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## References and Notes

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- (2) (a) M. Hamberg, J. Svensson, and B. Samuelsson, *Proc. Natl. Acad. Sci. U.S.A.*, **72**, 2994 (1975); (b) G. B. Kolata, *Science*, **190**, 770 (1975).
- (3) The presence of endoperoxides in these solutions has been inferred by convincing indirect evidence, and recently a solvent-free product was obtained but structural or elemental analytical evidence for their structures remains to be obtained; see ref 1h-j.
- (4) For example, 9 $\alpha$ ,11 $\alpha$ -epidioxy-15(S)-hydroxy-13-*trans*-prostenic acid has a half-life of 2.7 h at 20 °C in light petroleum-ether (1:1v:v) and in aqueous medium the half-life is only 30 min at 20 °C: ref 1i.
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- (10) The peroxides **10**, **11**, **12**, and **13** all gave positive peroxide tests with ferrous thiocyanate reagent: cf. R. A. Johnson and E. G. Nidy, *J. Org. Chem.*, **40**, 1681 (1975). Correct elemental analyses were obtained for these compounds which are all white crystalline solids (from ethanol): **10** mp 109.7-110.0 °C (71% yield); **12** mp 140.5-141.0 °C (26% yield); **13** mp 141.7-142.3 °C (11% yield).
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## Book Reviews

**The World of Quantum Chemistry.** Edited by R. DAUDEL (Centre de Mécanique Ondulatoire Appliquée) and B. PULLMAN (Institut de Biologie Physico-Chimique). R. Reidel Publishing Co., Dordrecht/Boston, 1974. xiv + 316 pp. \$37.00.

The proceedings of the First International Congress of Quantum Chemistry held at Menton, France, in 1973 are reported. Five symposia, chaired by P.-O. Löwdin, J. Koutecký, R. Daudel, R. Parr, and A. Pullman, deal with methods of quantum chemistry, the electronic structure and conformations of molecules, theory of chemical reactivity, the formation and evolution of molecular excited states, and environmental effects on molecules. These symposia are not intended to provide a comprehensive treatise of each subject; rather, they should be viewed as a perspective provided by several distinguished scientists and experts. Contributions range from a reporting of calculated results to an exposé of powerful theoretical methods and interpretive remarks. One is introduced to methods and learns of their successful application; however, the lectures are not generally a source for details and alternative approaches are often not discussed.

Professor J. C. Slater sets a discussion of the  $X\alpha$  method in an interesting and informative historical perspective. The excitement about the unfolding applicability of quantum mechanics during the past 50 years is conveyed by one who held much of it in his own hands. E. Davidson discusses the configuration interaction description of electron correlation and some of his own very significant work on the use of natural orbitals in the development and analysis of CI expansions. Some recent developments and current problems of the theory of intermolecular interactions are presented by W. Kolos who discusses perturbation theory, CI and SCF applications.

The second symposium is introduced by Professor J. Koutecký who remarks on simple theories for the calculation of electronic structure. J. Pople reports on the application of the ab initio SCF method using modest basis sets to the problem of internal rotation about single bonds. Results are reported for several molecules, and some discussion of an adequate level of treatment, the effect of polar substituents, and coupled interactions is included. B. Pullman lectures on recent conformational studies using the PCILO method (localized orbitals and local excitations to antibonding orbitals applied at the CNDO level). Implications of preferred conformational space calculations on pro-

teins are discussed with reference to X-ray data, and applications to torsion angles in polynucleotides and conformations of acetylcholine are described.

Professor R. Daudel introduces the third symposium on the theory of chemical reactivity and discusses the use of static and dynamical indexes of reactivity. M. Karplus considers the importance of quantum corrections to classical trajectory calculations of reaction attributes using the hydrogen exchange reaction to illustrate different levels of approximation. Charge and spin transfers in chemical reactions are discussed by K. Fukui with emphasis on orbital interactions. Illustrative reactions are interpreted using highest occupied and lowest unoccupied molecular orbital concepts.

The fourth symposium deals with the formation and evolution of molecular excited states. J. Jortner and S. Mukamel provide a unified theoretical scheme for the description of the diverse decay channels of excited electronic states of polyatomic molecules. This symposium is a much more toward a self-contained development of the subject. The basic principles of relaxation phenomena are presented in terms of a Green's function formalism for the determination of decay amplitudes of the system; interstate coupling schemes and the time evolution of excited molecular states are carefully discussed. E. Heilbronner begins his lecture on UV photoelectron spectroscopy by pointing out possible misunderstandings in the interpretation of data in terms of the theoretical construct of molecular orbitals and Koopmans' theorem. Limitations of the theory, correlations of data with theoretical calculations, and correlations involving closely related compounds are discussed.

The last symposium on environmental effects on molecules is introduced by A. Pullman who considers nonpolar and polar solvents and crystal environmental effects on hydrogen-bonded systems like valinomycin; a supermolecule approach utilizing possibly simple models for nearest neighbor molecules is advocated. A. D. Buckingham lectures on intermolecular forces and the electric and magnetic properties of molecules, concisely setting forth the fundamentals of polarizability and dipole moment effects with brief reference to magnetic susceptibility and nuclear magnetic shielding. O. Sinanoğlu expounds on three types of potentials needed to predict conformations of molecules in solution. The adiabatic potential for molecules in

vacuo, an effective pair potential modification, and a solvophobic potential expressed as a Helmholtz free energy are introduced and treated using Sinanoğlu's solvent effect theory. K. Morokuma, S. Iwata, and W. A. Lathan describe excited electronic states of complexes in terms of ab initio calculations utilizing in the analysis an electron hole picture and a scheme for decomposition of energy contributions. Applications to several hydrogen-bonded systems and charge-transfer complexes are emphasized.

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**Total Synthesis of Steroids.** By ROBERT T. BLICKENSTAFF (Veterans Administration Hospital, Indianapolis, Ind., and Indiana University), ANIL C. GHOSH (Sheehan Institute and Sharps Associates), and GORDON C. WOLF (Veterans Administration Hospital, Indianapolis, Ind.). Academic Press, New York, N.Y. 1974. xiii + 328 pp. \$29.50.

The steroids constitute a class of organic compounds of great biological and medical significance, and this book provides an extensive summary of the published accounts of those research groups which have attempted the preparation of steroids by way of total synthesis. The authors state that they "tried to approach the subject as one planning to synthesize a steroid and needing to know what has already been done", and that the book "is for the organic chemist who desires an overall view of steroid total synthesis". These two goals reflect both the strongest and weakest points of the book. Their efforts to provide a comprehensive summary of previously published work on the total synthesis of steroids are quite successful. On the other hand, the book would not serve as a good introduction for an organic chemist previously unfamiliar with the area.

The book's greatest weakness is the virtual absence of any critical evaluation of the syntheses. The relative merits of the various synthetic schemes presented within a particular chapter are not discussed. Similarly, the arrangement of material in the book sometimes requires that different synthetic approaches to a given steroid be presented in different chapters; as a consequence, comparisons of such different approaches are absent. For example, there is no discussion of the relative advantages and disadvantages of Sarett's synthesis of cortisone (Chapter 9: BC → ABC → ABCD) relative to the approach used by Woodward (Chapter 12: CD → BCD → ABCD). This lack of critical evaluation and comparison does not help the authors achieve their goal to "aid the chemist planning a new steroid synthesis".

Chapter 1 ("Designing Total Syntheses"), presumably aimed at the general reader, is the weakest part of the book. Most organic chemists, even if they have not worked with steroids, should be familiar with such basic reactions as the Michael reaction, alkylation, acylation, and the Wittig reaction. On the other hand, the Torgov reaction, which has been used almost exclusively in steroid synthesis, is treated in no greater detail; no reference is made to the subsequent and more extensive treatment of this reaction in Chapter 4. A second example is provided by the separate entries for the Reformatsky reaction and for "Ethylation"; while the latter is mentioned as an alternative to the Reformatsky reaction, the only reference cited is a doctoral thesis. This would have been an ideal opportunity to discuss the use of anions derived from ethoxyacetylene (e.g., in the several syntheses of aldosterone presented in Chapter 9) and the advantages relative to the Reformatsky reaction.

The subject material, title, format, date of publication, and length of this book all invite comparison with Akhrem and Titov's "Total Steroid Synthesis" [Plenum Press, 1970; see *J. Am. Chem. Soc.*, **93**, 3842 (1971) for a review]. Both volumes are arranged similarly with syntheses grouped by the order in which rings are formed (e.g., CD → BCD → ABCD) rather than by the particular steroid or structural class. The books are comparable in length and both are profusely illustrated, each having 1500–2000 structural formulas. While there may be some duplication (since references are listed at the end of each chapter), the present volume has a total of 1325 references with coverage of the literature through 1973; this is about 200 references more than in the earlier book which does not provide literature coverage past 1968. It is this additional reference material together with a chapter on "Biogenetic-like Steroid Synthesis" and an excellent (and unusually useful) author index which make the present book more valuable. On the other hand, the virtual absence of reaction yields is unfortunate as it limits the reader in evaluating the relative merits of various reactions; in the earlier volume per cent yields for reactions (or reaction sequences) appear frequently.

This is not the sort of book that one is apt to sit down and read for

relaxation; presumably the authors never intended it to be. Rather it is a valuable compilation and summary of the synthetic work on steroids that has been carried out over the past 40 years. Anyone working in the area of steroid synthesis probably already has the book; anyone who wants to learn more about organic synthesis could benefit from occasionally browsing through it.

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**Organotransition-Metal Chemistry.** Edited by Y. ISHII (Nagoya University) and M. TSUTSUI (Texas A & M University). Plenum Press, New York, N. Y. 1975. xiv + 398 pp. \$37.50.

This volume is comprised of 35 papers describing advances in organotransition-metal chemistry. Twenty-six of the papers were presented at the first Japanese-American seminar on "Prospects in Organotransition-Metal Chemistry" held in 1974. The remaining papers were solicited by the editors. The topics of discussion touch on nearly every aspect of organotransition-metal chemistry. The subject covered in greatest detail is homogeneous catalysis; the discussions cover both the mechanistic and synthetic aspects of this exciting area.

A number of papers deal with the structures of novel organotransition-metal compounds such as the metallocarboranes and ruthenium cluster complexes. The kinetics and mechanism of a number of organotransition-metal reactions are discussed in depth. Papers on the stereochemistry of certain of these complexes are also included.

The biological aspects of organometallic chemistry are covered in some detail including a discussion of the mechanism of mercury neurotoxicity.

The discussions of the papers presented at the Japanese-American seminar are included. These discussions add greatly to the value of the book, and they permit the reader to capture a bit of the "spirit" of what appears to have been a successful seminar.

The book is pleasant, easy reading. It should stimulate interest in this area of chemistry. It is unfortunate that the book has appeared nearly two years after the seminar was held which diminishes the timeliness of some of the reports.

**George W. Kabalka**, *University of Tennessee*

**Interfacial Electrochemistry: An Experimental Approach.** By E. GILEADI, E. KIROWA-EISNER, and J. PENCINER (Tel-Aviv University). Addison-Wesley Publishing Co., Inc., Reading, Mass. 1975. xviii + 522 pp. \$19.50 (paper \$13.50).

This is a good reference book for electrochemists and materials scientists interested in the kinetic processes that occur in the areas of corrosion, energy conversion using fuel cells, catalysis, and electroplating. It would also be useful to researchers interested in crystal growth and surface physics if they have the proper chemistry background. The authors correctly state that electrochemical and irreversible processes are neglected in physical chemistry textbooks. They have done much to remedy the situation with their quite complete book.

The book is divided into two parts—theoretical considerations and an outline of some experiments. Some of the major topics covered in the 13-chapter theoretical section are the ionic double layer, electrocapillary thermodynamics, electrode kinetics, adsorption, and activation and diffusion controlled processes. There are some 40–50 experiments outlined in the 14-chapter experimental section. The authors have done a good job outlining experiments which, to a large degree, do not require elaborate equipment. Some of the major topics covered in this section are the operational amplifier, the double layer, electrode kinetics, voltammetry, and adsorption.

While I can recommend this book as a reference book, I cannot recommend it as a textbook. I have a background in physical chemistry, thermodynamics, surface physics, crystal growth, and electronic materials, yet I often had to refer to other books in order to understand the points being made by the authors. For example, Pitzer and Brewer's version of Lewis and Randall's "Thermodynamics" helped me to understand the significance of separating the chemical potential into a chemical part and an electrical part. There is also a lack of continuity. For example, the microscopic nature of capacitance appears in the discussion of many topics—topics such as the Stern model, the small dielectric constant of the adsorbed water in the inner Helmholtz layer, the changes in the capacitance with the voltage, the large dielectric constant of conductive oxides, and the electrolytic capacitor—yet these topics are too often treated as unrelated phenomena. Another reason for not recommending this book to be used as a textbook is that the index is not as complete as it should be.

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