surya Prakash (University of Southern California), and Richard D. Chambers (University of Durham). John Wiley & Sons: New York. 1992. xii + 402 pp. \$95.00. ISBN 0-471-54370-5.

This book includes the research interests of the editors, who also contribute as authors. Professor Olah of the University of Southern California in the United States has shaped our modern understanding of carbocation and carbonium ion structures and mechanisms in organic synthesis using stable inorganic fluoroelement counteranions. Professor Chambers of the University of Durham, England, is the noted organic fluorine chemist and educator who has explored the inverse chemistry of synthesis via fluorocarbanion mechanisms. This book, with the able initiative of Dr. Prakash, has assembled seventeen current contributions by experienced authors originally presented at a symposium on synthetic fluorine chemistry in 1990 and now diligently expanded in the typeset book to review background and synthetic details sufficient to promise the unspecialized reader interest and perhaps an inspired solution to a current research problem.

Schrobilgen describes the fascinating Lewis acid chemistry of fluorinated noble gas cations. Christie, Wilson, and Schack discuss the controlled replacement of fluorine by oxygen in volatile highly reactive inorganic fluorides. Aubke, Cader, and Mistry review the transition metal derivatives of fluorinated acids. Seppelt outlines his studies of fluorine stabilized carbon sulfur multiple bonding. These are four chapters reviewing state of the art organic fluorination techniques by the authors Lagow, Bierschen, Juhlke, Hajimu, Kawa, Adcock, Rozen, Olah, and Li. Burton reviews perfluoromethyl and perfluoroalkenyl organometallics. Prakash reviews emerging interest in nucleophilic perfluoroalkylations using perfluoroalkyltrialkylsilanes. Farnham discusses silicon mediated synthesis of fluorocarbons especially as applied to bifunctional oligomers. Baum also reports routes to bifunctional fluorocarbon oligomers. Shteingarts summarizes his study of electrophilic ipso reactions of polyfluoroarenes. Takenaka and Lemal review interesting isomerizations in the perfluorobenzene oxide perfluoroaxepin system. Krespan and Dixon discuss perhalodioxins in their quest for new polymerizable fluoroolefins. Welch, Yamazaki, and Gimi use the fluoroacetamide acetal Claisen rearrangement in asymmetric synthesis. Chambers surveys examples of fluorocarbanion induced synthesis of unusual fluorinated alkenes.

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