

oxygen in three separate steps, enough being added in each step to oxidize II to III, we found a total of 2.06 mmoles of carbonyl.

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## BOOK REVIEWS

**Les Cyclitols. Chimie, Biochimie, Biologie.** Actualités Scientifiques et Industrielles 1294. By THÉODORE POSTERNAK, Professeur à l'Université de Genève. Editions Hermann, 115, Boulevard Saint-Germain, Paris VI, France. 1962. 491 pp. 17.5 × 24 cm. Price, 48 NF.

Although the prototype cyclitol, *myo*-inositol, was discovered in muscle tissue more than a century ago, no rapid progress in cyclitol chemistry was possible until the configuration of this key compound was determined. This difficult task was finally accomplished by Théodore Posternak of the University of Geneva during the period 1928–1942, stimulated by earlier work of his father, S. Posternak. Professor T. Posternak later elucidated the configuration and chemistry of numerous other cyclitols, and it is most fitting that the first major treatise on this subject now appears under his authorship.

The word cyclitol was at first applied only to ordinary inositol and a few closely related substances. Now in a much broader sense *cyclitol* might be taken to include any monoalicyclic compound whose ring bears at least one hydroxyl group and may also bear other groups. The results of cyclitol research now conveniently available in Posternak's book are of value in many areas of science, and this excellent monograph should be useful to a wide circle of chemists, biochemists and biologists.

The cyclitols are old friends to teachers and students of organic chemistry, because the nine isomers of inositol have long served as favorite illustrations of the stereoisomerism (and more recently, conformational analysis) of polysubstituted cyclic molecules. These isomers were already the basis of extensive classroom discussions at a time when most of the actual compounds were still unknown and the paths leading to their ultimate synthesis could not even be foreseen.

The study of cyclitols is a fascinating and challenging subject for the synthetic or structural chemist because of their complex stereoisomerism, numerous functional groups of similar reactivity, and special susceptibility to conformational analysis. The treatment of these compounds in "Les Cyclitols" benefits by the rather complete configurational knowledge now available. To a greater extent than in most previous reviews, Posternak has placed the structurally selective and stereospecific reactions of cyclitols on a rational basis made possible by modern conformational theory. Only brief mention is made of the application of n.m.r. and optical rotation predictions to these compounds, and it does seem that greater emphasis should be placed on these exciting new physical methods.

The material assembled in this volume should be of especially great value to the carbohydrate chemist, for whom the cyclitols are useful model substances with which to study typical secondary-alcohol group behavior of sugars, in the absence of ring-opening complications. The alicyclic or steroid chemist will also find much of interest here, since the cyclitols conveniently display many properties of the six-membered ring.

The Première Partie (272 pages) of this book consists of 14 chapters on "Chimie des Cyclitols." After a long introductory chapter on basic characteristics of the entire family of compounds (stereochemistry, conformation, reactivity, physical properties) there are individual chapters dealing with: *myo*-inositol; the other inositols; the pentols, tetrols and triols; the methyl ethers; cyclohexanes; anhydro and unsaturated derivatives; halogen and nitrogen derivatives; carboxylic acids; and phosphate esters. Although part of a "Natural Products" series, Posternak's book gives thorough coverage to synthetic cyclitols, and in fact these comprise the great majority of compounds mentioned.

In the Deuxième Partie (110 pages) there are ten chapters on "Biochimie and Biologie." These provide a useful review of a great variety of fascinating topics, including: occurrence in plants and animals; metabolism; biosynthesis; inositol lipids; antagonists of *myo*-inositol; lipotropic action; inositoria; effect on tumors.

The potentially great importance of inositols to the biochemist or biologist arises in part from the fact that *myo*-inositol occurs in every living cell, so far as is known. Perhaps even more important is the fact that *myo*-inositol belongs to that very select group of 22 organic compounds (including 13 amino-acids) which are *necessary and sufficient* for the survival and growth of isolated human cells. Although the essential cellular role of *myo*-inositol is not well understood, there can be little doubt that it is deeply involved in important biochemical processes.

The primary coverage of "Les Cyclitols" extends through 1959, but 50 additional papers from 1960 and 1961 are reviewed in 11 pages of *Addenda*. Altogether, not less than 1200 original articles were examined. Citations to these are given both in fine-print footnotes and in a 40-page alphabetized bibliography. This bibliography and the subject index and table of contents together consume not less than 85 large-type, single-column pages at the end of the book. This format, space-consuming though it may be, is a refreshing change from the supercondensed multi-column style which afflicts so much of today's scientific literature.

The author of any work on cyclitols faces some vexing problems of nomenclature, since the ways of naming these substances are almost as numerous as the groups working on them. Although uniformity is much needed, it appears that nearly every proposed nomenclature has some good features, which might well be preserved in the ultimate uniform system.

The difficulties arise primarily in designating the very numerous stereoisomers (*e.g.*, 32 for an aminodeoxyinositol). Three principal notations have been advocated, and since Posternak makes some use of all three, the reader has an opportunity to judge their relative effectiveness. The first notation uses 8 rather arbitrary prefixes (allo, muco, neo, etc.) for the cyclohexanehexols, 10 other prefixes for the cyclohexanepentols, and so on. The second notation tries to name nearly all cyclitols in terms of the 8 inositol configurations. The third notation employs fractional symbols, as in the name "14/23-cyclohexanetetrol." In the reviewer's opinion, this fractional notation, being nearly self-explanatory to any organic chemist, is by far the best system.

It does seem unfortunate that Dr. Posternak has chosen to perpetuate the name "*meso*-inositol" for the most common isomer, since seven *meso*-inositols are possible and all are now known. Although "*myo*-inos," meaning literally "muscle-muscle" (the Greeks had two words for it), is redundant, the name *myo*-inositol proposed by Fletcher, Anderson and Lardy is already widely accepted, and now seems the most practical way to escape the ambiguity.

This volume is unusually free of typographical or other errors. However, 1,2,4,5-cyclohexanetetrol (p. 121) should be credited with five (not four) theoretically possible diastereomers—the last of these were prepared this year. Also, more than one 1,2,4-triol (p. 126) has been reported in earlier literature. Also formula 115 (p. 100) needs revision.

"Les Cyclitols" is an attractively printed and bound paperback, which well deserves its selection by a French Graphic Arts Committee as one of "les 50 plus beaux livres de l'année" (non-scientific books included). The present volume is one of a promising series on the Chemistry of Natural Substances, to be edited by Professor Edgar Lederer, Director of the new Institut de

Chimie des Substances Naturelles (Paris). The authors will be from various countries, but with some exceptions, publication will be in French.

The English-speaking chemist who refers to the lucid pages of "Les Cyclitols" will be pleasantly reminded that scientific French is the easiest of foreign languages to read. Now that an increasing number of valuable French scientific works are reaching us, it is hoped that no imagined language problem will prevent the American chemist from making full use of them.

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**Developments in Inorganic Polymer Chemistry.** Edited by M. F. LAPPERT, Senior Lecturer in Chemistry, and G. J. LEIGH, Lecturer in Chemistry, both at the Manchester College of Science and Technology, University of Manchester (England). American Elsevier Publishing Company, Inc., 52 Vanderbilt Avenue, New York 17, N. Y. 1962. xi + 305 pp. 14 × 22 cm. Price, \$10.00.

The knowledge that inorganic compounds can combine into polymeric substances is not new, but until ten years ago the subject received scant attention. Recently, however, there has been a great deal of interest in it, and a voluminous literature on inorganic polymers is building up. Thus, this book is the third to appear within the last year and a half. All three are quite different, and all deserve attention, for not only is the chemistry involved very interesting, but there is reason to believe that practical results are not far in the future.

This volume records a series of lectures which were given at the Manchester College of Science and Technology in the fall of 1960. It is unfortunate that publication was delayed for two years, because in a field which is growing as rapidly as this one, many changes take place in that length of time. However, in spite of the delay, the information in these lectures, and the compilations of the hundreds of references which accompany them, are of great value.

Following a short chapter which serves as a general survey of the field, there are chapters on polymers containing boron and nitrogen, other boron compounds, phosphorus and nitrogen, sulfur and phosphorus, silicones, siloxanes (two chapters), and metal chelates. The last is the shortest chapter in the book, covering only seventeen pages. The reviewer feels that the author of that chapter is not as hopeful as he should be about the future of coordination polymers, though he agrees "that the difficulties are much greater than was foreseen." In general, the chapters are descriptive, and give little information on factors that influence polymer formation and thermal stability. Most of the reviews are reasonably complete, and in some cases, critical. The quality of the writing is good, and is more nearly uniform than in most books which have been prepared by a number of authors. Readability could have been improved by tabulating some of the information and by the use of formulas of compounds instead of their names; e.g., bis-(triphenylsiloxy)-diisopropoxytitanium, which few chemists will visualize without puzzling over it or writing the formula.

Because of the mass of detailed information which it contains, this volume is not easy to read for general background information. For the same reason, however, it will be highly useful to those interested in inorganic polymers and as a reference book on the chemistry of the non-metals.

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**Mass Spectrometry. Organic Chemical Applications.** By KLAUS BIEMANN, Associate Professor of Chemistry, Massachusetts Institute of Technology. McGraw-Hill Book Company, Inc., 330 West 42nd Street, New York 36, N. Y. 1962. xii + 370 pp. 16 × 23.5 cm. Price, \$13.75.

Since mass spectrometry is by no means a new physical tool nor does the field suffer from a dearth of recent books or review articles, the present opus should be reviewed in the light of the current status of the subject and its monograph literature. It is interesting to note that while mass spectrometry has been practiced in certain areas of organic chemistry (notably the petroleum field) for nearly twenty years, it has only recently begun to enter the every-day organic laboratory. This is not the fault of instrumentation—the usual reason for the lag between the development of a physical tool and its extensive use by the laboratory organic chemist—since some of the presently employed mass spectrometers have been available for many years. It cannot even be blamed on the relative non-volatility of the bulk of organic substances, because O'Neal and Wier introduced a heated inlet system over ten years ago.

In my opinion, the chief reason for this situation is implicit in a sentence taken from Biemann's introduction, namely "... that the most useful data are obtained if the originator of the problem and the person determining the spectrum are in close contact. The most ideal situation results if both the chemistry and the mass spectrometry required for the solution of a given problem are carried out by the same individual..." In other words, with few exceptions—most of them rather recent ones in Sweden, Austria, Australia, Great Britain and the U. S.—the bulk of mass spectrometric research was not performed by organic chemists. A second reason, again in the reviewer's opinion, is that much of the mass spectrometric information accumulated in the past has been published in journals, not generally read by organic chemists, and presented in a manner which was hardly likely to excite the reader. Some of the striking exceptions to this generalization, such as McLafferty, Stenhagen and Biemann, only seem to confirm its correctness. Fortunately, this state of affairs is changing rapidly and the present book is likely to accelerate the process. It is not the first book dealing with mass spectrometric applications to organic chemistry, but it is the first written by an organic chemist and for his purposes by far the best.

The first chapter, dealing with instrumentation, gives a brief description of the different mass spectrometers. As the author points out, fuller details can be found in other books dealing with mass spectrometry, but in my opinion it would have been very desirable for the average organic chemist if the various instruments were identified with existing commercial models (U. S.: CEC and Bendix; Great Britain: A.E.I.; Germany: Atlas; Japan: Hitachi) so as to help him in the potential choice of an instrument for his laboratory. Even more important would have been an authoritative comment, addressed to instrument companies, reminding them that the ideal mass spectrometer for general organic chemical work still needs to be produced.

Chapter 2 on "Sample Handling and Operating Techniques" is particularly valuable to the novice in the field and illustrates the various procedures practiced by the author in his own laboratory. Most readers will find that eventually each mass spectroscopist develops his own favorite methods, especially suited to his needs. Thus the reviewer's laboratory would take issue with Biemann's conclusion on p. 23 that the most valuable means of handling a "non-volatile" substance is to convert it into a more volatile derivative. Before attempting this, we would always examine first the direct insertion of the sample near the ion source, especially since this is now possible with mass spectrometers showing unit resolution to masses beyond 800. In the section (p. 42) on the presentation of data, Biemann favors figures containing plots of relative abundance *vs.* *m/e* over the historically more standard tabular presentations found especially in journals such as *Anal. Chem.* In the reviewer's opinion, this point cannot be made too strongly, because as far as the organic chemist is concerned, no other factor has made the reading of many mass spectrometry papers so unpalatable an experience.

The third chapter on "The Nature of Mass Spectra and Their Interpretation" is by far the longest. It commences with a very good discussion of the recognition of molecular ions, the first problem usually encountered by the organic chemist. There follows a detailed, and on the whole very clear, coverage of fragmentation mechanisms, utilizing the approach first pioneered by McLafferty and reviewed by him in an able manner in a recent chapter (Chapter 2 in "Determination of Organic Structures by Physical Methods," F. C. Nachod and W. D. Phillips, Ed., Academic Press, Inc., New York, N. Y., 1962), which may well make good introductory reading before delving into Biemann's book. This section abounds with mechanisms and thus represents the diametric opposite of Beynon's presentation of mass spectral fragmentation processes ("Mass Spectrometry and its Applications to Organic Chemistry," Elsevier Press, Amsterdam, 1960). If I would have to choose between these two extremes, I would certainly pick Biemann's exposition and expansion of McLafferty's views, but I would feel much more comfortable if many of the mechanisms were put forward in a more conditional manner. The very positive statements using mechanisms A, D, H, etc., represent a very tempting siren's song, which will lull the average organic chemist into a comfortable feeling of mechanistic security, which is quite unreal and unjustified at this stage of our knowledge.

While several fragmentations, notably the simpler ones, have been substantiated by deuterium labeling (e.g., p. 113), there are others (the vast majority) for which there exists as yet no verification. As far as possible, mechanisms should be supported by labeling experiments, and while this sermon is preached elsewhere in the book, it is not practiced very extensively in this section. In the absence of such support, it may still be preferable to suggest possible mechanisms for major fragmentations, rather than to use the earlier mass spectroscopist's proverbial wiggly line, but these mechanisms should be proposed cautiously and not *ex cathedra*. This is particularly important in a book of this kind, which is bound to influence the modern graduate student because it appeals to his desire for sophistication. As an example, an experimentally unsupported hydrogen transfer