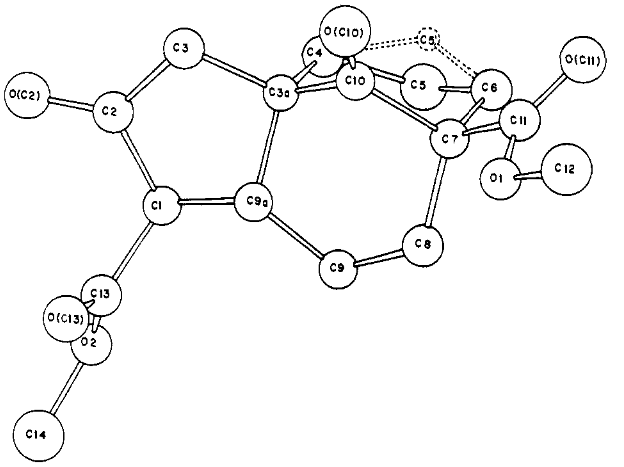
ture has thus far been refined to a reliability index,[8] R, of 0.050 for the 2491 reflections. The crucial configurational relationships to be noted are the trans fusion of the perhydroindane system and the trans relationship of the carbomethoxyl at C, and the C_4-methylene group attached to C_{3a}.

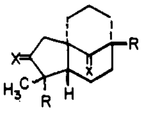
The X-ray study also revealed an interesting conformational feature which is reflected in a disordering of the position of C_5. The high occupancy site (~80%) corresponds to the chair–chair form with a C_5–C_9 separation of 3.11 Å. The low occupancy site (~20%) corresponds to a chair–boat arrangement with a C_5–C_9 separation of 3.66 Å. The chair–chair is the only one observed in previous crystallographic studies of derivatives of the bicyclo[3.3.1]nonane system.[9] These data are summarized in the structure of VI where the broken lines correspond to the low occupancy conformer.

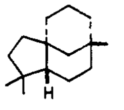


VI

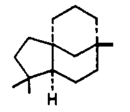
The definition of the stereochemistry of VI allows for the indicated assignment to its precursor Va and, hence to the bicyclic product, V. The transformation of IVa to Va is decisive in defining the stereochemistry at C_{9a} in the subsequent products. The extended prechair conformation postulated for IVa is well disposed to give rise to the equatorially oriented enolate in Va which is probably also thermodynamically preferred.[10]

Before the crystal structure of VI was in hand, it was converted to what can now be formulated as *dl*-epiclovane (XI). Methylation (1-TlOEt; 2-CH_3I)[11] gave the crystalline (mp 103–110°) but epimeric mixture, VII.[6] Double thioketalization gave epimers VIII, mp 145–150,[12] which upon desulfurization (Raney Nickel) provided the epimeric diesters, IX.[12] The latter were transformed ((i) $LiAlH_4$–ether, (ii) Collins oxidation,[13] (iii) ethanedithiol-BF_3) into the bis-(thioketal) epimers, X.[12] Desulfurization (Raney nickel) of X gave a single hydrocarbon, XI,[12] whose infrared, nmr (τ (CCl_4) 250 MHz, 9.03 (6 H, s), 9.15 (3 H s)) and mass spectra all differed in detail from those of authenic clovane XII (τ (CCl_4) 250 MHz, 9.02 (3 H, S), 9.13 (3 H, s), 9.15 (3 H, s)) whose cis fusion is well established.[14]





XI Epiclovane



XII Clovane

VII X=O, R=CO_2Me
VIII X=$S(CH_2)_2S$; R=CO_2Me
IX X=H_2, R=CO_2Me
X X=H_2, R=$CHS_2(CH_2)_2$

Further chemical and crystallographic studies of this new ring system are in progress.

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S. Danishefsky,* W. E. Hatch
Department of Chemistry, University of Pittsburgh
Pittsburgh, Pennsylvania 15213

M. Sax, E. Abola, J. Pletcher
Veterans Administration Hospital
Pittsburgh, Pennsylvania 15240

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(8) $R = \Sigma F_o - KF_c/\Sigma F_o$ where F_o and F_c are observed and calculated structure factors, respectively, and K is the overall scale factor.

(9) *Cf.* (a) W. A. C. Brown, J. Martin, and G. A. Sim, *J. Chem. Soc.*, 1844 (1965); (b) N. C. Webb and M. R. Becker, *ibid.*, 1317 (1967).

(10) For an analysis of conformations of bicyclo[3.3.1]nonanes, see J. M. McEuen, R. B. Nelson, and R. G. Lawton, *J. Org. Chem.*, **35**, 690 (1970).

(11) *Cf.* E. C. Taylor, G. H. Hawkes, and A. McKillop, *J. Amer. Chem. Soc.*, **90**, 2421 (1968). The use of conventional alkylating bases led to extensive amounts of *O*-methylated product,[6] mp 132–135°. Under the Taylor conditions this was reduced to 8% yield.

(12) The structure of this product is consistant with its infrared, nmr, and mass spectra.

(13) J. C. Collins, W. W. Hess, and F. S. Frank, *Tetrahedron Lett.*, 3363 (1968).

(14) *Cf.*, *inter alia*, A. Abei, D. H. R. Barton, A. W. Burgstahler, and A. S. Lindsay, *J. Chem. Soc.*, 4659 (1954); D. Becker and H. J. E. Lowenthal, *ibid.*, 1338 (1965); P. Doyle, I. R. McLean, R. D. H. Murray, W. Parker, and R. Raphael, *ibid.*, 2749 (1965).

Book Reviews

Catalysis in Chemistry. By A. J. B. Robertson (University of London). Methuen Educational Ltd., London. 1972. v + 56 pp. $2.75.

This book is one of about a dozen introductory surveys of science topics in the Methuen Studies in Science series. Ably written by Professor Robertson, it is composed of five chapters: (1) Historical Introduction, (2) The Adsorption of Gases by Solids, (3) The Rate of Heterogeneous Catalytic Reactions and the Adsorption Theory, (4) Catalysis and Solid State Chemistry, and (5) The Probable Importance of Active Catalytic Centres at the Catalytic Surface. The discussion emphasizes heterogeneous catalysis in general and the gas–solid interface, in particular. An historical approach has been used in developing the topics, and the text has been occasionally enlivened with brief accounts of controversies which occurred during the formulation of some of the basic concepts such as the nature of physical adsorption.

The material in this, as well as the other science topics in the series, is at the college preparatory or entering college level. The mathematical treatments do not go beyond simple algebra and are not extensive. The subject is covered in much more detail than is usually found in introductory chemistry textbooks and would best be used as supplemental reading for the interested student. It does not stand alone very well.

M. C. Hobson, Jr., *Virginia Commonwealth University*

Trace Analysis by Mass Spectrometry. Edited by A. J. AHEARN (Kensington, Maryland). Academic Press, New York, N. Y. 1972. xiv + 460 pp. $24.75.

Spark source mass spectrometry has become established as among the most sensitive of the available techniques for trace element analysis, and as virtually the only method applicable all across the periodic table. Six years have elapsed since the appearance of the last general review of spark source mass spectrometry, and so the present volume is very timely. There have been several significant instrumental advances in the field since 1966, as well as many important applications. Moreover, much important material has appeared in conference proceedings and other relatively inaccessible sources. The present volume provides a good introduction to that literature.

About three-quarters of the fourteen chapters is devoted to instrumentation, the remainder to applications. Two chapters describe the problems of photographic plates as detectors. One discusses the problems of electrical detection. The discussion of ion formation in the spark (J. Franzen) is particularly lucid. A chapter (B. Knox) on laser ionization and vaporization of solids prior to mass spectrometry is included. The topic is well treated but seems almost out of place after thirteen chapters largely given over to the details of spark source mass spectrometry.

The chapters on applications are well written but highly specialized. These contributions naturally emphasize work from the authors' laboratories and related studies and do not do justice to the wide range of applications of spark source mass spectrometry. Despite this minor drawback, the book is highly recommended to anyone interested in modern methods of trace element analysis.

Michael D. Morris, *University of Michigan*

Advanced Inorganic Chemistry. A Comprehensive Text. Third Edition. F. ALBERT COTTON and GEOFFREY WILKINSON. xxi + 1145 pp. Interscience Publishers, New York, N. Y. 1972. $15.75.

The earlier editions of Cotton and Wilkinson are well known to inorganic chemists, so, in reviewing the Third Edition, it is almost sufficient to tell how it differs from the Second Edition.

For those few inorganic chemists who are not familiar with the earlier editions of Cotton and Wilkinson, it may be stated that theirs is the most widely used of all of the texts for courses in advanced inorganic chemistry. It is a volume of over 1100 pages, but, unlike most modern textbooks, the price is not exorbitant. The wise student, when he has finished the course for which he purchased it, will save it for reference (many research laboratories have bought the earlier editions as reference books), for it contains such a wealth of material that he could not possibly have covered it all in a single college course, or retained all of the information in it, if he had.

Commonly, a book which goes through several editions grows larger with each edition, for the authors cannot bear to delete good material, and they see no way to add new chapters except by adding pages. Such is not the case here; the Third Edition is a bare nine pages longer than the Second. The difference is more than made up by an expansion of the index from 13 pages to 24. The reviewer heartily applauds this increase and hopes that in the Fourth Edition the authors will again double the size of the index. There are significant items that are discussed in this volume that are not mentioned in the index, for example, "ambidentate," "allotropic forms," and "five coordinate complexes."

In this edition, there has been extensive rearrangement of the subject matter. Careful examination shows that some passages have been lifted bodily from the Second Edition, but in many cases, phrases, clauses, sentences, and sometimes entire paragraphs have been deleted. In most cases, but not in all, nothing has been lost by these omissions. They have saved a good deal of space for the inclusion of new material. There are other, more significant rearrangements of subject matter. For example, the chapter on lithium has been deleted and that element is considered along with the heavier alkali metals. The separate set of chapters on the other first-row elements have been modified and are more closely associated with—or absorbed into—the chapters on the heavier elements of their respective periodic groups. The chapter on Stereochemistry and Bonding in Compounds of Non-Transition Elements has been rewritten to a large extent and moved into Part I of the book (General Theory). Most significantly, there has been a striking change in the handling of coordination compounds, which the authors now believe are not to be considered as a special class at all. They argue that since SF_6, VF_6^-, and SiF_6^{2-} are all isolectronic, it is not necessary to consider the last two as coordination compounds and exclude the first. All of them belong in a single class.

A good deal of new material has been added in the Third Edition, but only a few of the many examples which might be cited will be mentioned here. There is a new and timely chapter on Homogeneous Catalysis, a section on the structure of ice, and a section on dinitrogen complexes (only two pages, but seventeen references to recent journals). The discussion of molecular orbital theory is considerably expanded, as is that on dioxygen complexes.

This is an excellent book, and it will undoubtedly find wide use, as its predecessors have.

John C. Bailar, Jr., *University of Illinois*

Cellulose and Cellulose Derivatives. Parts IV and V. Edited by NORBERT M. BIKALES and LEON SEGAL. Wiley-Interscience, New York, N. Y. 1971. Part IV: xix + 718 pp. Part V: xix + 693 pp. $64.75 for the set.

While it is widely recognized by chemists that cellulose is the most abundant naturally occurring polymer, its extensive use as a raw material in industry is frequently overlooked. On a worldwide basis more than 70% of the textile fibers are based on cellulose, in excess of 90% of the world's paper is cellulosic, and many plastic substances are chemical derivatives of cellulose. Furthermore, despite the increasing use of synthetic polymers, cellulose and chemical derivatives of cellulose are expected to play a dominant role in the years ahead. The scientific and patent literature dealing with cellulose is among the most widespread in the world, with nearly all countries contributing from their private, governmental, and academic sectors. Thus, "Cellulose and Cellulose Derivatives" is a most welcome successful attempt to systematize and summarize the extensive available literature. Parts I, II, and III of the second edition of "Cellulose and Cellulose Derivatives," edited by Emil Ott, H. M. Spurlin, and M. W. Grafflin, appeared in 1954. Parts IV and V, the subjects of this review, were edited by N. M. Bikales and L. Segal. According to the editors, the new parts are intended as supplementary volumes to cover new developments, and to address those aspects of cellulose science and technology that challenge contemporary chemists. In keeping with previously established patterns, the editors called upon recognized experts to prepare authoritative discussions. The usual problems associated with collaborative works are not evident here. There is minimal overlap in the treatment of the various topics, and there is good uniformity in depth and extent of coverage among the sections. The editors obviously scrutinized each contribution and exerted a strong influence of their own. Each chapter contains an extensive tabulation of references to the original literature, including, where appropriate, the pertinent patents. Clearly, Parts IV and V have maintained and even extended the high levels of excellence which have been set by the earlier parts of this invaluable treatise.

The principal chapter in Part IV deals with investigations of structure, emphasizing modern methods of structure analysis. Included are discussions of infrared spectroscopy, X-ray and electron diffraction, nmr spectroscopy, and microscopical examination. An excellent discussion of swelling is contained in this chapter. Other chapters in Part IV deal with investigations of solutions, mechanical properties, and biosynthesis. Since cellulose is most extensively used as an element of construction, the chapter on mechanical properties is of particular importance. The discussion here deals with the mechanical behavior of fibers, principally cotton, and the deformation mechanics of fiber assembly networks, principally paper. These discussions are especially useful in a book that deals mainly with chemical and structural details.

Part V contains three chapters dealing with derivatives, degradation, and new developments in cellulose technology. The chapter on derivatives deals with the whole range of possible chemical derivatives of this reactive substrate including ethers, esters, graft copolymers, cross-linked cellulose, and others. In the chapter on degradation one finds a discussion of the usual acid, alkaline, thermal, photochemical, and enzymatic processes. Of particular value is the chapter on new developments in the technology of cellulose and its derivatives. Included here are excellent summaries of the new high-wet-modulus and other rayons, durable-press treatments of fabrics containing cellulosic fibers, triacetate fibers, films, membranes, and several other topics.

Ludwig Rebenfeld, *Textile Research Institute, Princeton, New Jersey*