Book review

Rodd's Chemistry of Carbon Compounds; Supplement to the 2nd Edition, Volume I, Aliphatic Compounds, Part FG: edited by MARTIN F. ANSELL, Elsevier Scientific Publishing Company, Amsterdam and New York, 1983 xvi + 372 pages + Subject Index, \$115.00, Dfl. 270.00.

This supplement to the 2nd edition of "Rodd" is intended to update the coverage of carbohydrates and related compounds in Chapters 22-25 thereof. It, therefore, contains chapters on polyhydric alcohols, monosaccharides, oligo- and poly-saccharides, and tetrahydric alcohols, written by experts in these fields. As stated in the Preface, the principal objective of "Rodd" is to allow a knowledgeable chemist or biochemist an immediate access to a particular area of organic chemistry. Therefore, this supplement should provide a concise but comprehensive survey of developments in carbohydrate chemistry during the past 15 years. Considering the enormous number of relevant publications during this period, actual literature citings must necessarily be very selective, but they should be representative of the most important advances. Certainly, this book does not attempt to duplicate in any way The Chemical Society's Specialist Periodical Reports; neither is it an in-depth review of the Advances type. However, the authors have been careful to include useful lists of appropriate reviews near the beginning of each chapter or section. Generally, these citations cover the period 1965-1980, although the preface to the book is dated Dec. 1982.

Chapter 22, by R. J. Ferrier, on "Polyhydric Alcohols (Alditols)", is brief, because the alditols were fully covered in the 2nd edition. It surveys the occurrence, conformational analysis, synthesis, and reactions of the compounds, with reference mainly to work published in the late 1960's and early 1970's.

The same author has written a much longer chapter (No. 23, 210 pages) on "Monosaccharides and Their Derivatives", even though the nucleosides are not included. This chapter is a very clearly written and thorough survey of monosaccharide chemistry, again with emphasis on topics not fully treated earlier by Hough and Richardson. The text is illustrated by a large number of clearly drawn schemes of formulae, which are generally placed exactly where they are needed by the reader to avoid page turning. As in the other chapters, literature references take the form of insertions within the text, also a convenience for the reader. As in chapter 22, there are almost no references from the 1980's, which can be a problem for fast-moving areas of carbohydrate chemistry, especially as most of the reviews cited are from the period 1967–1973. Thus, in the very thorough treatment of conformational analysis, n.m.r.-spectroscopic methods are stressed, but the intentional

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emphasis is on ¹³C, the inference being that the newer technique has more exciting possibilities than ¹H-n.m.r. spectroscopy. However, the advent of 2-dimensional methods (not mentioned) has surely changed this perspective, especially when the problem of sensitivity is considered. Because of the requirement for repetitive pulsing and the need to obtain various modes of proton-decoupled spectra, the cost of ¹³C-n.m.r. spectra becomes prohibitive for many laboratories in terms of computer time. Also, the need for 10–100-mg samples is against the current trend towards the analysis of ever smaller samples (µg levels for the newer ¹H-applications), which is a serious limitation on ¹³C methods for isolation of natural products occurring at very low levels in plant or animal tissues, or for the end-products of long, multistage syntheses. Otherwise, this chapter contains an excellent treatment of such factors as shielding and bonding effects that decide the ¹³C-chemical shifts in the spectra of a variety of monosaccharides.

After a brief treatment of other analytical and separatory methods, and a very brief mention of synthesis from non-sugar precursors (c.f., the long review by Zamojski and co-workers in Advances in Carbohydrate Chemistry and Biochemistry, Vol. 40), there is a more extensive discussion of oxidation of monosaccharides, with emphasis on the value of the products as synthetic starting-materials.

Strategies for different approaches to glycoside synthesis, including the 1,2-cis-glycosides, are thoroughly reviewed, and several of the methods that have led to spectacular recent progress, particularly for oligosaccharide synthesis (see later comments) are described. This comprehensive coverage of synthetic methods is continued in a survey of all the major classes of protective groups, with emphasis on recent developments. Other sections cover the synthesis and reactions of amino sugars, deoxy sugars, branched-chain compounds, thio sugars, and unsaturated sugars. Treatment of the last group is especially thorough, reflecting the author's particular expertise in this area, and the versatility of these compounds as synthetic intermediates, but some erroneous nomenclature detracts from this section.

Chapter 24, "Oligosaccharides, Polysaccharides, and Related Compounds", by R. Khan, J. K. Wold, and B. S. Paulsen, begins with a survey of synthetic methods, and physical methods of structure-determination. Unavoidably, the section on synthesis cannot reflect the spectacular recent progress in this field, even though it is heavily documented (with references to work performed in the 1970's). Thus, any reader requiring an authoritative and systematic discussion of the factors affecting the yields and stereochemistry of oligosaccharide-forming reactions should consult a more recent review, such as that by Hans Paulsen [Angew. Chem., Int. Ed. Engl., 21 (1982) 155–224]. There is some overlap between chapters 23 and 24 on this subject, but this is not a problem, and the synthetic procedures are illustrated by very clear reaction-schemes. It is surprising to find no discussion of silver triflate as a condensation promoter, especially as its use is noted in the section on individual oligosaccharides (e.g., on page 288). For the section on n.m.r. spectroscopy, similar comments apply, because of the speed of recent development (see earlier comments). Again, there are very extensive literature-citations, but

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anyone seeking familiarity with the utility of n.m.r.-spectroscopic methods for oligosaccharides would need to consult current literature or recent reviews. The discussion of mass spectrometry primarily concerns the applications of electron-impact methods, but fragmentation mechanisms are well reviewed, and it is pleasing to note some reference to the "soft ionization" methods that have revolutionized the mass spectrometry of complex carbohydrates in recent years. After a few pages on X-ray crystallography, primarily of common disaccharides, there follows an extensive "catalogue" of individual oligosaccharides, including melting points, optical rotation, brief notes on method of synthesis, and literature reference. This format is based on that employed by Aspinall et al. in the 2nd edition.

After a forty-five-page treatment of polysaccharide occurrence and structure determination, the remainder of Chapter 24 consists of a discussion of the major classes of polysaccharides, treated individually. In the "structure" section, there is a good survey of methylation analysis and Smith degradation, but, surprisingly, no discussion of endoglycosidases as structure probes. The coverage of plant and seaweed polysaccharides is comprehensive, with a well balanced and extensive selection of literature citations up to 1980. The overwhelming impression gained from this, and the following sections on complex saccharides of bacterial and mammalian origin, is one of an amazing diversity of structures. This results from the unequaled potential of sugars to exist in various combinations of sequences, linkages, anomeric configurations, and branching patterns, with presence of O- and N-substitution (by, for example, acetyl, glycoloyl, methyl, 3,6-anhydro, lactyl ether, pyruvic acetal, sulfate, phosphate), and conjugation with lipids and proteins. The section on lipopolysaccharides is very brief, with only a few references to the large amount of work on this topic coming from the Swedish and German groups. Glycoproteins and proteoglycans are covered in nine pages, which means that only the surface of this extremely important topic is skimmed, and an interested reader would need to consult one of the excellent recent reviews (some of which are cited). There is a serious error on page 336, which states, for the N-glycoproteins, "In the first group the pentasaccharide core is substituted exclusively by β -D-mannopyranose residues", when all except the first of these residues is, in fact, α -linked. There is the interesting observation (page 340) that true repeating-sequences are not found in glycoproteins (as distinct from proteoglycans). This view may have been commonly held until recently, but the occurrence of "lactosaminoglycans" [repeating β-D-Galp-(1→4)-D-GlcpNAc units] is now a familiar feature of many important glycoproteins.

Chapter 25, "Tetrahydric Alcohols, Their Analogues, Derivatives and Oxidation Products", by R. A. Hill, reviews the occurrence, synthesis, properties, and reactions of erythritol, threitol, their derivatives, and related compounds. The reactions are illustrated by large, clear, schemes of formulae, and the literature coverage is through 1979.

A very useful feature of this supplement to "Rodd" is the comprehensive subject index. Most of the entries are the names of compounds, but some reactions

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and techniques are also included. The names employed for compounds are a mixture of trivial and supposedly systematic (i.e., those used by the authors), and the latter are not always in conformity with the Rules, as is apparent from the "Contents" pages of Chapters 23 and 24. The book consists of a very clear reproduction of the original typescripts, unlike the 2nd edition, which was typeset. Apart from aberrations of nomenclature, there are very few errors, and the supplement continues the tradition of high quality of presentation established in the original volumes of "Rodd".

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