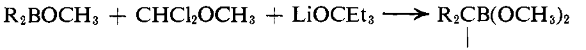
proceeds with retention of configuration at the migrating carbon. Such retention has been previously established for carbonylation[11] and for the cyanoborate reaction.[12] Consequently, in combination with the remarkable characteristics of the hydroboration reaction these procedures provide highly valuable methods for assembling carbon structures in a stereospecific manner with the aid of boron.

The following procedure is representative. A dry 500-ml flask, fitted with a septum inlet, magnetic stirrer, and reflux condenser, was flushed with nitrogen and maintained under a static pressure of the gas. In this flask was placed 19.6 ml of a 2.55 *M* solution of borane (50 mmol) in THF and 20.0 ml of THF. An ice bath was placed about the flask and 9.6 g (100 mmol) of cyclohexene was added. After 1 hr at 0°, 1.6 g (50 mmol) of methanol was added slowly to form the ester, methyl dicyclohexylborinate. To the reaction mixture was added 5.0 ml (6.53 g) (~10% excess) of DCME, followed by 25.4 ml of a 1.97 *M* solution of lithium triethylcarboxide (50 mmol) in hexane over 5 min. (The base was prepared from *n*-butyllithium and triethylcarbinol.) The reaction mixture was allowed to come to room temperature and maintained there for 0.5 hr. A heavy white precipitate, presumably lithium chloride, was observed. Then 20 ml of 95% ethanol was added, followed by 4 g of sodium hydroxide and 15 ml of 30% hydrogen peroxide (slow!). The oxidation mixture was cautiously heated and maintained at 50–60° for 1 hr to complete the oxidation. The aqueous phase was separated by saturation with sodium chloride. Distillation of the dry tetrahydrofuran phase yielded 8.2 g of dicyclohexyl ketone: bp 96–98° (1.2 mm); $n^{20}\text{D}$ 1.4838; yield, 85%.

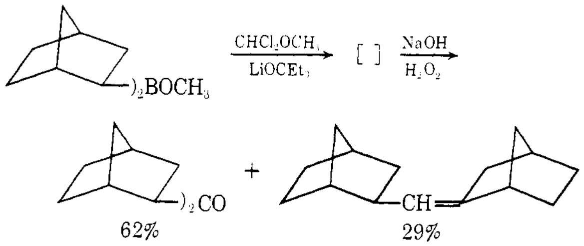
The hydroboration of cyclohexene, methylcyclopentene, and 3-methyl-2-butene can be controlled to yield the dialkylborane, readily convertible to the methyl borinates by treatment with methanol, as in the above procedure. All other olefins were converted to the dialkylchloroboranes by hydroboration with monochloroborane diethyl etherate,[1] and the latter was converted to the methyl esters by treatment with 100% excess methanol at 0° for 0.25 hr. The excess methanol, diethyl ether, and hydrogen chloride were removed under reduced pressure with an aspirator, THF was added to make a solution, ~1 *M*, and the reaction with DCME was carried out as above.

The intermediate in this base-induced reaction of methyl dialkylborinates with DCME has been identified as an α-chloroboronate[13] (eq 3). It was observed that



$$R_2BOCH_3 + CHCl_2OCH_3 + LiOCEt_3 \longrightarrow R_2\underset{\displaystyle Cl}{\underset{|}{C}}B(OCH_3)_2 \quad (3)$$

in some cases involving secondary alkyl groups there was formed, in addition to the ketone, small to moderate amounts of internal olefins.[14] These apparently arise from a competing elimination reaction of the intermediate. For example, methyl bis(*exo*-norbornyl)-borinate produced 62% of bis(*exo*-norbornyl) ketone and 29% of *exo*-norbornylmethylene-2-norbornane (eq 4). This side reaction promises to provide a valuable new route to such olefins.



(4)

The present procedure provides a facile route from olefins to ketones. It appears to be of wide generality accommodating even bulky groups without apparent difficulty. It makes evident still another fascinating facet of the remarkable chemistry of organoboranes.

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[11] H. C. Brown, M. M. Rogić, M. W. Rathke, and G. W. Kabalka, *J. Amer. Chem. Soc.*, **91**, 2150 (1969).

[12] See Pelter, *et al.*, footnote *g*, Table I.

[13] For example, the α-chloroboronate in the representative reaction above was isolated prior to the oxidation in 82% yield. It was identified by nmr, ir, mass spectral, and elemental analysis.

[14] A similar phenomenon has been observed in the cyanoborate reaction: M. G. Hutchings, Ph.D. Thesis, University of Manchester.

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Book Reviews

Physical Methods of Chemistry. Part III.D. Edited by A. Weissberger and B. W. Rossiter (Eastman Kodak Co.). Wiley-Interscience, New York, N. Y. 1972. xiv + 705 pp. $32.00.

Part III.D of the Techniques of Chemistry Series treats X-ray crystal structure, electron diffraction of gases, neutron scattering, Mössbauer spectroscopy, photoelectron spectroscopy, molecular beams, neutron activation analysis, positronium annihilation, measurement of radioactivity, and γ-ray spectrometry. These subjects all fall in the broad fields of optical, spectroscopic, and radioactive methods. No better collective presentation of the basic material involved in the fields presented occurs in the literature than in Volume III.D of the Physical Methods of Chemistry Series. The book therefore will appeal to the specialist in one or more of these fields who may need an authoritative reference at hand containing information which he need not commit to memory, and will more strongly appeal to a beginner in any of these fields since here is the fundamental material necessary to the understanding of the field.

The basic pattern in the presentation of the physical methods in chemistry included in this volume is (a) an introduction generally giving the fundamentals of the method under consideration, its application, and, if two or more methods are applicable to the same phenomenon or phenomena, which method is advantageous to the problem at hand; (b) a rather complete presentation of the theory and the mathematical formulation of the theory, including the application of the mathematical formulas to data in order to obtain the quantity or quantities desired; (c) the apparatus or apparatuses used and the methods of usage, including the variables to be controlled and the precision of control in obtaining raw data; (d) quantities to be calculated and examples of calculations, including graphical and tabular dependence of the desired quantities on pertinent variables; (e) the precision of calculated results; (f) the limitations of the method and any modifications of apparatuses and procedures evolved to improve precision and to mitigate the limitations.

The above order of presentation of topics is not always adhered to, but the topical contents given generally prevail; and these contents, together with their clear and rather in depth presentations by authorities in the fields, make this volume a great contribution to physical methods in chemistry.

Edward S. Amis, *University of Arkansas*

Biosynthesis. Volume 1. A Specialist Periodical Report. Senior Reporter and Editor, T. A. Geissman. The Chemical Society, London. 1972. iv + 249 pp. $12.50.

The well-written Specialist Report on "Biosynthesis" reviews the progress in this area between 1970 and 1971 and includes prior references only when essential to the text. Under the able editorship of T. A. Geissman, five chapters are produced which deal predominantly with biosynthetic studies of alkaloids and terpenoid compounds. The first chapter by S. A. Brown on "Methodology" concentrates primarily on isotopic trace methods and excludes "all but incidental mention of enzymological techniques," much to the regret of authors who consider this to be "ultimate tool of biosynthesis investigation." This chapter is well constructed and singularly detailed for a review (162 references) and sets the stage for the subsequent topics. Chapter 2, "Biosynthesis of Terpenoid Compounds: C_5-C_{20} Compounds," by J. R. Hanson, assembles recent works on mevalonic acid, hemiterpenoids, monoterpenoid compounds, iridoids, sesquiterpenoid, and diterpenoid compounds. Works on the "Biosynthesis of Triterpenes, Steroids and Carotenoids" are summarized by H. H. Rees and T. W. Goodwin in Chapter 3. The material focuses, as expected, heavily on cholesterol and steroid biosynthesis. J. B. Harborne's chapter on "Biosynthesis of Phenolic Compounds," is well organized under phenols and phenolic acids, phenylpropanoid compounds (including coumarins), lignins, flavanoids, xanthones, stilbenes, and quinones. The remaining chapter on the "Biosynthesis of Alkaloids," by E. Leete, concentrates on indole alkaloids, particularly the role of amino acids in biosynthesis of indole and aporphine alkaloids. There is also a section on stereochemistry of hydroxylation involved in alkaloid formation. Essential findings from enzyme studies are summarized briefly, and the majority of the results are compiled in an *extensive* table under the plant studied, compounds administered the labeled alkaloids isolated, and present incorporation of label.

The extensive research published in this area over the past several years is clearly reviewed by experts in the area. Their interpretations of the results are concise and their mechanisms illustrated amply with clear structures. These reviews are well coordinated and the book is well written. The formulas are beautifully reproduced. This Report will serve as source material to lecturers and students alike in natural product chemistry, pharmacognosy, and botany. It is a stimulating account of recent progress in this area.

Ludwig Bauer, *University of Illinois at the Medical Center*

Applied Spectroscopy Reviews. Volume 6. Edited by Edward G. Brame, Jr. (E. I. du Pont de Nemours & Co.). Marcel Dekker, Inc., New York, N. Y. 1973. xiv + 375 pp. $21.50.

"Applied Spectroscopy Reviews" is an international publication dealing with principles, methods, and applications of and the latest information on spectroscopy in various fields of science. This volume has been written practically entirely for the researcher and physicists as well as other scientists, in addition to chemists and biochemists who could be interested in it. There are six reviews in this volume as follows: "Dichroic Spectra of Biopolymers Oriented by Flow" by W. Wada from Tokyo, "Rapid-Scan Fourier Transform Spectroscopy" by P. R. Griffiths, C. T. Foskett, and R. Curbelo of Philadelphia and Cambridge, "Neutron Scattering and Vibrational Spectra of Molecular Crystals" by T. Kitagawa of Osaka, "Diagnostics of High-Temperature, High Density Plasma by Radiation Analysis" by H. Conrads of Germany, "Spectroscopy of Liquid Crystals" by S. Chandrasekhar and N. V. Madhusudana of Mysore, and "Metals Analysis in Particulate Pollutants by Emission Spectroscopy" by R. D. Sacks and S. W. Brewer, Jr., of Ann Arbor and Ypsilanti.

Although in general the principles are well defined, the theory of the various techniques is given in such a condensed form that the book is hardly suitable for a beginner. However, by means of the many references given, the reader can find details of relevant theory and of experimental procedures in the papers cited. Nevertheless, the book is interesting because it does give the reader a good survey of the latest and most sophisticated methods in the six fields discussed. The review on liquid crystals is especially long and replete with many phenomenological descriptions of numerous liquid crystal systems. The review on metal analysis in particulate pollutants deals, of course, with a very timely subject, but again the reader would have to turn to the original literature for details of the procedures. In this review the references to each type of metal are conveniently given in tables as well as at the end of the review. In the case of the review on plasmas it is difficult to see anything there of interest to a chemist except to give him an introduction to the theory of such phenomena as self-pinching discharges and the emission spectra of highly ionized atoms at temperatures of many thousand degrees Kelvin. For the average chemist wishing to obtain a good summary of the latest spectroscopic techniques, probably the first three reviews would be of greatest interest; at least they were to this reviewer. In general, the book can be highly recommended as a source book for summaries of theories and techniques of the subjects discussed and especially for the very extensive and up-to-date literature references.

Malcolm Dole, *Baylor University*

Biochemistry of the SH Group. By P. C. Jocelyn (University of Edinburgh Medical School). Academic Press, New York, N. Y. 1972. xx + 404 pp. $20.00.

This timely book pulls together from a wide variety of sources much of what is known about the nature and role of sulfur-containing substances in living systems. It is intended for readers who range from those having a basic background in organic chemistry and biochemistry to researchers in the field. On the whole, the author's attempt has succeeded rather well. The opening chapter catalogs the naturally occurring thiols and disulfides, and the next five chapters are devoted to the structure, chemistry, and assay of thiols and disulfides. This provides a valuable if not exhaustive review of the subject. The remaining chapters trace the presence and function of thiols and disulfides in enzyme-catalyzed reactions, in subcellular particles, in blood, in animal tissues, in plants, in microorganisms, in the interactions with vitamins and hormones, in radioprotection, and in pharmacology.

The book has over 2000 references and about 11% of these are dated 1970 or later. A substantial number of misprints was noted. The author uses a system of cross referencing which is quite helpful.

Libraries will certainly want to acquire this valuable reference work and, at $20.00, many workers in the field may wish to get it for their personal use.

David W. Emerson, *The University of Michigan—Dearborn*

Organic Polymer Chemistry. By K. J. Saunders (Ryerson Polytechnical Institute, Toronto). Chapman and Hall Publishers, London. 1973. ix + 473 pp. $18.00.

A more accurate title for this book would have been: An Introduction to the Organic Chemistry of Some Technologically Important Polymers. The complete absence of physical-organic and quantitative aspects of organic chemistry has disturbed this reviewer. For example, it is very difficult to discuss rubbers without mentioning Tg. On the positive side, this book is useful for teachers and students who seek a concise up-to-date survey of the field of commercially-technologically significant polymers including brief descriptions of monomer manufacture, polymer synthesis, polymer structure, and some qualitative property information. The material is well organized and presented; the writing is fresh. The first chapter, ∼10% of the book, Basic Concepts, is an introduction to organic polymer chemistry. The rest of the 19 chapters summarize technologically important polymer classes, *e.g.*, Polyolefins, Polystyrene and Styrene Copolymers, Poly(vinyl chloride) and Related Polymers, Poly(vinyl acetate) and Related Polymers, Acrylic Polymers, Fluoropolymers, Polyethers, Polyamides and Related Polymers, Polyesters, etc. Each chapter is followed by an inadequate set of original references, but a good list of general bibliography. Appendix I is a list of some trade names and a satisfactory subject index is provided. This reviewer agrees with the author: "This book is . . . intended for . . . students . . . specializing in the field of polymer science and . . . graduates who require an introduction to this field."

Joseph P. Kennedy, *The University of Akron*