

observed major products (3 and 4) did not arise directly from 2, but rather from an isomer, the oxirane 6. We suggest that warming first transforms the  $\alpha$ -lactam into oxirane 6, which species fragments into cyclohexanone and *t*-butyl isocyanide. The nature of the transformation of 2 to 6 (free-radical, ionic, or carbene) is not obvious on the basis of the evidence at hand.

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DEPARTMENT OF CHEMISTRY JOHN C. SHEEHAN  
MASSACHUSETTS INSTITUTE OF TECHNOLOGY ISTVÁN LENGYEL  
CAMBRIDGE 39, MASSACHUSETTS

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## BOOK REVIEWS

**Organische Chemie in Einzeldarstellungen. Band 7. Die Photochemie der Organischen Farbstoffe.** By HANS MEIER, Dr. rer. nat., Diplomchemiker, Staatliches Forschungsinstitut für Geochemie, Bamberg. Springer-Verlag, Abteilung VI, 1 Berlin 31 (Wilmersdorf) Heidelbergerplatz 3, West Berlin, Germany. 1963. xvi + 471 pp. 16 × 24 cm. Price, ganzleinen, DM 79.

The photochemistry of organic compounds is a field having many different aspects; this subject is primarily of interest to physical chemists. The fading of dyed textiles and other substrates, however, is a problem which has been investigated mainly by dye chemists and technologists. Investigations of light-catalyzed organic reactions have increased appreciably in recent years and the importance of photochemical processes in biology has been clearly recognized.

There is no previous monograph which discusses the photochemistry of organic compounds with visible light. This book covers this topic and is therefore most welcome.

The author opens with a general survey of the theory of light absorption by organic compounds in relation to their constitution and their states of aggregation. Two chapters are devoted to fluorescence and phosphorescence. A discussion of photochemical reactions of dyes then follows. The central and largest part of the book contains five chapters on the photoconductivity of dyes. In the later chapters some specific effects are discussed, namely the sensitization of photographic layers and of inorganic semiconductors by dyes, the photodynamic damage of biological substrates, the nature of human vision, the photosynthesis of organic compounds in plants, and a short discussion of the problem of energy transportation in biological materials.

In the preface the author states that he wishes to review the whole field of the photochemistry of dyes by discussing as many literature references as possible. Indeed, the number of papers cited (some 1200) is extremely high. One therefore expects comprehensive coverage of the whole subject. This is not always true. For example, from our own files on the fading of dyes on textiles, which is by no means comprehensive but contains 107 references, we found only six in this monograph. The name of C. H. Giles, an author who has made substantial contributions to the fundamental understanding of the lightfastness of dyeings, does not appear in the context; some of his papers are mentioned by the name of the first author with the appendix, *et al.* Whereas the photodynamic effect of dyes on the degradation of biological systems is discussed in detail, only two pages are devoted to the tendering effect of certain anthraquinone dyes on cellulose; only Dörr's paper is discussed in this field, although there are at least ten valuable contributions to this problem.

Although the free electron method of H. Kuhn and N. S. Bayliss has been more successful than other methods in the calculation of absorption bands of dyes in the visible spectrum, the MO treatment certainly merits more than 1.5 pages.

Organic chemists will miss structural formulas of many dyes; very often a certain dye's behavior in some photochemical respect is discussed in detail which might be more illustrative if its constitution were given. A more thorough discussion, including formulas, would also be desirable for photodegradation products of dyes.

In several places one has the impression that the author is not well acquainted with physical organic chemistry (p. 10,  $-\text{NH}_3^+$  is not a  $-M$ -substituent in Ingold's nomenclature; on page 112 one feels that Hammett's  $\sigma\rho$  relationship could be something specific for the rate of fading; on pp. 72–73 the author seems to think that the decrease of acidity of phenols and the increase of basicity of anilines are different effects).

On the other hand, it should be emphasized that the central part of the book—photoconductivity of dyes—is excellent and authoritative. Those parts of the book in which the author discusses the importance of photoconductivity for complex processes, e.g., for biological processes such as the assimilation of  $\text{CO}_2$  in plants catalyzed by the chlorophylls, are very remarkable.

This discussion will stimulate further work in this field, especially because the author differentiates clearly between experimental facts, definite conclusions drawn from these facts, and hypotheses which need further work in the laboratory. The discussion on the photoelectric theory of the photodynamic effect (pp. 338–351) is a good example of this.

In conclusion, this book can be highly recommended for all who are interested in photoelectric and photodynamic effects of dyed molecules. Beginners as well as experts will find the book stimulating. The book is, in spite of the remarks in this review, also useful for chemists who are interested in dyes in the technological sense (dyeing of fibers, plastics etc.) or in the organic chemistry of the processes involved in the reactions between dyes and light. For these, however, it does not emphasize the main problems, but provides suggestions of a different point of view. In this sense it is also welcome for this group of chemists.

DEPARTMENT OF INDUSTRIAL AND ENGINEERING CHEMISTRY HEINRICH ZOLLINGER  
SWISS FEDERAL INSTITUTE OF TECHNOLOGY  
ZURICH, SWITZERLAND

**Handbuch der Präparativen Anorganischen Chemie. Band II.** Edited by GEORG BRAUER, Professor für anorganische Chemie an der Universität Freiburg im Breisgau. Ferdinand Enke Verlag, 7000 Stuttgart W, Hasenbergsteige 3, Germany. 1962. xii + 1611 pp. 16.5 × 24.5 cm. Price, geheftet, DM 102; ganzleinen, DM 108.

Brauer's "Handbuch" is not a text-book. It is a reference work with contributions from a distinguished and highly capable group of inorganic chemists who have accepted responsibility for selecting those synthetic procedures with which each is thoroughly familiar through teaching and research. Reproducibility of experimental procedures is therefore guaranteed. That such a compilation should come from Germany is itself an indication that teaching and research in inorganic chemistry in the German speaking countries still strongly accent preparative and experimental chemistry, as contrasted with the physico-chemical approach which characterizes the English speaking world.

In its organization the second edition follows the pattern set by the first edition which appeared in 1954. Both are divided into three "large" chapters dealing with (I) Preparative Methods, (II) Elements and Compounds, and (III) Special Classes of Substances. The original one-volume edition (1439 pages) has been expanded into two volumes totaling 1611 pages (including a complete formula index and a subject matter index in Volume II). Volume I (pages 1–877) appeared in 1960 and was reviewed (*J. Am. Chem. Soc.*, **83**, 505 (1961)) by Anderson. Volume I included the general chapter on Preparative Methods and the first 18 sections of Chapter II covering the preparation of the elements and compounds of hydrogen and the seven regular groups in the Periodic Table. Volume II (pages 878–1611) with the date line 1962 includes: (a) eleven additional sections devoted to the preparative chemistry of the transition elements, thus completing Chapter II and (b) all of Chapter III on Special Classes of Substances.

The preparative chemistry of the transition elements and their compounds is the work of Glemser and Sauer (Cu, Ag, Au), Wagenknecht and Juza (Zn, Cd, Hg), Wetzel (Sc, Y, the rare earths), Ehrlich (Ti, Zr, Hf, Th), Brauer (V, Nb, Ta), Hein and Herzog (Cr, Mo, W, V), Lux (Mn), Glemser (Re), Lux (Fe), Glemser (Co, Ni), and Grube (Pt metals).

Particularly interesting are the sections which make up Chapter III, although it is not clear why the five specific topics should have been selected, except that the authors of each are well-known for their researches in the respective fields. The section by Wagner on Adsorption and Catalytically Active Substances is especially to be commended for its coverage of a wide variety of materials which find use as catalysts (active metals, compound

catalysts, simple and mixed oxides, gels). Scholder's section on Hydroxo-Salts is essentially a review of the preparative aspects of his own researches. The material on Iso- and Heteropoly Acids by the late G. Jander and one of his students, Gruettner, goes beyond the vanadium, molybdenum, and tungsten iso- and heteropoly derivatives to mention the polysulfates, -chromates, -arsenates, -tungstates, and -niobates, but neglects entirely any discussion of the polyphosphates and polymetaphosphates. The section by Seel on carbonyls and nitrosyls is devoted almost entirely to the preparative accomplishments of the Hieber school. The fifth and final section on alloys and intermetallic compounds by Brauer represents an excellent compilation on high temperature experimental methodology, with illustrative procedures for preparation of silicides, borides, and amalgams.

Professor Brauer is to be commended for his efforts in editing (and himself contributing to) this very excellent treatise on preparative inorganic chemistry. Its scheduled appearance in English will enhance its value to American chemists.

DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING  
UNIVERSITY OF ILLINOIS L. F. AUDRIETH  
URBANA, ILLINOIS

**Zone Electrophoresis in Blocks and Columns.** By H. BLOEMENDAL, Department of Biochemistry, Antoni van Leeuwenhoekhuis, The Netherlands Cancer Institute, Amsterdam (The Netherlands). American Elsevier Publishing Company, Inc., 52 Vanderbilt Avenue, New York 17, N. Y. 1963. viii + 219 pp. 13.5 × 19.5 cm. Price, \$6.50.

This is a good book. It is for the user of electrophoresis—the migration of solute with respect to solvent in a d.-c. field. "Zone" refers to the arrangement in which the space occupied by the initial sample is narrow compared to the distance available for electrical migration. Omitting only paper and agar gel subtypes, the author covers block, gel (starch, silica, and polyacrylamide), continuous, column, and density gradient techniques. These are each deftly treated in categories of apparatus, electrodes, preparation of supporting medium, introduction of sample, the run itself, influence of temperature and electroosmosis, location of the resolved zones, recovery, evaluation, and applications.

The 444 references appear to be complete through 1961 with a few from 1962. They are especially well cross-indexed and described appropriately.

It might have been better to indicate in the title that this is a practical book, for there is no theory to speak of, except as it pertains to engineering design. Often the theory as listed is so sketchy as to be misleading. For example, in the review of droplet sedimentation the explanation given on page 160 is reversed. Sucrose diffuses into the sample zone faster than protein diffuses out. The tendency to an inverted density gradient because of the additional sucrose leads to a stream of droplets originating from the lower boundary.

Nevertheless, the practicality of the text is superb. Not only are there many pictures and diagrams of commercial equipment and its operation, but there are excellent descriptions of simple, inexpensive apparatus made from ordinary items found in any laboratory. There are many tables giving working conditions for numerous chemical and biological substances and for the various supporting media; yet the book is small and compact.

The monograph fills a vacancy left by other publications and can be recommended as practical reference in a physical biochemistry course and as a laboratory manual for those using electrophoresis.

PLUM ISLAND ANIMAL DISEASE LABORATORY  
U. S. DEPARTMENT OF AGRICULTURE RODES TRAUTMAN  
GREENPORT, L.I., NEW YORK

**Thermodynamics of Small Systems, Part I.** By TERRELL L. HILL. W. A. Benjamin, Inc., 2465 Broadway, New York 25, N. Y. 1963. 171 pp. 16 × 24 cm. Price, \$4.95 paper, \$9.00 cloth.

The fundamental importance of classical thermodynamics to the physical chemistry of matter in bulk is that it places ex-

perimental measurement within the context of a comprehensive deductive scheme, whose assumptions are clearly stated. To an increasing extent, quantitative research activity has become directed toward matter in states of greater subdivision (*e.g.*, colloids, powdered absorbents, dilute macromolecules) than was the case during the early years of thermodynamics. Professor Hill has anticipated the resulting need for extension and generalization of the usual thermodynamic concepts to include description of small systems. This book is the first half of an exposition of that extension.

The dominant feature of small system thermodynamics is that quantities such as energy and entropy, which are extensive in character for macroscopic systems, will exhibit nontrivial size variations for small systems. In this manner, system size itself becomes an interesting thermodynamic variable (even though it may only indirectly be subject to change, for example, by examining a sequence of colloidal suspensions with varying size distributions). Accordingly, considerable emphasis is given in this text to isolating these nonextensive deviations, and to deriving those thermodynamic identities that are important for small systems, but which are either lacking in the usual macroscopic formalism, or which reduce to trivialities in that limit.

The author devotes a good deal of effort toward distinguishing the operational differences between the various "environments" in which the small systems are immersed, and by which one may control particle and energy interchanges with the small systems, and exert stresses. Although it is pointed out that the thermodynamic relations may be derived once and for all without any reference to particular environmental variables, it was deemed important to handle each case separately, since the magnitudes of various thermodynamic properties are not the same in each case (though the small system thermodynamic relations remain invariant), and since the quantities have differing experimental significances when they are fixed or can fluctuate. Of the six chapters included in this first installment, four are devoted to specific environments.

The major fraction of the examples given by the author have come not from experiment, but from statistical mechanical theory, where it is relatively easy to construct model small system partition functions, and to effect at least approximate evaluations of the thermodynamic quantities, with results that explicitly show size dependence. Lattice gases and model polypeptides undergoing simplified helix-coil transitions are called upon repeatedly as illustrations. Indeed, it seems fair to say that this development of small system thermodynamics was largely motivated by recent statistical mechanical theory, in a way historically that classical thermodynamics could not have been comparably motivated.

Two particularly interesting applications of small system thermodynamics covered are chemical and phase equilibria (Chapter 5). In the case of the latter, the author remarks that even though phase change in its ordinary interpretation (discontinuities in certain thermodynamic functions) cannot exist here, extrapolation procedures can identify vestigial "phase change," and lead to novel "equal-areas" constructions. Some model calculations are included by way of estimating rate of convergence to macroscopic first-order transition behavior with increasing size.

Assuming that the soon-to-be-available second part of this exposition resembles the first in stress and style (as is indicated by the reprinted paper, included at the end of this volume, from which both parts stem), the result will amount to a systematized handbook of available knowledge on small system thermodynamics. It is thus not a source of scintillating light reading for graduate students or mature scientists with casual interest. Workers in the fields of colloid and protein chemistry, as well as those concerned with surface films (systems small in at least one dimension), however, should give the subject of this book a serious perusal, since it may harbor potentially useful tools. Assuming that aggressive exploitation of small system thermodynamics by both theoreticians and experimentalists develops, it seems reasonable to look forward to a combined second edition of "Thermodynamics of Small Systems" with new quantitative examples taken directly from experiments on real systems.

BELL TELEPHONE LABORATORIES FRANK H. STILLINGER  
MURRAY HILL, NEW JERSEY