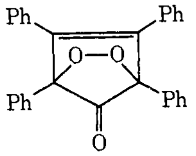
authentic specimen) which has been isolated recently and characterized.[7] The reaction using 1,3-diphenylisobenzofuran as the diene had a rate 30 times greater than that of tetraphenylcyclopentadienone and gave a 30% yield of 1,2-dibenzoylbenzene (mp 146–147° (lit. 148°) undepressed in admixture with an authentic specimen obtained by photosensitized oxygenation). A control incubation performed under identical conditions but with boiled enzyme gave, in each case, no detectable reaction.



I

The enzyme-catalyzed formation of the endoperoxide I from tetraphenylcyclopentadienone finds direct analogy in the addition of singlet oxygen to 1,3-dienoid systems. In this case, the mild conditions of the enzymic reaction led to the isolation of the endoperoxide which undergoes facile reactions under more drastic conditions.[7] The conversion of 1,3-diphenylisobenzofuran to 1,2-dibenzoylbenzene, here catalyzed by lipoxidase, is a known reaction of singlet oxygen[8] involving its addition to the 1,3-dienoid system present in the furan. That the oxygenation of the dienes is not due to the product(s) of lipoxidation of ethyl linoleate is shown by incubation of ethyl linoleate, under the same conditions, prior to the addition of the diene; this led to at least a tenfold decrease in the rate of oxygenation of the dienes. Kinetic studies further indicated that the disappearance of the diene had a maximum initial rate that occurs concurrently with the maximum rate of the oxidation of ethyl linoleate. The results reported here are therefore consistent with a reaction sequence in which the dienes trap, in a fast reaction, an intermediate formed during the oxidation of ethyl linoleate.

The observation that two modes of oxygenation analogous to the reactions of singlet oxygen are catalyzed by soybean lipoxidase raises the interesting question whether such excited molecular species, either free or bound to a group on the enzyme, are involved in the catalysis of this enzyme. As oxygen is usually the only high-energy reactant present in reactions catalyzed by lipoxidase, the generation of singlet oxygen would involve raising one molecule of oxygen to this excited state by the free energy released upon the reduction of another.[9] Previous studies[10] have given no indication that more than 1 mol of oxygen is consumed per mole of linoleate oxidized. They have, on the other hand, shown the absence of prosthetic groups and heavy metal ions on the enzyme[11] and have pointed to the participation of free radicals which are not involved in chain reactions.[12] Apart from these investigations, little is known about the way oxygen is involved in reactions catalyzed by soybean lipoxidase. The results discussed here indicate that an intermediate is generated during the lipoxidase-catalyzed oxidation of ethyl linoleate that is a close analog of singlet oxygen. Thus, it is reasonable to assume the existence of enzymes that catalyze the addition of the elements of molecular oxygen to 1,3-dienoid systems in specific substrates in the biosynthesis of natural products having structures that suggest this mode of derivation. Further studies on the relationship between the reactions of singlet oxygen and enzymic oxygenations including the possible presence of singlet molecular oxygen in biological systems is in progress.

Acknowledgment. The author is grateful to the Gulbenkian Foundation for a Research Fellowship at Churchill College, Cambridge, England, to the United Kingdom Agricultural Research Council for financial support, and to Mr. C. M. D. Beels for a sample of 1,3-diphenylisobenzofuran.

(7) H. W.-S. Chan. *Chem. Commun.*, 1550 (1970).

(8) C. Dufraisse and S. Ecary, *C. R. Acad. Sci.*, **223**, 735 (1946).

(9) This only applies to free molecular singlet oxygen. There can, of course, be oxygen bound to the enzyme that is "singlet-like" without having an excess of 22 kcal of electronic energy. This would fall into the category of oxygen activation that is often invoked in the discussion of reactions catalyzed by dioxygenases and may be involved in the present case.

(10) (a) R. T. Holman, *Arch. Biochem.*, **15**, 403 (1947); (b) H. L. Tookey, R. G. Wilson, R. L. Lohmar, and H. J. Dutton, *J. Biol. Chem.*, **230**, 65 (1958).

(11) A. L. Tappel, *Enzymes*, **8**, 275 (1963).

(12) A. L. Tappel, P. D. Boyer, and W. O. Lundberg, *J. Biol. Chem.*, **199**, 267 (1952).

Henry W.-S. Chan
University Chemical Laboratory
Cambridge, United Kingdom

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*Book Reviews**

Physical Organic Chemistry. Second Edition. By LOUIS P. HAMMETT, Columbia University. McGraw-Hill Book Co., New York, N. Y. 1970. 420 pp. $13.95.

Second editions usually closely resemble first editions, but this is not the case with the book under review. Instead of being satisfied with assessing progress in the great contributions of the first edition (sigma–rho theory, H_0 acidity function, *i*-factors), Hammett has chosen a more ambitious goal. Briefly, it is to examine the consequences of thermodynamics and transition-state theory on reaction rates.

This second edition is unusual in another way. It is published thirty years after the first.

It will be convenient to review Chapters 11 and 12 first, since they stand somewhat apart from the rest of the book. Chapter 11 is entitled "Quantitative Relationships Involving Structure and Reactivity." This is Hammett's sigma–rho theory, and it must give the author tremendous paternal pride to see how well it has

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* Unsigned book reviews are by the Book Review Editor.

stood the test of thirty years. Since Taft's extension of the theory to aliphatic chemistry, the field has stabilized. This allows Hammett to do a masterful job in succinctly summarizing the contributions of the various investigators. Every organic chemist can read this chapter with profit.

Chapter 12 is entitled "Effect of Structure on Enthalpy and Entropy Changes." The emphasis is on enthalpies and entropies of activation. The validity of isokinetic relationships (proportionality between $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$) and the existence of isoentropic and isoenthalpic series are discussed. This is recommended as initial reading in the field, and for many, it may terminate their reading. The impression is left of "The Waywardness of Enthalpy and Entropy Effects" (a section heading), and that examination of the effect of temperature on rates has still to shed much light on mechanisms of organic reactions.

The rest of the book is largely concerned with the various aspects of the effect of solvent on rates and the requisite thermodynamic background for an understanding of the area. This subject would appear to be of the greatest importance to organic chemists, yet it is largely ignored in texts. The reasons for this hands-off policy soon becomes apparent. Although the problem can be readily formulated in terms of the Brønsted equation and γ and μ^0 values, no general quantitative theory of μ^0 as a function of structure and solvent has emerged. Although Hammett becomes somewhat entangled in the morass, at least he has made a noble attempt to bring order out of chaos. This is preferable to the device of most physical chemists (stay aquocentric or gaseous) or the device of most organic chemists (ignore thermodynamics). Let us consider the chapters in order.

Chapter 2 takes up the thermodynamic basis and three knotty problems are soon encountered. The first is the notorious lack of conformity of symbolism among texts on thermodynamics, which is merely annoying.

The second problem concerns the thermodynamic symbolism to use for transfer of species between different solvents. Hammett uses activity coefficient (γ) to describe variations of activity with concentration and standard potential (μ_0, this was f in the first edition) to describe variations with solvent. This leads to cumbersome symbols like $K^{\circ\circ}$ and $\mu_1{}^{\circ\circ}$. It seems that some simpler notation should be possible.

The third problem is more subtle and serious. Numerical values of rate constants and equilibrium constants are dependent on what is counted for concentration. Hammett uses the example of boat and chair cyclohexane where one investigator might regard the reactant as boat cyclohexane and use the actual boat concentration in calculating k and K, whereas another would use the sum of boat plus chair. In the past, the terms stoichiometric and true concentrations were often used. Hammett proposes the terms "primitive" and "sophisticated" (in connection with chemical potential and, by inference, concentration). If there were but two possibilities, such a division would be adequate, but the reader need only recall the variety of Fe(III) species in a typical aqueous solution to appreciate the complexity of the problem. At least, we are indebted to Hammett for focusing attention on this problem.

Chapter 3 deals with statistical mechanics. Although Hammett spares us most of the elegant formalism of this subject, even the brief treatment has only a nominal effect on the subsequent chapters.

Chapter 4 on "The Evaluation of Rate Data" is a gem. Important practices in the art such as determining reaction order from initial rates, the advantages of stirred-flow reactors, and diffusion limits are discussed. The historical notes at the end are illuminating.

Chapter 5 develops transition-state theory. Emphasis is placed on the fact that kinetics cannot give information on the path between reactants and transition states. This is illustrated with the question (judged meaningless) as to which conformer of 1-chloropropane eliminates HCl. Structural and solvent isotope effects are beautifully summarized including the astounding k_H/k_D ratios of 24 found by Lewis and Funderburk.

Chapters 6–10 develop what is known about the effect of solvent (including acidity and basicity) on rates. It is the most complete treatment yet presented. It includes salt effects, solvent variation (including the dramatic effects of polar aprotic solvents), and the present status of acidity functions.

More than anything else, reading the second edition gave again those sparks of illumination, those glimpses of insight, and those inspirations for research that were experienced on reading the first edition thirty years ago.

Norman C. Deno, *Pennsylvania State University*

Chemistry of the Alkaloids. Edited by S. W. PELLETIER, University of Georgia. Van Nostrand-Reinhold Co., New York, N. Y. 1970. xx + 795 pp. $24.95.

It has been many years since a one-volume book has been available which offers a broad yet detailed and contemporary view of alkaloid chemistry. A complete survey of the field in one volume is of course impossible, and any selection must be arbitrary; yet this book, which consists of chapters by twenty-two different contributors, achieves a very good balance. Simple aromatic alkaloids, isoquinolines, Ipecacuanha alkaloids, the morphine series, Amaryllidaceae and Erythrina alkaloids, colchicine, indole, ergot, and Cinchona alkaloids, furoquinolines, betalains, pyrrolidines, piperidines, tropanes, Lycopodium alkaloids, and diterpenoid and steroidal alkaloids are covered. There is also a chapter on alkaloid biosynthesis and a welcome review of alkaloids from the viewpoint of biochemical systematics. The contributions are authoritative and well written. This book should be of interest to all investigators in natural products chemistry, and graduate students should find it absorbing and helpful.

P. W. Le Quesne, *University of Michigan*

Ethylenimine and Other Aziridines. By O. C. DERMER and G. E. HAM, Oklahoma State University and the Dow Chemical Co. Academic Press Inc., New York, N. Y. 1969. xiv + 592 pp. $27.00.

This ambitious work immediately arouses comparison with other reviews of aziridine chemistry, particularly those that are part of the two major treatises in heterocyclic chemistry. The aziridine chapter in the series edited by Weissberger is four years older and covers the subject in only 75 pages, with less than one-tenth the number of references in the present work; the chapter in the series edited by Elderfield, published in 1950, is smaller still. The present book is thus in no way redundant, and it has the valuable function of providing a nearly encyclopedic coverage.

This book is divided into eight chapters, covering formation, physical properties, reactions, polymerization, industrial applications, biological properties, analytical methods, and handling and storage. Synthesis is treated, but it is mixed in with the material on formation. With such a large amount of material to cover, the authors have had to forego a critical treatment, but short critical comments do appear throughout the work. The references, all 4212 of them, are grouped together at the end of the text. This unusual arrangement is not the easiest to use, and it must have taken an exceptional effort of organization for the authors to handle. However, the literature coverage is said to be complete through 1968, which is quite an achievement. It has the additional value that it includes a comprehensive coverage of the patent literature.

Collected Works. By JOHN D. ROBERTS, California Institute of Technology. W. A. Benjamin, Inc., New York, N. Y. 1970. xxv + 1278 pp. $20.00

This hefty volume contains all the scientific papers, including book reviews, of Professor Roberts, covering a span of thirty years. They have evidently been reproduced directly from the original articles. In addition, there is an appreciation by George Hammond, a list of twelve articles in press, a list of books by Professor Roberts, an index of coauthors, a subject index, and an entire chapter from "Organic Reactions" (Cyclobutane Derivatives). Apart from the general value of having the writings of one of the most influential organic chemists of the times in one place, this book will be especially appreciated by those who have had to wrestle painfully with the Author Index in *Chemical Abstracts* in order to locate all of Professor Roberts' contributions on a given subject, for his name is seldom first in the list of authors of an article.

Enamines: Synthesis, Structure, and Reactions. Edited by A. G. COOK, Valparaiso University Marcel Dekker, Inc., New York, N. Y. 1969. xi + 515 pp. $35.75.

Enamine chemistry has burgeoned since the publication of the major review of the area by Smuszkovicz ("Advances in Organic Chemistry," 1963), and there has developed ample need for a book-length treatment. The subject is covered in eight chapters, devoted to structure, properties, formation, various types of reaction, and utilization in synthesis. The authors (S. K. Malhotra, L. W. Haynes, E. J. Stamhuis, G. H. Alt, J. V. Paukstelis, A. G. Cook, O. Červinka, and M. E. Kuehne) are all well known in the field, and have produced a valuable book. The literature coverage appears to be through 1968; one chapter alone has 731 references! There is an author index and a substantial subject index.

Chemical Reaction Mechanisms. By George M. Fleck, Smith College. Holt, Rinehart & Winston, Inc., New York, N. Y. 1971. xi + 235 pp. $10.95.
A Guidebook to Mechanism in Organic Chemistry. Third Edition. By Peter Sykes, University of Cambridge. John Wiley & Sons, Inc., New York, N. Y. 1970. xii + 301 pp. $5.50 softbound.
Organic Reaction Mechanisms, 1968. Edited by B. Capon and C. W. Rees, Universities of Glasgow and Leicester. Interscience Publishers (John Wiley & Sons Ltd.), London. 1969. 583 pp. $24.95.

Of these three books on the same general subject, the first is a textbook for a laboratory course, the second is intended as supplementary material for introductory courses in organic chemistry, and the third constitutes a detailed review of the research published in 1968 on the subject.

Professor Fleck's book is strongly oriented toward kinetics, and might be considered suitable for an undergraduate course in the subject. However, it would not be a part of the conventional chemistry curriculum. At Smith College, it has been used in a freshman course on "Structure and Energetics in Chemistry." It consists of twelve chapters, of which the first is only a short general introduction. The others take up both methods of following rates and methods of handling the data, using reactions taken from organic, inorganic, and biological chemistry. The approach is always initiated at an easily comprehended, elementary level, but leads on to fairly sophisticated concepts. Very little mathematical facility is assumed, but the tools and concepts that are needed are introduced when required. An unusually large set of appendices explains such things as determinants and exponential functions. The nature of the treatment recommends this book to those who may need to rehabilitate themselves in the elements of kinetics on a practical as well as theoretical basis, especially those chemists who received their education before mechanism was recognized as a proper part of the curriculum.

Dr. Sykes' book focuses on results rather than methods, although one chapter out of the eleven is devoted to energetics, kinetics, and investigation. The fundamental types of reactions—additions, eliminations, displacements, etc.—are described in the light of what is known about their mechanisms. The approach is essentially didactic, with no attempt to provide rigorous arguments for the mechanisms presented. However, the more important evidence is quoted, and the author has carefully avoided dogmatism by pointedly qualifying statements and conclusions where the evidence is incomplete. There are no references, but only a two-page bibliography for further reading, entirely in book form. There is no mention of the Hammett equation anywhere, a surprising circumstance in a book that has chapters entitled "Structure, Reactivity, and Mechanism" and "The Strengths of Acids and Bases." Presumably the intent was to keep the presentation strictly qualitative, drawing a sharp line between physical organic chemistry and mechanism. The mechanisms that are described are generally up to date and accurate, although there is an unfortunate tendency to give prominence to intermediates that have been disproved, such as nitrenium ions in the Beckmann rearrangement, while playing down the actual mechanism.

The Capon–Rees book consists of fourteen chapters, of which six were written by the editors, devoted to the principal types of reactions or reactive intermediates. Each one is a heavily documented review, in moderate detail, of the advances published through November 1968, presented knowledgeably but without strong critical comment. The result is quite readable, and provides a most helpful way to become, or keep, reasonably current in the broad field of mechanism. It is pleasant to find the references at the foot of each page, a convenience to the reader that in recent years has been sacrificed to economy all too often. There is an author index occupying 64 pages; in this sort of work, such an index is particularly useful. The subject index, 23 pages, is cumulative over previous volumes in the series (1965–1968).

Naturally Occurring Insecticides. Edited by Martin Jacobson and D. G. Crosby, U. S. Department of Agriculture and University of California at Davis. Marcel Dekker, Inc., New York, N. Y. 1971. xii + 585 pp. $33.75.

The subject of this book is, obviously, a highly timely one. Not only is interest intense in natural alternatives to synthetic agricultural chemicals, but more progress in the chemistry of natural insecticides has been made in the last two decades than in the preceding century. The overwhelming abundance of the citations from the 1950's and 1960's in the extensive bibliographies in this book amply document this view.

There are eleven chapters, spread among three main divisions: Botanical Insecticides, Insect-derived Insecticides, and Bacterial and Fungal Insecticides. The fifteen authors form an international group, with a Canadian, an Australian, and six Japanese; most of the authors are associated with government laboratories. Each chapter covers occurrence and discovery, isolation, structure proof, synthesis, insecticidal activity, and toxicology and pharmacology, but the strongest part is the chemistry, which is presented with a high degree of competence. There is much tabulated information, lots of structural formulas, and a few photographs. The literature coverage appears to be through 1968, with a few 1969 references. There is both an author and a subject index. The style is such as to lead the nonspecialist gently but efficiently into the subject of each chapter, although it inevitably becomes a bit dry further in. This book is intended to be a comprehensive source book; it appears to be a good one.

Transition Metal Organometallic Chemistry: An Introduction. By R. Bruce King, University of Georgia. Academic Press Inc., New York, N. Y. 1969. ix + 204 pp. $11.50.

This book is based on one of the ACS "short courses". It consists of eight chapters, the first of which is relatively long and is devoted to General Principles, and the last, on organometallic derivatives of the coinage metals, is but two pages. The subject matter is heavily concerned with cyclopentadienyl and carbonyl derivatives, which are so richly represented in the transition metals. The chemistry of the various types of compounds is presented in a balanced way, and the introductory chapter supplies a perspective that is very helpful in visualizing the whole of the field. Each chapter has a selected bibliography of 50 or so references, and a supplementary reading list of books and reviews. There is both an author and a subject index. The value of this book will be to acquaint the nonspecialist with a field whose importance has grown greatly in the last decade; it could also serve as a text for a course at the intermediate level.