

Book Reviews

Carbohydrate Building Blocks, By M. Bols. Wiley: New York, 1996, 182 pp, hardback. £ 40. ISBN 0-471-13339-6.

It is now well recognized that carbohydrates represent an extremely rich class of highly functionalized enantiopure molecules. In spite of their elaborated structure, many of them are relatively inexpensive and some are amongst the cheapest organic compounds, being produced in large quantity and high purity. In spite of these advantages, the potential of carbohydrate derivatives for chemical synthesis has been exploited only recently, even though the interest in sugar derivatives as starting material spread rapidly through the synthetic chemist community after this idea was launched by some outstanding contributions and in particular S. Hanessian's book "*Total synthesis of natural products. The chiron approach*". However, the complexity of sugar is a fact explained mainly by the possibility of structural modifications of monosaccharides (open and cyclic forms, either furanose or pyranose) and the diversity of oligosaccharides, in terms of regio- and stereoisomers. This is why many of those who are not familiar to carbohydrates may feel reluctant to undertake a sugar-based synthetic work, having in mind that the classical selective manipulation of hydroxyl groups might constitute a tedious task, in a not so easy field. The new book proposed by Mikael Bols "*Carbohydrate Building Blocks*" is conceived to help and guide them in the sense that in contrast to comprehensive treatises, it focuses on data which is most valuable for preparative work.

After an introductory section dealing with the source and cost of the most important sugars, the first part of the book contains 11 chapters which correspond to the main classes of sugar derivatives. For each of them, the classical reactions for either preparation or transformation are presented. Hence, this concise survey gathers a large number of high-yielding procedures leading to selectively protected (acetal, acetyl, acyl, ether...) carbohydrate derivatives, oxidation products (aldonic acids, lactones), reduction products (carbohydrate polyols), 1,6-anhydro sugars, products of base/acid treatment and disaccharides, mainly. The general trends which explain the selectivity of a particular reaction, such as the relative reactivity of hydroxyl groups for example, are indicated, thus providing a rationale for the presented data. In addition to the text, a rather extended graphic representation makes this book attractive, easy to read, with the more

important data (structures, references, yields) at hand.

This is followed by a compendium of building blocks classified according to the types listed before. Most of them can be prepared in four steps, or less, from a cheap precursor. In addition to the pictorial representation of a particular structure, its registry number according to *Chemical Abstracts* is indicated, followed by a reference to the literature for its preparation, the name of its precursor and the number of synthetic steps to be completed from the starting material. In all, a collection of 619 structures and about six hundred references are proposed. The fact that long-known and well-established synthetic procedures are often cited is certainly not a weakness of this book. However, quotation of quite recent synthetic work or review articles on specific topics would have been advantageous for those interested in more comprehensive information, alternative methods or updated point of view.

The last part of the book provides the key for retrieving data to be used at the retrosynthetic stage. Four indexes can be found there. The first and most important one is a stereochemical index, containing up to 98 different chemical sequences made of up to 7 chiral centers. In many cases, the sequences, shown in an extended *zig zag* representation, are of the polyol type. However, the carbinol groups, not necessarily contiguous, might be separated by one or more methylene groups. Additional patterns resulting from the replacement of hydroxyl groups by either a heteroatom (halogen, nitrogen) or a carbon substituent, are also included. For each sequence, the appropriate configurations in the *D* and *L* series are quoted as well as the numbers corresponding to possible precursors to be found in the compendium. Partially protected polyol derivatives originating from 10 common pentoses, hexoses and ketoses are listed next. This makes the identification of diversely configured sugar derivatives with either one or several free hydroxyl groups a straightforward task. This should be most helpful in the case of functional group conversion, protection/deprotection strategies and oligosaccharide synthesis. Finally, two indexes for compounds containing either a carbocyclic ring or a branched carbon chain are provided.

In summary, this book exploits the vast practical experience accumulated in the carbohydrate field. It has been deliberately elaborated to provide practical means for an easy selection of enantiopure building blocks, amongst a large array of easily accessible sugar derivatives. This is the first attempt to provide

the synthetic chemists with an extended data collection and indexes to facilitate and even optimize the search of suitable building blocks. The novelty of this procedure will, no doubt, contribute to the appreciation of this book and to a more effective use of sugar derivatives in organic synthesis.

J.-P. Praly, Université Claude-Bernard Lyon 1, France

Carotenoids Volume 2: Synthesis. Edited by G. Britton, S. Liaaen-Jensen, H. Pfander. Birkhäuser: Basel, 1996, 359 pp, hardback. DM 168. ISBN 3-7643-5297-3.

Several of the most prominent groups presently working in the field of carotenoid synthesis have put together a well organized book that describes the current state of the art in carotenoid synthesis. It should be an essential reference book for anyone involved in research related to these important natural pigments. The techniques covered in this monograph will be useful for the synthesis of new natural and artificial polyene based compounds. It is hoped that the availability of these pigments would enhance the research into known functions and properties of carotenoids and catalyze the search for new roles of carotenoids in natural and synthetic systems.

Carotenoids Volume 2: Synthesis, is organized into three chapters. Chapter 1 includes a historical overview of the development of carotenoid synthesis and perspectives of the field, strategies for building the carbon skeleton and methodology used in the characterization of the final products of the synthesis as well as the intermediates.

Chapter 2, entitled "Coupling Reactions", is divided into four parts and describes with numerous examples the most important reactions used in the assembly of the conjugated system, namely, the enol ether and aldol condensations, organometallic reactions, Wittig olefination and the sulfone coupling reaction. Because the synthesis of carotenoids played an important role in the development of organophosphorous chemistry, Part III, which describes the Wittig and Horner-Emmons olefination reactions, figures prominently. Mechanistic considerations and classic examples of the synthetic strategies discussed in Chapter 1 are given.

Chapter 3 is divided into nine parts. Part I, "Polyene Synthons", together with Appendix I and the Tables in Chapter 2 provide a comprehensive list of the synthons used in carotenoid synthesis. Parts II and III emphasize the synthesis of the end groups and the construction of the carotenoid molecule. Although the field is not covered comprehensively,

key groups and carotenoids are treated. Some of the most abundant naturally occurring carotenoids have the polyene chain modified by the presence of allenic groups (e. g., peridin, a photosynthetic light-harvesting pigment in some algae). Its C₃₇-skeleton, abnormal arrangement of side-chain methyl groups, presence of a butenolide ring structure, five asymmetric carbon atoms and a chiral axis in the allenic structure provided a major challenge for its synthesis in the natural optically active form. The synthesis is described in a schematic manner in Part IV and includes a new synthetic methodology (the sulfone method) that has been developed for the construction of conjugated alkylidenebutenolides. Part V presents the total synthesis of (Z) isomers and gives practical advice for the design and synthesis of geometrical isomers at different points on the polyene chain. Isotopically labelled carotenoids and retinoids have proven valuable for the study of function and structure of these pigments in their protein environments. In Part VI the tools for synthesizing labelled carotenoids are discussed. Uses and synthesis of ¹³C and ²H labelled synthons are described starting from simple isotopically enriched materials such as acetonitrile, acetic acid, methyl iodide and bromoacetate. The technical syntheses of Part VII tie together laboratory scale work with industrial methodology and illustrate the development of environmentally friendly procedures for the large scale synthesis of carotenoids.

At the end of the book eight worked examples with experimental procedures are included. These examples are well chosen and developed in such detail that they are ready to be incorporated in the laboratory sections of organic chemistry classes.

The numbering system of the naturally occurring carotenoids in Carotenoids Volume 2 coincides with the numbering used in the Key to Carotenoids, a compendium listing all of the known carotenoids. The reference information one can obtain from the combination of these two books is comprehensive and remarkably easy to access due to the impeccable organization of both volumes.

Ana L. Moore, Arizona State University, Tempe, Arizona, USA

Advances in Metal-Organic Chemistry, Volume 4, Edited by L. S. Liebeskind. JAI Press: Greenwich, 1995, 317 pp, hardback. £ 62.50. ISBN 1-55938-709-2.

Volume 4 of Advances in Metal-Organic Chemistry presents contributions in the areas of organocopper chemistry, industrial prostaglandin synthesis, chromium(0)-promoted cycloadditions, synthetic applications of diene tricarbonyliron complexes, and transition-metal catalyzed carbonylations. An internationally recognized group of authors covers

these diverse topics with a refreshing mix of personal style and scholarly breadth.

B. Lipshutz dedicates much of his chapter on recent progress in his group in higher order cyanocuprate chemistry. This personal account covers synthetic aspects of transmetalation schemes of silicon- and tin-intermediates, alkenylalanes, and zirconocenes. In addition, spectroscopic evidence for the existence of "higher order" cyanocuprates is discussed. This is obviously a topic of continued discussion in the current literature that is fueled by the indisputable synthetic utility of cyanocuprates. References through mid-1993 have been considered in Professor Lipshutz' analysis.

J. R. Behling, P. W. Collins, and J. S. Ng present the Searle process for prostaglandin synthesis. In a practical extension of the cyanocuprate chapter, this report focuses on vinylstannane-cuprate transmetalation after a short discussion of the historic background of the conjugate addition strategy. An important step in the large-scale synthesis of the antiulcer agent misoprostol takes advantage of an exchange between a vinyl stannane and $\text{Me}_2\text{CuCNLi}_2$ followed by an in situ conjugate addition, enolate trapping sequence. The optimization of this process is discussed in detail and includes experimental protocols.

J. H. Rigby describes transition metal-promoted higher order cycloaddition reactions. The high levels of stereocontrol, accommodation of extensive functionalization, and the high level of convergency are attractive features of $[6\pi+2\pi]$ and $[6\pi+4\pi]$ cycloaddition reactions and receive special attention in this treatise. Synthetic applications of cycloheptatriene-tricarbonylchromium(0) cyclo addition chemistry range from thermally and photochemically induced bicyclo[4.4.1]undecane preparation to the elaboration to diquinane and

heterocycle synthesis. Reference coverage extends through 1992.

R. Gree and J. P. Lellouche present a thorough abstract of the use of cyclic diene tricarbonyl iron complexes in organic synthesis. In addition to general data on the synthesis, resolution, and reactivity of neutral complexes, preparation and reactivity of complexed cations are discussed.

Special chapters introduce the reader to the synthesis of arachidonic acid metabolites and other polyunsaturated natural products and heterocycles with this methodology. Particularly useful is an appendix that lists synthetic operations that are compatible with the dienyl tricarbonyliron moiety. The extensive tabular collections establish this chapter as a powerful reference source. With the inclusion of 1994 and some 1995 references, this is also the most up-to-date chapter in this volume.

M. Hidai and Y. Ishii review their work on novel carbonylation reactions catalyzed by transition metal complexes. Synthetic and mechanistic concepts of the palladium- and platinum catalyzed cyclocarbonylation of allylic esters are presented. A second part of this chapter is directed at the use of homogenous multimetallic catalysis for the hydroformylation of olefins and the formylation and carbonylation of aryl iodides. Proposed catalytic cycles, solvent effects, and effects of metal variations are discussed. Two references from 1994 and 1995 are included.

The high quality of text and drawings and the broad general utility and interest of the subject chapters establishes the series and Volume 4 specifically as a highly recommended addition to any chemistry library. It will also be a useful source for graduate students and anyone interested in synthetic applications of organometallic reagents.

Peter Wipf, University of Pittsburgh, USA

Book reviews are generally by invitation. Publishers should send books to Dr Sarah Ryan, Book Review Editor, Synthesis Editorial Office, Georg Thieme Verlag, Rüdigerstrasse 14, D-70469 Stuttgart, Germany.