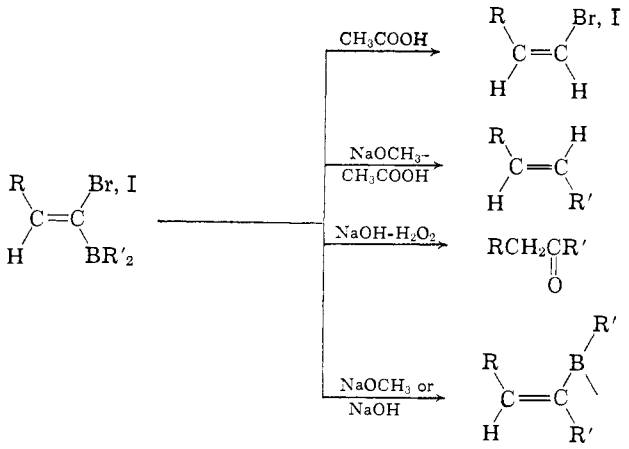

A representative procedure for the preparation of ketones from α-halovinylorganoboranes is given as follows. To a suspension of 30 mmoles of dicyclohexylborane[9] in tetrahydrofuran at 0° was added 30 mmoles of 1-bromo-1-hexyne. After maintaining the reaction mixture for an additional 30 min at 20–30°, 15 ml of 3 *N* sodium hydroxide was slowly added while keeping the temperature at 20–30°. The resulting organoborane was then oxidized at 30–40° by adding 15 ml of 30% hydrogen peroxide. The ketone formed was extracted into ether and the combined extracts were washed with saturated sodium chloride solution. Distillation gave 4.33 g of cyclohexyl pentyl ketone (79%), bp 99–100° (3 mm), n^{22}D 1.4545.

(9) Prepared by hydroboration of cyclohexene with borane in tetrahydrofuran in a 2:1 ratio of 0°.

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Book Reviews

Peptide Synthesis. By MIKLOS BODANSZKY and MIGUEL A. ONDETTI, The Squibb Institute for Medical Research, New Brunswick, N. J. Interscience Publishers, John Wiley and Sons, Inc., 605 Third Ave., New York, N. Y. 1966. x + 294 pp. 16 × 23.5 cm. $9.50.

In 1949, the extant information on the synthesis of peptides was critically reviewed by J. S. Fruton in 82 pages in Volume 5 of *Advances in Protein Chemistry*. Fruton's article not only reported in tabular form all of the known peptides, but also included a critique of the various methods of peptide synthesis. This article set the style for a number of reviews which have appeared periodically since that time, the most recent being the two-volume treatise on "The Peptides" by E. Schröder and K. Lübke.[1] The present book represents a departure from these earlier works in that no attempt is made to catalog the properties of the various peptides. Rather, the authors have concentrated on a delineation of the merits and limitations of the methods involved in peptide synthesis. After short introductory chapters on the historical aspects and on the over-all problems of peptide synthesis, the book takes up seriatim the topics of protective groups, peptide bond formation, racemization, and strategy. In each topic the advantages and disadvantages of the methods are thoroughly discussed and documented. Few if any of the myriad pitfalls present in peptide synthesis have been omitted. The authors through their wide experience have a fine appreciation for the unexpected side reaction which may be overlooked by the novice (and often by the experienced investigator) and which may defeat an otherwise perfect synthesis. Their thoughtful discussion of these problems is alone a sufficient reason for reading this book. The book ends with a chapter outlining the synthesis of a number of biologically active peptides. These schemes not only illustrate the historical developments of peptide synthesis but serve as useful guides for charting the synthesis of new peptides.

This book will be most useful to the novice in peptide synthesis. Its readable and clear exposition will be much appreciated by the graduate student as well as by the experienced investigator who is suddenly immersed in a problem involving peptide synthesis. The reactions are amply illustrated by structural formulas which are presented with surprisingly few errors. The book does not attempt to catalog the various peptides, and in this sense will not be useful as a source book to the established investigator. Understandably emphasis is placed on the contributions of the senior author to peptide chemistry, but with few exceptions other contributors are dealt with quite fairly. To this reviewer, more discussion should have been placed on Merrifields' "solid-phase" synthesis. In part, this deficiency may be due to the problem of timeliness. Even though the authors have made a few citations to the literature in 1965, this book is based largely on the information available through 1964. Much new material has appeared since 1964, and, although in most cases it is supplementary rather than contradictory to the themes espoused in this book, the "solid-phase" technique has had some successes which were not foreshadowed in this writing. This minor criticism on timeliness should not deter the potential purchaser. The authors have carefully illuminated the problems involved in peptide synthesis. These *problems* are timeless. It is the *solutions* which, hopefully, will yield to the passage of time and require a revision of the text.

(1) For a review see G. W. Anderson, *J. Am. Chem. Soc.*, **89**, 2510 (1967).

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The Analytical Chemistry of Cobalt. By ROLAND S. YOUNG, Department of Mines and Petroleum Resources, Victoria, B. C., Canada. Pergamon Press Inc., 44-01 21st St., Long Island City, N. Y. 1966. vii + 170 pp. 15 × 22 cm. $7.00.

Until recent years, a relatively neglected sector of the analytical chemical literature has been the analytical chemistry of individual elements. This lack is now being filled by monographs appearing as members of major series or singly. Thus, the V. I. Vernadskii Institute of Geochemistry and Analytical Chemistry of the Academy of Sciences of the USSR is publishing a series of some 50 volumes on the analytical chemistry of individual elements, which are being translated into English. Young's "Analytical Chemistry of Cobalt" is an independent monograph. It deals as comprehensively as most analysts might wish with chemical, physicochemical, and physical methods for the determination of the element. In addition, sampling, separation methods, and some other topics are treated. Detailed procedures are presented for a considerable number of chemical methods. Because of his experience in the field, the author is able to make helpful recommendations.

The author has conscientiously listed hundreds of references on the determination of cobalt. In the chapter of colorimetric methods,

more than 60 reagents, in addition to the principal ones, are mentioned. Are so many reagents needed for cobalt or any other element? Most of them have no advantages over the three or four standard colorimetric cobalt reagents. As aptly put by Szabadvary, some analytical methods end their careers the day they are published. Some of us are ready to cry hold, enough, and would only feebly, if at all, protest a moratorium on new reagents for such chromogenic elements as cobalt, iron, and copper. Sometimes, not to publish would be a small benefaction and a kindness.

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Elements of Thermodynamics. By D. ter Haar, Oxford University, and H. Wergeland, Norwegian Institute of Technology, Trondheim. Addison-Wesley Publishing Co., Inc. Reading, Mass. 1966. xiii + 160 pp. 16 × 23.5 cm. $9.75.

When the influential Greek skeptic, Pyrrho (365–275 B.C.), declared that all theories are probably false, he was no doubt referring to philosophy, theology, and politics. After reaching his conclusion, Pyrrho would have done well to turn his attention to burning fuel and boiling pots of water, thus anticipating Hero of Alexandria in the invention of the steam engine. Going even farther, he might have discovered the first two laws of thermodynamics, and thus a theory to which there are no known verifiable exceptions as to its truth for macroscopic systems, including living creatures. But history chose a different course, and thermodynamics as a body of rigorous theory did not flower until the 19th century after the steam engine was already a commercial item, mainly in the western world.

On the theoretical side some of the most important advances in thermodynamics came from the studies of J. Willard Gibbs (1838–1903) of Yale University. Gibbs' work turned out to be of special interest to chemists. On both the theoretical and experimental side, thermodynamics first came west of Dodge City when G. N. Lewis went to Berkeley in 1912. Before 1912 the men west of Dodge City were busy defending their cows, their riparian rights, and their women; and they slept with their six guns. The remarkable book by Lewis and Randall—later revised by Pitzer and Brewer—played an important role in the development of chemistry both in America and abroad.

But now let's turn to the small, somewhat expensive book by ter Haar and Wergeland. It is, as the authors plainly state in their preface, a theoretical text, and it is meant for college seniors and graduate students. The subject matter is treated mainly by the methods of Gibbs. Atoms, molecules, and quanta are mentioned more than once, but these concepts are not used in the main development of thermodynamics. Only ordinary algebra and the calculus are used in the book; one finds no exotic algebras, wave equations, and the like here. No mention is made of Pyrrho, Hero of Alexandria, steam engines, or Dodge City.

After the preface and a better than ordinary table of contents, we come to a three-page "Introduction" which states briefly and clearly the first and second laws of thermodynamics, followed by short historical account of these two laws. The authors, being theoretical physicists, call the two laws "empirical propositions;" chemists and engineers would say that the laws have been established by many, and often difficult, experiments on real substances. (Joule spent much of his adult lifetime in determining the mechanical equivalent of heat.) In the historical account such men as Count Rumford, Humphrey Davy, Carnot, Clapeyron, Mayer, Joule, Kelvin, and Clausius are rightly credited together as the discoverers of the first two laws of thermodynamics.

Following the "Introduction" are the nine chapters of the book proper. Chapters 1 and 2 are entitled, respectively, The First Law, and The Second Law. They are meant as reviews or refreshers on the two laws. In the latter part of Chapter 1 the term "reversible process" is introduced, even though this term implies the second law, if one is interested in rigor. But the first two chapters do give clear expositions of such concepts as equations of state, internal energy, heat, work, Carnot cycles, and entropy; even Boltzman's famous equation $S = k \log W$, receives deserved attention, as does also Carathéodory's approach to thermodynamics *via* Pfaffin differential forms. Like most writers in the field, the authors fight shy of defining temperature.

The remaining seven chapters bear the titles, respectively, Equilibrium Conditions, Thermodynamic Potentials, Transformation of Variables, Systems of Variable Mass, Chemical Equilibrium, The Third Law, and Systems in External Fields. These titles should give some idea of the subjects treated as well as the spirit of the book. Thermodynamics is now considered to be a "closed" science, but the book is quite up to date. There are a number of problems throughout the text, together with their solutions (Olé!). A few well-chosen references are to be found here and there.

At the end of the text there are four interesting appendices entitled, respectively, Some Numerical Values, Critical Points, Mathematical Index (Lagrangian Multipliers, Legendre Transformations, Jacobians), and Negative Temperatures. The Mathematical Index contains material that is to be found in books on advanced calculus, but, of course, such books are usually not at hand when most needed.

As a text for seniors and graduate students I (= this reviewer) believe that "Elements of Thermodynamics" deserves some praise; it opens the door to the more lofty treatises by P. S. Epstein, Fowler and Guggenheim, Lewis and Randall, and Stephen G. Brush. A distinguished chemist of yesteryear opined that there were two distinct views held about science. In one view, science is likened to a cow that is admired for the butter and cheese she provides; in the other view, science is a lovely goddess who is worshipped for herself alone. "Elements of Thermodynamics" is partial to the goddess.

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