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Book reviews

Oxidation in Organic Chemistry: Part C, edited by WALTER S. TRAHANOVSKY, Academic Press, New York, 1978, xi + 380 pages + Subject Index, $34.00.

This is the third part of a treatise on oxidation in organic chemistry [Part A, K. B. Wiberg (Ed.) (1965); Part B, W. S. Trahanovsky (Ed.) (1973)], and the editor of and contributors to Part C are to be congratulated on maintaining the extremely high standard of production apparent in the earlier volumes. The book consists of five contributed chapters, and all of the authors are recognized authorities. The oxidation reactions covered are not limited to special classes of organic compounds; indeed, they are applicable to carbohydrates and other structurally related compounds.

A chapter by H. J. Reich (which occupies over one-third of the whole book) presents in a masterly way all important facets of new organoselenium reagents as applied to organic synthesis; it may be supplemented with the author's recent review on the same subject [H. J. Reich, *Acc. Chem. Res.*, 12 (1979) 22–30]. The text discusses the preparation of various organoselenium reagents, and includes six large Tables of numerous examples of their practical application, giving structure, reaction conditions, and yield. In addition to the known selenium dioxide oxidations [R. Rabjohn, *Org. React.*, 24 (1978) 261–320], the new diphenyl selenoxide reagent has been used for oxidation of hydrazides, amines, and catechols; also, the new benzeneseleninic anhydride has been successfully applied for the oxidative hydrolysis of dithiolanes and hydrazones to ketones, and for the oxidation of phenols to *o*-quinols and *o*-quinones. Some of the methodology described in this chapter has a counterpart in organosulfur chemistry [B. M. Trost, *Chem. Rev.*, 78 (1978) 363–382; *Acc. Chem. Res.*, 11 (1978) 453–461)]. Although a trace of selenium is very important in human nutrition, selenium and its compounds on the whole are toxic. However, the relative ease of selective oxidation at selenium and sulfur, and the much greater facility in cleavage of C–Se as compared to analogous C–S bonds makes organoselenium compounds the preferred reagents for performing oxidative transformations under mild conditions. The most important oxidative transformations include: (*i*) selenoxide *syn*-elimination to yield alkenes (frequently regiospecific), (*ii*) conversion of α-phenylseleno carbonyl compounds into carbonyl olefins, and (*iii*) 2,3-sigmatropic rearrangements. The chapter concludes with a discussion of mechanisms of selenium dioxide oxidation.

R. A. Johnson provides a chapter that is concerned with oxygenations by micro-organisms. Despite its specificity and the impressive results achieved, the use of microbial oxidations has not become commonplace. The unfamiliarity of chemists with the techniques of fermentation, and the inability to predict the micro-organisms that should be used to achieve a desired oxidation, have forced many to choose some alternative route. The chapter treats in considerable detail the oxygenation and hydroxylation of steroids, as well as several other substrates. A series of specific micro-organisms described includes *Pseudomonas putida*, *Sporotrichum sulfurescens*, *Rhizopus japonicus*, and *Canonetria decora*. The microbial oxygenations of olefins and the 1,2-dihydroxylation of aromatic rings are also discussed. The chapter, indispensable to all fermentation chemists and biologists, can now be supplemented by a recent study on microbial epoxidation of long-chain olefins (a 100% stereospecific synthesis) [H. Ohta and H. Tetsukawa, *J. Chem. Soc. Chem. Commun.*, (1978) 849–851].

Oxidations with peroxy acids and other peroxides are surveyed in a chapter by B. Plesnicar. The text discusses the preparation, and physical and some chemical properties, of organic peroxy acids, alkyl hydroperoxides, and peroxy esters, and gives a guide to experimental techniques. The oxidation of almost all types of organic compounds with peroxy acids and other peroxides is expertly covered, including the important epoxidation of olefins. Despite a considerable literature on the topic, the author has succeeded in providing a concise, yet clear, description of the present state of the art of organic oxidations with peroxides.

A chapter by Y. Ogata is devoted to oxidations with nitric acid or nitrogen oxides. It is a brief, but thorough, presentation of all major aspects of vapor- and liquid-phase oxidations with nitric acid and dinitrogen tetraoxide (N_2O_4). Fuming nitric acid acts as a nitrating agent for olefins and arenes, for example, electrophilic substitution by the ionic species NO_2^+; however, the nitration of alkanes in the vapor phase proceeds *via* a free-radical mechanism. The oxidation by nitric acid requires the presence of an initiator, such as nitrous acid or nitrogen dioxide (NO_2), and these conditions are found in dilute nitric acid. However, the reaction of nitrogen tetraoxide with olefins is conducted under oxygen in order to eliminate nitrogen oxide (NO), which yields dinitro compounds and nitro-nitrites. The chapter also reports on the reaction of nitric acid and dinitrogen tetraoxide with alcohols, alkyl halides, ethers, ketones, organo-nitrogen compounds (*e.g.*, heterocyclics), and organo-sulfur compounds. The kinetics and mechanism of action of the oxidants are presented and discussed.

S. K. Chakrabartty has written a chapter that deals with alkaline hypochlorite oxidation, still another useful "old" method. Oxidation by means of alkaline hypohalite solution has a notable record in carbohydrate chemistry, and this work is a useful supplement to an earlier study on its reactions with sugars. The chapter discusses the chemical nature of the oxidant, and the kinetics and mechanism of the classical haloform reaction; oxidation of saturated carbocyclic compounds, epoxidation, shortening of the chain length by oxidative decarboxylation (*e.g.*, the preparation of D-arabinose from D-glucose by a two-stage, hypohalite oxidation), and the cleavage of aromatic rings are also surveyed. The book concludes with a Subject Index, but an Author Index is not provided.

Because of its wide applicability, this book should be useful to organic synthetic chemists, biologists, biochemists, and chemists involved in pharmaceutical and medical research. In general, it is an excellent and scientifically sound monograph, containing an abundance of high-quality, structural formulas and reaction schemes; it is essential that a copy be in the chemical library, and most chemists should acquire a personal copy as the price is so reasonable.

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Xylitol, edited by J. N. COUNSELL, Applied Science Publishers, Ltd., London, 1978, xiv + 191 pages, $25.00.

This book is a compilation of the papers given at a symposium held in May, 1977, to discuss the food technology, biochemistry, and dental aspects of xylitol. There are ten chapters covering these three divisions, and each division is followed by a neatly edited discussion-section. Although the symposium was sponsored by industry, it is a credit to the symposium organizers and speakers to find that the material presented is not generally a commercial appeal for the use of xylitol as a sugar substitute in foods and confections, or as a "new" food ingredient. Each chapter is documented with references, and there are ample graphs and charts, and also metabolic and absorption schemes. There is very little overlap of the subject matter.

A few errors in the text need to be pointed out. A structure shown for D-xylan on page 3 is an unorthodox depiction having the anomeric carbon atom of each xylosyl residue at the left instead of at the right, is devoid of free hydroxyl groups and glycosidic oxygen atoms, and contains alternating β-L- and β-D-xylopyranoside units. The long-accepted, disaccharide repeating-unit for D-xylan is, of course, 4-*O*-β-D-xylanopyranosyl-β-D-xylopyranose. An attempt to rationalize the absorptive difference between xylitol and D-glucitol (sorbitol) on page 47 suggests that, whereas sorbitol possesses a chiral center at C-4, xylitol does not! Finally, the molecular weight of all forms of D-glucose, including D-glucopyranose, is 180, not 162 (page 47).

The book may be of value to food chemists and food technologists who need background information on the properties and uses of xylitol in foods. The price seems reasonable.

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