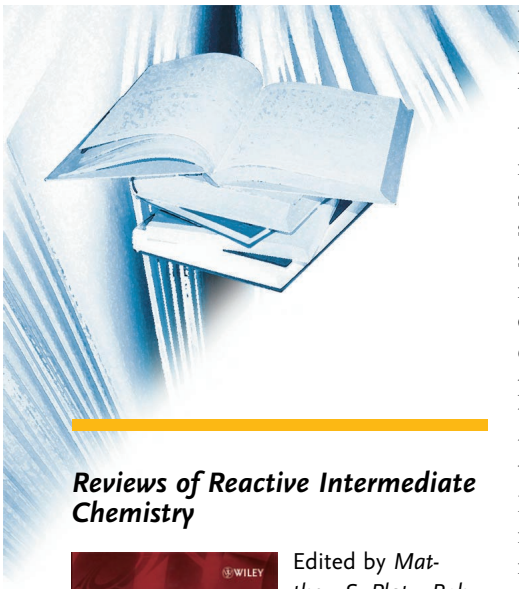
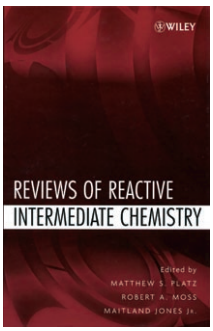


Reviews of Reactive Intermediate Chemistry



Edited by *Matthew S. Platz*, *Robert A. Moss*, and *Maitland Jones*. John Wiley & Sons, Hoboken 2007. 472 pp., hardcover € 99.90.—ISBN 978-0-471-73166-5

A second title for this book published recently by Wiley-Interscience is "New Insights into Reactive Intermediates that Can Help You Design New Reactions". The volume is intended as a supplement to the book *Reactive Intermediate Chemistry*, which was edited by the same experienced team: Matthew S. Platz, Robert A. Moss, and Maitland Jones, Jr. Like the previous work, this too is essentially a collection of reviews of important topic areas and methods of physical organic chemistry, although this one also touches on some related topics in the biosciences ("The Chemical Reactions of DNA—Damage and Degradation") and theoretical chemistry ("Conical Intersection Species as Reactive Intermediates").

The book is divided into two parts, "Reactive Intermediates" and "Methods and Applications". The first part, the shorter one, consists of two review articles, entitled "Tetrahedral Intermediates Derived from Carbonyl Compounds" and "Silicon-, Germanium-, and Tin-Centered Cations, Radicals, and Anions". The former one presents a very nice systematic discussion of the role of tetrahedral intermediates in the reactions of carbonyl compounds.

The second, longer, part of the book begins with chapters on various modern methods of physical organic chemistry, such as time-resolved resonance Raman spectroscopy, time-resolved infrared spectroscopy, and the application of mass spectrometry techniques to the characterization of highly reactive molecules. Although these chapters do not provide introductions to help the reader towards mastering these complicated techniques (which anyway would not be a sensible aim for a volume of this kind), they will at least enable the reader to evaluate the potential of the methods described. Moreover, each chapter ends with a list of recommended literature for further reading, which is certainly helpful for readers who want to explore the subjects in greater depth. The subsequent chapters of the book describe applications of the various methods to investigations of specific topical problems, such as "Reactive Intermediates in Combustion", "Reactive Intermediates in Crystals", the previously mentioned review article on damage to DNA caused by reactive intermediates, and one on conical intersection species, ending with a very nice detailed review article on the role of quantum-mechanical tunneling in the chemistry of reaction intermediates.

Like almost every other book, this one is not entirely free of errors. To mention two examples: benzophenone is a very unsuitable precursor molecule for the photochemical synthesis of diphenylcarbene (Murray and co-workers used diphenyldiazomethane), and although the photolysis of santonin in the crystalline phase does indeed give a highly unstable cyclopentadienone derivative, this dimerizes spontaneously (pp. 272, 273). However, I found no other factual errors.

I certainly recommend that one should buy this book, especially to be used together with *Reactive Intermediate Chemistry*, which is also published by Wiley-Interscience. The two books in combination should provide everybody interested in organic chemistry and related fields with important and stimulating ideas—exactly in the way described by the second title mentioned at the beginning of this review.

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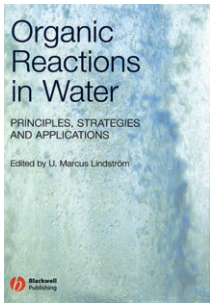
Organic Reactions in Water



Edited by *U. Marcus Lindström*. Blackwell, Oxford 2007. 414 pp., hardcover € 99.50.—ISBN 978-1-4051-3890-1

Organic reactions in water have attracted increasing interest in the last few decades, and they have become an important alternative for many types of reactions. That popularity is based firstly on the cheapness and environmentally benign properties of this solvent, but also on some special benefits with regard to reaction rates and selectivity. This book is not original in its choice of subject, but its structure gives it a unique character. It consists of 12 more or less independent chapters in which outstanding experts discuss problems in the area of chemical reactions in water, some of which are already well known and others that are highly topical today. The youthful editor proves himself to be a good "overview man".

The book begins with a sort of self-portrait: Ronald Breslow, a pioneer in the area of organic chemistry in water, reviews his research over a period of 50 years, and in that context offers an insight into the interplay between system and chance as a route to understanding. Especially for interested younger readers, this can serve as more than just a historical reminiscence.

The second chapter (by J. B. F. N. Engberts) is devoted to the structure and properties of water, and aims to give an insight into the special characteristics

of the medium. Organic chemists especially will appreciate this concise and easily readable overview, which is of a quality that is hard to find. Two particular highlights are the comparison between normal and heavy water in the form of a table, and a critical discussion of the hydrophobic effect. Beginning with Chapter 3, specific classes of organic reactions in water are discussed. First, C. Ogawa and S. Kobayashi describe examples of reactions catalyzed by Brønsted acids and water-stable Lewis acids. This area of research has recently expanded very rapidly, and such reactions have also played an important role in asymmetric syntheses. The introduction of micellar systems has been found to produce surprising effects.

Chapter 4, by C.-J. Li, on metal-mediated C–C bond-forming reactions in aqueous media, is the longest in the book, and provides a wealth of widely different examples. Particular attention is focused on the Grignard–Barbier type reactions using organo-indium compounds that have been developed in the author's laboratory. In this article too there is a special focus on asymmetric syntheses. The chapter lists 330 literature references.

An important addition to the discussion of C–C bond-forming reactions is provided by Chapter 5, which deals with pericyclic reactions. Whereas these reactions are unaffected by the polarity of most solvents, special effects are found in water. The Italian authors (F. Fringuelli, O Piermatti, F. Pizzo, and L. Vaccaro) again report work on Diels–Alder reactions, including biocatalytic variants, but here they also give detailed and precise descriptions of 1,3-dipolar additions, [2+2] photocycloadditions, and Claisen rearrangements. The role of water is mainly treated from a phenomenological standpoint. Chapter 6, by T. V. RajanBabu and S. Shin, surveys catalytic reductions in water. Some surprising successes are reported, especially in the areas of hydrogenations and transfer hydrogenations. The article focuses especially on asymmetric reactions, and provides an excellent survey of the literature and an optimistic forecast.

As one might expect, that is followed by a chapter on oxidations (by R. A. Sheldon). The author discusses prospects for reactions such as the epoxidation and dihydroxylation of olefins, the oxidation of alcohols and aldehydes, and sulfoxidation reactions, and also gives details of practical aspects. This contribution carries particular implications for the development of "green chemistry" methods.

The topic of Chapter 8, by D. Sinou, is less obviously predictable from the reader's viewpoint: nucleophilic additions and substitutions in water, again for C–C bond formation. This article too makes very easy reading, with a clear emphasis on enantioselective reactions, although there is some overlapping with Chapter 3, which was probably unavoidable. The literature coverage is excellent.

In the following chapter, C. L. Liotta, J. P. Hallett, P. Pollet, and C. A. Eckert give an introduction to reactions in near-critical water. Here the polarity is significantly less than for water near room temperature, but not yet so greatly altered as in supercritical water. The article begins with a very good and readable introduction to the physical chemistry of water in the near-critical region. It continues with a description of the chemistry that again demonstrates possibilities, but points to the need for further experiments. The authors mention that there are experimental limitations, as the apparatus is expensive because of the corrosive effects of the hot water.

Chapter 10, by K. Nakamura and T. Matsuda, is devoted to biocatalysis in water. For these reactions water is the natural solvent, and the special feature is the use of enzymes for the synthesis of organic compounds. The chapter also describes important new initiatives based on enzyme-mimetic processes. However, one must ask whether such a large area of research as biocatalysis can be compressed into one chapter of a book. Nevertheless, it is a very well-written article and could serve as an introduction for advanced students. The extensive bibliography is severely compressed, and consequently not very clear.

Chapter 11, by S. Narayan, V. V. Fokin, and K. Barry Sharpless, introduces some new aspects under the title "Chemistry 'on Water'—Organic Synthesis in Aqueous Suspension". Experiments in the authors' laboratory show that water can be an excellent medium even when the reactants are only slightly soluble. However, because of that, the desired reaction may be affected by competition from the breakdown of the reactants by water. A remarkable number of reaction types can already be included in this category, such as nucleophilic substitutions, rearrangements, pericyclic reactions, and free-radical reactions. However, the outcome may depend on whether the method offers good prospects for future applications.

In the last article, the prospects for industrial applications of chemistry in water are discussed by two experts with experience in this field, E. Wiebus and B. Cornils. As one existing process for more detailed consideration, they choose the hydroformylation of propene (the RCH/RP process), and some other processes are also mentioned. Some important laboratory processes are also summarized. According to these authors, the decisive criteria for any technological applications are that the catalyst should be recoverable, and that the process should be economically viable and environmentally benign. This realistic conclusion of the book shows that the establishment of "green chemistry" in industry is a complicated task.

In summary, the book is a modern scientific text that should give the younger generation of readers some interesting new insights, and should provide the older generation with an easily readable survey of this area of research, which is growing year by year. The presentation and typography are attractive, the contributions are pleasingly up-to-date, and the choice of topics and the literature coverage are wide-ranging. I hope that the book will find a way into many libraries and laboratories.

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