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Book review

Methods for the Oxidation of Organic Compounds: Alcohols, Alcohol Derivatives, Alkyl Halides, Nitroalkanes, Alkyl Azides, Carbonyl Compounds, Hydroxyarenes and Aminoarenes, by Alan H. Haines, Academic Press, London, 1988, xx + 447 pages + Subject Index, $129.00; £69.50.

This is a companion volume to an earlier book by the same author on oxidation of hydrocarbons (A. H. Haines, *Methods for the Oxidation of Organic Compounds: Alkanes, Alkenes, Alkynes, and Arenes*, Academic Press, London, 1985; see *Carbohydr. Res.*, 152 (1986) c1). Here, the scope has been expanded to include the oxidation of various types of polar compounds, and the author is to be congratulated on the success of the immense task of assembling a vast array of best synthetic methods on oxidation into one coherent volume.

The book covers over a hundred reagents, and about half of them are treated in depth (over 1550 references cited). It is divided into eight chapters, and each of these deals with a different class of substrate; sections are further subdivided on the basis of reagents or the type of reaction. Each sub-section contains examples of detailed preparative procedures in which the relevant theory is applied to optimizing practical results. Most of these are carefully worked out methods which have proved themselves in the exacting area of the synthesis of natural products. Discussion of reaction mechanisms, including questions of reactivity, selectivity, and stereochemistry provide the reader with additional information to help in deciding whether the method is suitable in a particular case.

Although the book is designed for practising organic chemists in general, in the opinion of this reviewer, carbohydrate chemists will benefit immensely from this volume. The introductory chapter deals primarily with the scope and organization of material; it also outlines the arrangement of some functional groups according to their oxidation state. Chapter 2 discusses a series of reagents for oxidation of alcohols to carbonyl compounds, and all these are important to carbohydrate chemists; the section includes the catalytic oxidation (platinum-on-carbon plus oxygen, the Heyns method), oxidation by halogens, oxidation by silver carbonate on Celite, and many others. Dimethyl sulfoxide–acetic anhydride reagent is effective in conversion of methyl 6-deoxy-2,3-*O*-isopropylidene-β-D-allofuranoside into the 5-ulose (81% yield), and ruthenium tetraoxide (preferred to the more poisonous osmium tetraoxide) is a specific oxidant for conversion of 1,6-anhydro-2,3-*O*-isopropylidene-β-D-mannopyranose into the 4-ulose (85% yield). Steric and stereoelectronic factors have been observed in the

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oxidation of certain sugars with active manganese dioxide. This reagent has proved to be effective in the stereospecific synthesis of carbazole alkaloids and related natural products [H.-J. Knölker, M. Bauermeister, D. Bläser, R. Boese, and J.-B. Pannek, *Angew. Chem., Int. Ed. Engl.*, 28 (1989) 223–225; H.-J. Knölker and M. Bauermeister, *J. Chem. Soc., Chem. Commun.*, (1990) 664–665; 1468–1470].

Chapter 3 examines the oxidation of esters and alkyl halides; a useful procedure involves conversion of primary alcohols into aldehydes *via* the photolysis of their pyruvic esters; for example, $H_2CCOCOCO \xrightarrow{h\nu} CHO$ and the preparation of 1,2:3,4-di-*O*-isopropylidene-α-D-*galacto*-hexodialdo-1,5-pyranose. Chapter 4 is devoted to oxidation of ethers, acetals, and metal derivatives of alcohols. The stereospecificity of some reagents is particularly interesting in certain oxidations of sugars. Chromium trioxide in acetic acid will oxidize acetals of aldehydes to esters. In this respect, glycosides (*e.g.*, hexofuranosides), being acetals, are oxidized by the reagent with ring rupture, to give esters of 4-hexulosonic acids. With pyranosides, the reaction is specific to β-glycosides, whereas, with furanosides, both the α- and the β-glycoside undergo oxidation.

Chapter 5 concerns the oxidation of amines, nitro compounds, and azides. Of importance to the carbohydrate field is the Nef reaction, by which α-L-glucose can be prepared from 1-deoxy-1-nitro-L-glucitol in 59% yield.

Chapter 6 describes the oxidation of aldehydes and ketones to carboxylic acids by old and new oxidants, including halogens, ozone, and potassium permanganate and other manganese-based reagents. Acetals can be oxidized by ozone to esters with remarkable stereocontrol, and this is illustrated with the ozonolysis of methyl glycopyranosides. The per-*O*-acetylated β anomers of methyl D-gluco-, D-manno, D-galacto-, and 2-deoxy-D-*arabino*-hexo-pyranosides, on treatment with ozonized oxygen in a solution of acetic anhydride containing sodium acetate, are converted into the corresponding per-*O*-acetylated methyl D-aldonates, whereas the corresponding α-glycosides are completely inert towards ozone under the same conditions.

Chapter 7 is dedicated to the classical oxidative cleavage of 1,2-diols and related 1,2-bifunctional compounds by periodic acid and periodates, by lead tetraacetate, by organic compounds of polyvalent iodine, and by bismuth-based reagents. The mode of oxidation is thoroughly discussed, and supported by many schemes. However, this chapter must be supplemented with a missing reference to a review of oxidation with periodic acid and periodates [A. J. Fatiadi, in *Synthetic Reagents*, Vol. 4, J. S. Pizey (Ed.), Ellis Horwood, Chichester, 1981, pp. 147–335].

Chapter 8 explores the oxidation of hydroxyarenes, aminoarenes, dihydroxyarenes, diaminoarenes, and aminohydroxyarenes to quinones. A series of reagents are available today for preparation of 1,2- or 1,4-benzoquinones from hydroxyarenes, and all of these are examined for their usefulness. The preferred reagent for oxidation of phenols to 1,4-benzoquinones is potassium nitrosodisulfonate (Fremy's salt; the Teuber oxidation), and the reagent suggested for forming 1,2-benzoquinones from phenols is benzeneseleninic anhydride (the Barton reagent). It can be added at this point that oxidation of phenols and dihydroxyarenes with sodium periodate (the Alder oxidation) or with lead tetraacetate (the Wessely oxidation) can afford unique coupling-products that cannot be prepared by any other means yet known. In this respect, there is an excellent book on the subject [M. Hudlicky (Ed.), *Oxidations in Organic Compounds*, ACS Monograph Series No. 186, American Chemical Society, Washington, D.C., 1990].

A very useful appendix consisting of tables from which the reader can find additional suitable reaction-conditions, products, yields, and key literature references is provided.

The author has produced an extremely practical book for chemistry students and for chemists in industrial and university laboratories. This reviewer has no hesitation in recommending that this book be acquired by every chemical library. Those who are particularly interested in the subject should buy a personal copy.

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