





Book review

Monosaccharide Sugars: Chemical Synthesis by Chain Elongation, Degradation, and Epimerization

by Zoltán Györgydeák and István F. Pelyvás, published by Academic Press, San Diego, 1998, xvii + 508 pp., ISBN 0-12-550360-1, Price \$89.95 (hardcover, with a foreword by Sir Derek Barton)

This handsome book is intended as a sourcebook for the practising carbohydrate specialist and for the general organic chemist who seeks to make use of the unique opportunities for stereocontrolled transformations offered by sugar-based starting materials. It critically summarizes in a most comprehensive fashion the available strategies for the practical preparation of sugars and derivatives, as well as chiral building blocks obtainable from their modification, according to the three fundamental principles mentioned in the title.

The book provides access to a vast body of literature—some 1700 references—thus relieving the reader of much tedious search in the library. It covers the subject from Emil Fischer's and other early pioneers' seminal work, with time-honored but still dependable procedures, up to early 1996 with the multifarious developments of modern reagents and novel transformations. (A note added in the proof contains numerous 1997 references.) A certain limitation lies in the fact that the methodologies compiled are taken from the field of nonbranched sugars exclusively. Discussion of either functional-group transformations involved in the methods presented, or enzyme-mediated reactions, is not within the scope of the book.

Ch. 1, 'Ascending Synthesis of Monosaccharides', is the longest (370 pp.) of three

chapters. Beginning with the formose reaction and synthesis from glyceraldehyde, it surveys the cyanohydrin synthesis, the formation of acid derivatives by means of nucleophilic substitution, the nitroalkane syntheses, chain extensions with diazoalkanes, malonic esters (Knoevenagel type), and phosphoranes (phosphonium ylides). Miscellaneous other methods for chain elongation include, for example, the use of Grignard and lithioorganic reagents; organo-silicon, -tin, and -boron compounds, and sodium dicarbonylcyclopentadienyliron; aldol condensation and the Reformatski reaction; extensions starting from glycals and acetylene derivatives, and reactions of aldehydo-sugars with formyl anion equivalents.

Ch. 2 (94 pp.) entitled 'Descending Syntheses of Monosaccharides', summarizes the MacDonald-Fischer degradation of sugar dialkyl dithioacetals via their disulfones, the Ruff degradation of calcium aldonates, the Wohl-Zemplén degradation of sugar oximes or aldononitriles, chain shortening by means of periodate or lead tetraacetate oxidation, the Curtius and Hofmann degradations of glyconyl azides and glyconic or glycuronic amides, respectively, and various further oxidative procedures, including electrochemical oxidation as well as photochemical chain descent.

A small final chapter (20 pp.) deals with preparative applications of the long-known isomerization of saccharides in alkaline medium, and the more recently developed epimerizations mediated by molybdate complexes or by amine complexes of transition or alkaline earth metals. A 10-page subject index concludes the book.

The daunting task of organizing the formidable amount of data published over

more than a century in countless journals (including many non-English ones) has been tackled admirably. The three chapters referred to are divided into 21 sections comprising 41 subsections. Each section begins with a concise introductory explanation of the nature and background of the chemical transformations involved, and then proceeds to give sevexamples of applications relevant considered of particular usefulness and reliability by the authors, and illustrated by clear formula schemes. The book is replete with detailed experimental descriptions drawn from the original literature (offset by smaller print, and translated into English where applicable), with characterization of products by physical data. These descriptions are complemented by accompanying tables enumerating analogous applications, with listings of educts, products, reaction conditions, yields, and other parameters as appropriate.

This reviewer has found few glaring omissions in the coverage, and no serious errors. In some places only one might have wished, for the sake of completeness, for inclusion of important work which has been omitted. For example, the path-breaking work of R. Kuhn and co-workers on cyanohydrin synthesis starting with glycosylamines and leading, after catalytic hemihydrogenation of the resulting

aminonitriles, to all possible 2-amino-2-deoxy-D-hexoses and all 2-amino-2-deoxy-D-pentoses, is not mentioned in the cyanohydrin section. Similarly, the versatile method of nitromethane cyclzation of sugar dialdehydes (generated by periodate oxidation of methyl glycosides), which leads to 3-deoxy-3-nitro (and thence 3-amino-3-deoxy) aldopyranosides, is missing from the otherwise very detailed section on nitroalkane syntheses, even though the methodology represents a chain extension 'from within'.

The style of presentation throughout the book is easily comprehensible, and the quality of print, figures, tables, and general layout is first-rate, as may be expected from an edition of a renowned publishing house. The book should grace the shelves of every chemical library, and every chemist engaged in synthetic carbohydrate projects or the procurement of chiral synthons might be well advised to have a personal copy handy on his desk. It should also be a treasure trove for those who wish to prepare graduate lectures in the field.

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