

Book Reviews

Stereochemistry of Radical Reactions. Concepts, Guidelines, and Synthetic Applications. By D. P. Curran, N. A. Porter, B. Giese. VCH: Weinheim, 1996, 280 pp, hardback. DM 148. ISBN 3-527-29372-8.

During the last fifteen years, radical reactions applied to organic synthesis have become a field of intensive research and exciting developments. Efficient ways of conducting inter- and intramolecular reactions have been developed and spectacular progress has been made in stereochemical control. The three authors of this book have played a key role in this field and it is therefore very fortunate that they have decided to team up to write a comprehensive review on the stereochemistry of radical reactions.

The book is divided in 6 chapters grouping the reactions according to the type of stereochemistry (substrate control, chiral auxiliary control) and the nature of the radicals and of the radical traps (cyclic and acyclic). This organization is logical and very convenient for the reader entering this field as well as for the experienced reader looking for specific information.

Chapter 1 is an introduction describing the basic principles which allow to run efficiently radical reactions. This chapter underlines also the stereochemical analogies between radical, ionic and pericyclic reactions.

Chapter 2 deals with substrate control in cyclization reactions. A large body of literature is available on this topic and the authors have organized this chapter so that the reader will be able to find rapidly guidelines to rationalize and predict the stereochemical outcome. Butenyl and pentenyl radicals are discussed first but the major part is devoted to cyclization of hexenyl radicals. The well-known Beckwith-Houk model is explained with clarity, the scope and limitations of the model are expressed. The part devoted to group-selective cyclizations is highly interesting but could have been shorter.

Chapter 3 is dedicated to substrate control in cyclic systems. This chapter is clear, concise, and the rules which govern the stereochemistry are very apparent. Steric and stereoelectronic effects are discussed on judiciously selected examples.

Chapter 4 describes substrate control in acyclic systems. This field has grown very rapidly within the last few years. The different models which have

been developed are presented and the basic principles are simple to understand. However, more comments on analogies and differences between radical and ionic reactions would have been useful to illustrate the specificity of radical reactions.

Chiral auxiliary control is presented in Chapter 5. General considerations about radical conformations are mentioned and used to show some unique possibilities offered by chiral amides. Uses of C₂-symmetry, steric interactions and dipole-dipole interactions are discussed with interesting consideration on possible future developments. Chiral esters and chiral auxiliaries of electron rich radicals are also discussed.

In Chapter 6, several particular cases not easy to classify such as radical-radical reactions (coupling and dismutation), rearrangements (acyloxy migration, phosphatoxy migration and allylperoxy rearrangement) and alkene-forming reactions are treated.

The goal of this book, which was to explain the important concepts and guidelines for stereoselectivity control of radical reactions is fully achieved. It represents a unique and comprehensive source of information allowing synthetic organic chemists to introduce radical steps in retrosynthetic analysis. Even people not directly involved in radical chemistry will benefit from its reading since the principles developed in this book are general for asymmetric synthesis and may also be used to design new ionic or pericyclic reactions. It should be present in the library of all departments and groups engaged in organic synthesis. Moreover, due to its outstanding didactic approach and the announcement of a soft-cover version, this monograph is recommended for personal purchase by researchers, graduate students and postgraduate students involved in asymmetric synthesis. Further, this book would be well suited as a textbook for an advanced course in the field.

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Synthetic Methods of Organometallic and Inorganic Chemistry, Volume 1. By W. A. Herrmann, A. Salzer. Edited by W. A. Herrmann. Thieme: Stuttgart, 1996, 182 pp, hardback. DM 124. ISBN 3 13 103021 6.

Every generation of synthetic chemists "grows up" with reference series that collect, or provide citations to, common preparations and techniques. Those that are updated with annual volumes often become unwieldy or less user friendly. However, those that are not continuously updated sacrifice timeliness. Furthermore, new editions constitute major editorial undertakings.

It is to the great advantage of all synthetic chemists that a classic German language compendium, Georg Brauer's "Handbuch der Präparativen Anorganischen Chemie", has been reissued in English in a thoroughly updated and modernized format. This reference first appeared in 1954, with second and third editions following in 1960 and 1975-1981. The eight volume 1996 version is edited by W. A. Herrmann, and retitled as "Synthetic Methods of Organometallic and Inorganic Chemistry". However, many procedures describe reagents or catalysts commonly used in organic transformations, thus providing a valuable resource for the organic community as well.

The contents of Volume 1 are concisely described by its title. A 6 page review of the inorganic and organometallic literature is provided first. Textbooks that cover main group and transition metal organometallic chemistry are distinguished from those that cover only the latter. Other works that collect detailed preparative procedures are listed, and annotations on particularly useful features are provided. Although there is currently little in the way of relevant internet-based resources, this will certainly not be the case for subsequent editions.

A 20 page review of common laboratory techniques is then provided. Gas and solvent purifications, and Schlenk techniques, are emphasized. More specialized procedures are detailed, with clearly rendered figures, in the individual compound preparations. Some guidelines on safety and toxicity are given. However, users are left to their own judgment, knowledge, and common sense on many points. For example, the explosive properties of diazomethane and carcinogenicity of Cr(VI) are adequately stressed, but no precautions accompany the mechanical grinding of platinum-on-asbestos into fibers.

The bulk of Volume 1 consists of preparations of commonly used starting materials. The subsequent seven volumes, which will be reviewed in later issues, are organized by element. Although a separate volume for starting materials is logical, it is of course a subjective decision as to what should be included. Syntheses of substituted cyclopentadienyl ligands, and diazoalkanes, are clearly appropriate. However, it is not as obvious which phosphines constitute common starting materials, and which are best placed in Volume 3, where other phosphorus compounds are grouped. Organolithium and organomagnesium compounds are similarly split between two volumes. Thus, the apparent lack of a comprehensive index for all eight volumes is a shortcoming. There are also some oversights. For example, the synthesis of 1,2,4-tris(*t*-butyl)cyclopentadiene is described, but no guidance is given for the requisite bis(*t*-butyl)cyclopentadiene starting material.

Regardless, there are numerous exceptionally useful procedures. In selected cases, alternative routes are also supplied. Key physical properties are given for most compounds. Especially modern or topical procedures include C₆₀, the water soluble phosphine P(3-C₆H₄SO₃Na)₃, and chiral titanium "TADDOL" complexes that see use in enantioselective organic synthesis. There are also useful preparations involving silica and glass supports, and the immobilization of chromium or manganese species. Some recycling procedures, such as for rhodium residues, are also described.

A formula index has been eschewed in favor of a format that appears to list every conceivable synonym or heading for a compound. For example, (η^5 -C₅H₅)Co(CO)₂ is found under "carbonyl complexes" and "cobalt compounds" as "dicarbonyl(η -cyclopentadienyl)cobalt". It is also listed under "cyclopentadiene complexes" as "(η^5 -cyclopentadienyl)dicarbonylcobalt". However, some substituted cyclopentadienes are collected under the heading "cyclopentadiene", whereas others are not.

In summary, this is the inaugural volume in an immensely useful series. All readers of this journal will want to have the same access to "Synthetic Methods of Organometallic and Inorganic Chemistry" as "Organic Synthesis", "Fieser and Fieser", or the more recent "Encyclopedia of Reagents for Organic Synthesis".

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