**Table II.** Bond Lengths, $\sigma$ Orbital Hybridizations, and Hyperconjugative Interactions[a]

| system | C–N length, Å | $\sigma$ hybridization | | | | | hyperconjugation energy | |
|---|---|---|---|---|---|---|---|---|
| | | C | N | CH $\sigma$ | NH $\sigma$ | lp | lp → CH $\sigma^*$ | NH $\sigma$ → CH $\sigma^*$ |
| $H_3C{-}NH_2$ | 1.454 | $sp^{2.7}$ | $sp^{2.1}$ | $sp^{3.0}$ | $sp^{3.2}$ | $sp^{4.2}$ | – | – |
| $H_3C{-}NH_3^+$ | 1.507 | $sp^{3.6}$ | $sp^{2.2}$ | $sp^{2.8}$ | $sp^{3.3}$ | – | – | – |
| $H_2C{=}NH$ | 1.248 | $sp^{1.7}$ | $sp^{1.3}$ | $sp^{2.1}$ | $sp^{3.6}$ | $sp^{1.8}$ | 15.0 | 9.1 |
| $H_2C{=}NH_2^+$ | 1.262 | $sp^{1.9}$ | $sp^{1.4}$ | $sp^{2.0}$ | $sp^{2.4}$ | – | – | 7.4 |

[a] See ref 8 for the methods used to determine the orbital hybridization and hyperconjugative interactions.

**Table III.** Orbital Energies

| system | molecular orbitals | | localized orbitals | | | |
|---|---|---|---|---|---|---|
| | HOMO | LUMO | $\sigma$ | $\sigma^*$ | $\pi$ | $\pi^*$ |
| $H_3C{-}NH_2$ | −0.385 46 | 0.158 22 | −0.937 82 | 0.643 69 | – | – |
| $H_3C{-}NH_3^+$ | −0.787 08 | −0.081 46 | −1.207 00 | −0.281 58 | – | – |
| $H_2C{=}NH$ | −0.425 61 | 0.158 74 | −1.215 76 | 0.972 22 | −0.452 80 | 0.226 02 |
| $H_2C{=}NH_2^+$ | −0.781 65 | −0.139 58 | −1.501 55 | 0.639 01 | −0.781 27 | −0.071 04 |

the molecule that explains the enhanced reactivity toward nucleophilic addition of protonated Schiff bases or carbonyl groups and the enhanced nucleofugacity of the oxonium ion compared to the hydroxyl group. Further work is in progress to explore the chemical implications of these results.

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# *Book Reviews**

**Molecular Dynamics in Restricted Geometries.** Edited by Joseph Klafter (Tel Aviv University) and J. M. Drake (Exxon Corporation). John Wiley & Sons: New York and Chichester. 1989. x + 437 pp. $75.00. ISBN 0-471-60176-4.

When molecules are confined within a restricted geometry, their static and dynamic properties are often much different from those for the same molecules in the bulk phase. Examples of such situations are fluids adsorbed in porous solids (e.g. silica, activated carbons, clays, zeolites, rocks, etc.), polymer molecules confined in thin films, and molecules in micelles, vesicles, monolayers, and Langmuir-Blodgett films. This book contains 15 chapters devoted to the study of the dynamics of molecules in such confined situations. The main emphasis of the book is on experimental studies, particularly through the use of probes such as luminescent dyes and NMR. Theoretical methods for interpreting the dynamics are also covered, including classical probability ideas, fractal treatments, and statistical mechanics. Molecular dynamics computer-simulation studies are not included. Among the topics discussed are electronic excitation transfer and photoinduced electron transfer in vesicles, micelles, silica gels, filaments, membranes, zeolites, and polymer chains; photochemical probes for orientational and translational diffusion, as well as the dynamics of reactions; cyclization of polymers; the application of NMR to study local motions in amorphous polymers, diffusion in porous media, and characterization of porous materials; orientational dynamics of supercooled liquids in porous sol-gel glasses; and the reaction kinetics of charge carrier reactions in colloidal semiconductor particles and on semiconductor films.

This book will provide an up-to-date account of experimental and theoretical research on dynamics in confined systems and will be useful to specialists in these areas. It will also be of interest to scientists and engineers doing research in porous materials and polymers.

**Keith E. Gubbins,** *Cornell University*

**General and Synthetic Methods. Volume 11.** Edited by G. Pattenden (University of Nottingham). The Royal Society of Chemistry: Cambridge. 1989. xiii + 700 pp. $260.00. ISBN 0-85186-924-6.

This long and richly illustrated volume is intended to review new and improved methods of synthesis that were reported in the literature during the year 1986. Earlier volumes cover the literature from previous years. There are 2000+ references cited in the nine subject chapters of this work. Pattenden has succeeded in the formidable task of generating a coherent review of synthetic methods and applications from the large volume of literature that was published during 1986.

The organization is inherently logical. Pattenden starts with a generous Table of Contents and then follows with five chapters devoted to the wide spectrum of functional group interconversions, three chapters on organometallics and saturated cyclic compounds, and finally a chapter on the synthesis of natural products. A list of newly (1986) published reviews on General and Synthetic Methods and an Author index complete the book. The excellent organization of the book and the detailed Table of Contents make a subject index unnecessary.

In contrast to anthologies published 5–10 years ago, this volume is weighted more toward specific examples and less toward general methodology. A particularly noticeable trend is toward asymmetric synthesis, an area that has gained importance over the last few years. There are numerous stereo- and regioselective examples cited in each chapter.

This book is not meant as a textbook, and as such it is not light reading. It is written as a reference for the practicing chemist, who wishes to maintain awareness of the directions that chemical synthesis is going. It can also help suggest solutions to problems based on the successful newer methods that are cited in the book.

**James A. Thomas,** *Parke-Davis Pharmaceutical Research*

**Oxidations in Organic Chemistry.** By Milos Hrdlicky (Virginia Polytechnic Institute). American Chemical Society: Washington, D.C. 1990. xx + 433 pp. $49.95 (softbound); $89.95 (hardbound). ISBN 0-8412-1781-5 (soft), 0-8412-1780-7 (cloth).

This is a practical book that presents a lot of experimental experience in abbreviated but carefully organized form. An opening chapter systematically summarizes the principal oxidizing agents used by organic chemists. For the most part, one paragraph suffices; it gives succinct information on the scope and principal uses, with key references. The second chapter, relatively short, is devoted to dehydrogenation. Chapter 3 (216 pages) describes oxidations of specific functional groups and also presents a lot of specific information in tables. The organization is thus according to substrate rather than oxidizing agent. This chapter is followed by one composed of preparative procedures, including preparation of reagents. Finally, there is a large group of "correlation tables", in which specific starting structures (e.g., methyl ketones) are organized according to desired product and the reagents. The whole is made even more useful by a complete author index and a thorough subject index.

**Diterpenoids of Flowering Plants. Compositae (Asteraceae).** By F. Seaman (University of Texas), F. Bohlmann and C. Zdero (Technical University of Berlin), and T. J. Mabry (University of Texas). Springer-Verlag: New York, Berlin, Heidelberg. 1990. vi + 638 pp. $99.00. ISBN 0-387-97058-4.

The Compositae (Asteraceae) are among the most advanced and widespread of the families of flowering plants. Their alkaloids, flavonoids, sesquiterpenoids, and polyacetylene metabolites have been extensively studied, but the diterpenoid constituents, which are also numerous

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*Unsigned book reviews are by the Book Review Editor.

and structurally varied, have lacked an up-to-date overview until the publication of this compendium. The book consists of a compilation of compound names, structures, and sources, to which are appended chapters on diterpenoid biogenesis, distribution within the plant family, and biological activity.

The main utility of the book is the listing of compounds grouped into structural categories. It is easy to find whether a given diterpenoid has been isolated previously, and from what source. But it is striking that, given the widespread occurrence of diterpenoids as secondary metabolites in this family, so little is yet known about their biological activity. There has been some progress with studies of plant–animal interactions, but the variety and complexity of the relationships mediated by the diterpenoids of the Asteraceae can as yet only be guessed at.

All four authors are distinguished contributors to the field. Natural products chemists, botanists, and chemical ecologists will find this book a valuable reference and a source of many intriguing ideas about the biological functions of these compounds.

**Philip W. Le Quesne,** *Northeastern University*

**Behavior-Modifying Chemicals for Insect Management: Applications of Pheromones and other Attractants.** Edited by Richard L. Ridgeway (U.S. Department of Agriculture), Robert M. Silverstein (State University of New York), and May N. Inscoe (U.S. Department of Agriculture). Marcel Dekker: New York and Basel. 1990. xvi + 761 pp. $195.00. ISBN 0-8247-8156-2.

This book was developed from a symposium held at an unspecified date and site. However, it is more than a volume of proceedings, even though a number of the contributions are reports of original research, down to experimental detail. The Editors have attempted with some success to make it "an international review to obtain a realistic evaluation of the status of behavioral chemicals in pest control". The papers provide a substantial amount of introductory background that puts the topic in perspective.

There are seven sections into which the contributed papers are placed: Principles of Research and Development; Pests of Horticultural Crops; Forest Insect Pests; Pests of Field Crops; Stored-Product Insect Pests and Insects Affecting Animals; Development, Registration, and Use, and Prospects. Chemistry is discussed only peripherally, but here and there structural formulas of pheromones can be found. The conclusion reached is that "the time is ripe to put insect control with pheromones into practice".

The book is set in type and has a 10-page List of Commercial Suppliers as an appendix and a 29-page subject index.

**Solubility Data Series. Volume 41. Alkaline Earth Metal Perchlorates.** Edited by C.-Y. Chan, I. N. Lepeshkov, and K. H. Khoo. Pergamon: Oxford and New York. 1989. xxii + 280 pp. $85.00. ISBN 0-08-040198-8.

The solubility data for the perchlorates of beryllium, magnesium, calcium, strontium, and barium fill this volume. Both aqueous and nonaqueous systems are included, covering binary, ternary, and more complex systems. The evaluated data are presented in the tabular manner uniform in this series, augmented by phase diagrams where appropriate. Brief descriptions of the experimental methods are included. Where appropriate, a critical evaluation of the data in a delimited area is given. The volume closes with the usual formula and CAS Registry Number and Author Indexes.

**Solubility Data Series. Volume 42. Hydrogen Halides in Nonaqueous Solvents.** Edited by P. G. T. Fogg and W. Gerrard. Pergamon: Oxford and New York. 1990. xvi + 477 pp. $85.00. ISBN 0-08-023925-0.

The published solubility data for HF, HCl, HBr, and HI in a large variety of nonaqueous solvents, including inorganic as well as organic liquids, are tabulated in this volume. Most of the information is in tables, with a very small amount of graphical display. The usual information on methods, purity of materials, and estimated error is given where available. Discursive critical evaluations of selected areas are to be found throughout (e.g., for hydrogen chloride in aromatic hydrocarbons). A System Index and Registry Number Index complete the volume.

**Analytical Biotechnology: Capillary Electrophoresis and Chromatography. ACS Symposium Series 434.** Edited by Csaba Horvath (Yale University) and John G. Nikelly (Philadelphia College of Pharmacy and Science). American Chemical Society: Washington, D.C. 1990. x + 213 pp. $49.95. ISBN 0-8412-1819-6.

This volume contains eleven chapters on high-performance liquid chromatography (HPLC) and capillary electrophoresis developed from a symposium held in 1988. HPLC has reached a level of maturity that includes high sensitivity, resolution, and speed, and new applications therefore constitute the leading edge at present. The status of capillary electrophoresis (CE), the topic of about half of the chapters, is less advanced but is following a similar path. Developments in instrumentation of CE are reported in this book, which includes an introduction to the technique and a discussion of some of its important applications. One chapter of the book is devoted to displacement chromatographic techniques, which is "primarily a preparative technique", but is now being used for enrichment of trace components.

**Molecules to Models. Advances in Neuroscience. Papers from Science, 1986–1989.** Edited by Katrina L. Kelner and Daniel E. Koshland, Jr. American Association for the Advancement of Science: Washington, D.C. 1989. vi + 456 pp. $37.50. AAAS Publication No. 89-17S.

This is a volume of articles reprinted from *Science*, 1986–1989. They review different aspects of the exceptionally intriguing question of how the brain works. A group of seven articles grouped under the heading "Ion Channels" is the most chemical. Six articles are included in the section "Neural Development", five under "Learning and Memory", five under "Cortical Function and Behavior", four under "Neural Modelling", four under "Addiction", and two under "Neurological Disease". The period covered is one that includes major breakthroughs in understanding such subjects as neurobiology and electrophysiology, and this collection is therefore timely. It is well presented, with color plates and a good index.

**Organic Reactions. Volume 38.** Edited by Leo A. Paquette. John Wiley & Sons: New York and Chichester. 1990. xvii + 805 pp. $89.95. ISBN 0-471-51594-9.

This is the fattest volume yet in the Organic Reactions series. It consists of three chapters: The Peterson Olefination Reaction (D. J. Ager), Tandem Vicinal Defunctionalization (M. J. Chapdelaire and M. Hulce), and the Nef Reaction (H. W. Pinnick). The second of these makes up over half the book.

The Peterson olefination reaction resembles the Wittig reaction, with silicon in place of phosphorus; it consists of the condensation of an $\alpha$-silylcarbanion with a carbonyl compound, with eventual elimination from an $\alpha$-hydroxysilane. Its principal use dates from 1968. The chapter on Tandem Vicinal Difunctionalization is concerned with $\alpha,\beta$-unsaturated carbonyl compounds, which undergo addition of anions at the $\alpha$ carbon to form an enoblate anion, which then can be treated with an electrophilic reagent to substitute the $\beta$ carbon. This has assumed great importance in organic synthesis, as shown by the fact that the tabulated examples fill more than 350 pages.

The Nef reaction, by which aliphatic nitro compounds are converted through their anions to aldehydes or ketones, is nearing its centennial, and it is appropriate to have it reviewed. It has taken on renewed importance in synthesis. Modern applications of it have expanded the reported examples to such an extent that the tabular survey requires 90 pages; applications are to be found in a wide variety of areas, including steroids, carbohydrates, and macrocycles.

This volume concludes with an index of chapters and topics for Volumes 1–38.

**Chitin Sourcebook: A Guide to the Research Literature.** By E. R. Pariser (The Chitin Company, Inc.) and Donald P. Lombardi (Massachusetts Institute of Technology). John Wiley & Sons: New York and Chichester. 1989. ix + 623 pp. $150.00. ISBN 0-471-62423-3.

Chitin, and closely related chitosan, are nitrogenous polysaccharides that occur widely in nature, not only on the shells of crustacea. They have assumed industrial importance in many areas, and the growing literature has been organized in this compendium with funding by the MIT Sea Grant Program, the Chitin Co, Inc., H.J. Baker and Brooker Inc., John Wiley & Sons Inc., and private sources. The result is this nine-section book. The largest section (534 pages) is the bibliography, which is composed of entries with full titles and keywords. The other sections are indexes, which are the key to the bibliography. The cut-off date of the literature is not obvious, but the preface is dated September 1988.