A Radical Read

Radicals in Organic Synthesis. Vol. 1+2. Edited by *Philippe Renaud* and *Mukund P. Sibi.* Wiley-VCH, Weinheim 2001. 1110 pp., hardcover € 399.00.—ISBN 3-527-30160-7

The discovery of radicals happened more than 100 years ago. In the meantime, research resulted in the development of powerful reagents and synthetic intermediates, without which modern synthetic chemistry would be less diverse.

This monograph provides, within two volumes, a very good overview of the well-established areas in radical chemistry. The book deals with aspects of synthetic organic chemistry. P. Renaud and M. P. Sibi organized numerous well-known scientists to write contributions of their respective fields, and essentially review the advances made in the past three decades. If older reviews exist they are mentioned. Most parts of this monograph are of textbook quality!

Volume I focuses on the principles of radical chemistry and is divided into six chapters. Firstly, initiators and sources for radicals are systematically treated in several contributions. Two contributions are devoted to the importance of Barton-analogue reactions. Even modern developments, such as solid phase or fluorous phase based initiators are considered. In the second part of this volume, single-electron transfers are discussed. The individual contributions are arranged according to the transition-metal reagents used, but also include electrochemical and light-induced generation of radicals. In this particular chapter iodine(III)-reagents should have a definite place, but they are not even mentioned! In the following chapter the synthesis of radicals with relevant properties are discussed in detail. Therefore, radical clocks, calculations, and stabilizing effects of radical systems are described. A subsequent chapter on the stereoselectivity of radical transformations follows, wherein all contributions are well-coordinated and provide a consistent picture. The review about enantioselective radical reactions is appropriately placed, but major parts are repeated in the second volume of this monograph. The first volume is completed by two contributions about radicals in polymer science.

The second volume is devoted to the practical aspects of radicals in organic synthesis. The book is again divided into six chapters. The first part deals with carbon–carbon bond formation. The different multiple bonds which might serve as radical acceptors are treated systematically. Isonitriles and carbonylation reactions are discussed in individual contributions because of their synthetic significance. The most important section of the volume is the next chapter, devoted to the formation of carbon–heteroatom bonds. Basically, C-H-activation and heteroatom multiple bonds in radical reactions are discussed. This part also provides significant and comprehensive discourses on cyclization reactions and rearrangements. After having outlined the concepts and methodologies, the following chapter deals with recent applications in the total synthesis of natural products. The well-chosen examples and didactic outline demonstrate in 120 pages the potential of these new synthetic methods. A subsequent chapter is devoted to nitrogen, oxygen, and sulfur radicals, and provides a good overview of these topics. The book ends with a discourse on biomaterials, wherein radical transformations on amino acids, peptides, and carbohydrates are described.

Compared to the size and content of the book, the index is too small and restricted to each volume. Looking for a specific subject involves some effort for the reader. A listing of abbreviations would be useful. The monograph has been carefully prepared and well done. The schemes are clearly arranged and the numbering is systematic. Typos in the written part and the schemes are rare.

In summary, this monograph provides an excellent overview of the recent developments in radical chemistry. In the topics covered, the book fills the gaps left by previous reviews in the literature. Based on its completeness and cutting-edge nature, this monograph will become a leading piece of literature and a compulsory reading for chemists working in these areas.

Therefore, this valuable monograph should have a definite place in every good library.

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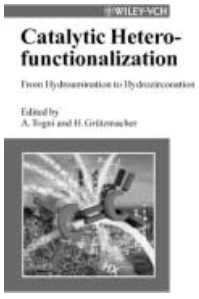
Catalytic Heterofunctionalization. Edited by *Antonio Togni* and *Hansjörg Grützmacher.* Wiley-VCH, Weinheim 2001. xiv + 289 pp., hardcover € 129.00.—ISBN 3-527-30234-4

Olefins and acetylenes are usually considered to be suitable starting materials for selective introduction of heteroatoms into organic molecules. Within this context, one of the most important reaction principles relies on the addition of H–X molecules to unsaturated bonds. A book that reviews the progress made on the development of catalytic variants should therefore be of major interest to synthetic chemists. The present book, edited by A. Togni and H. Grützmacher, offers such a concise summary.



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The volume is divided into eight chapters. In the first one, N. Miyaura describes different catalyzed reactions of olefins and acetylenes with boranes, diboranes, silylboranes, and stannylboranes. There is a general discussion for each different case which is followed by more special reactions dealing with synthetic applications and asymmetric versions. From a didactical point of view, the detailed schemes in this chapter are of major importance since they will provide easy understanding for readers who are not familiar with catalytic processes. The contribution then closes with a short discussion on cross-coupling reactions.

Chapter 2, by M. Lautens and M. Dahlmann, focuses on hydroalumination reactions. In the first part, differences in comparison with hydroborations are pointed out, followed by a discussion of the different catalyst systems known so far. The second part is devoted to hydroalumination reactions as key steps in the construction of more complex organic molekules as they have been developed mainly by Lautens himself.

Chapter 3 is dedicated to catalytic hydrosilylation and has been authored by J. Tang and T. Hayashi, well-known authorities in this area. In view of the highly sophisticated level that this reaction has reached over the past decade, only enantioselective examples have been included. On 17 pages the authors discuss the respective mechanisms, followed by all the important particular aspects that range from substrate geometry to intramolecular variants.

The currently very actively investigated area of catalytic hydroamination is summarized in Chapter 4. J.-J. Brunet and D. Neibecker give a very thorough review of the current situation in hydroamination of olefins and acetylenes, and also include a detailed historical description and comment on heterogenously catalyzed processes. Unfortunately, one of the inherent disadvantages of all review articles is also present in this chapter: since the literature coverage could only be updated to the end of 1999, there are no references to important recent work by Hartwig.

When one remembers the paramount importance of chiral phosphorus ligands in asymmetric catalysis, the interesting possibilities offered by related hydrophosphonylation reactions will be immediately evident. Current efforts in this area are summarized by D. K. Wicht and D. S. Glueck. As well as acetylenic and olefinic substrates, the authors focus on related additions to carbonyl groups. Compared to the advanced stage of development of related hydroaminations, hydrophosphorylations are still at the beginning of their development.

The next contribution by Y. Kataoka and K. Tani, one of the pioneers of heterofunctionalization, is divided into two topics: it begins with a discussion on synthesis and isolation of hydrido(alkoxo) transition metal complexes and related structures. Some readers may feel that such a detailed description (nearly 20 pp.) on inorganic structural chemistry is inappropriate here. While it remains unknown whether or not the compounds discussed might serve as future catalysts or catalyst precursors, there is a general tendency in review articles on catalytic processes to omit the chemistry of the metal complexes involved or that of related complexes. The present work is a pleasant exception, inviting readers to reflect on future developments for suitable catalysts. Following this part, the known catalytic addition reactions to alkenes and alkynes are reviewed in depth. It becomes evident that our present knowledge of such reactions is very small and that, given the lack of mechanistic insight, a significant effort will be required to drive this area into truly efficient catalysis.

The common assumption that sulfur compounds will inevitably shut down catalyst activity is refuted by H. Kuniyasus. In his contribution it is shown that activation of both S–H and S–X/S–S groups is generally possible, which leads to new reactivity in heterofunctionalization processes. A short digression on stoichiometric reactions closes this section.

The book ends with a chapter on hydrozirconation, authored by A. Igau. With a content of 30 pages this chapter is relatively short, especially considering the many recent applications of this reaction in organic synthesis. Nevertheless, it gives a concise summary emphasizing the synthetic potential of this reaction and important issues such as selectivity, reactivity, and substrate specificity.

Despite all these high quality contributions, the book does not give the impression of a unified treatment but rather a collection of reviews. Most certainly, it was not a good idea to opt for an alphabetical listing. It would probably have been better to rely on conceptual aspects. For example, hydroalumination and hydrozirconation are thematically closer than their positions in the book suggest. Although those readers who only wish to use the reviews as separate information sources are well served, a good monograph requires a stronger connection of the individual chapters. The schemes and artwork contain a relatively small number of mistakes; where they occur, they can be corrected easily within the context. As it is often the case, the stereochemical descriptors have not been chosen with sufficient care: for example, three different descriptors are present at once on pages 158–9 where one of them would have been sufficient! A more important drawback is the inadequate index, which also contains several mistakes. For example, the names of Sharpless and Shibasaki do not appear on the listed pages but on the following ones. Moreover, it is not easy to understand how a book on catalytic reactions can contain only a single index reference each to key words such as “catalyst” and “palladium”. Experts on catalysis will find it easier to search through the table of contents. All these objections do not detract from the impression that the chapters have been written in a very accurate and stimulating manner. The non-specialist reader will certainly encounter some difficulties in integrating the respective chapters within the area of asymmetric catalysis as a whole, and those who want only a brief overview will be better served by the book *Transition Metals for Organic Synthesis* by Beller and Bolm. For all experts and others interested in catalysis chemistry, and for PhD students who wish to become familiar with the subject, the present book offers a good source of sound knowledge on a variety of modern aspects of catalytic heterofunctionalization reactions.

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