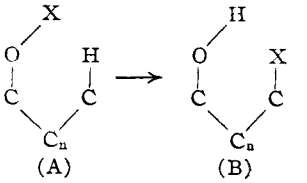
gen). This reaction has been observed by Professor Cheves Walling[2] for the hypochlorites of certain aliphatic alcohols. We now wish to report two examples of the reaction in the steroid series. In both cases the chlorhydrins formed have been characterized by base treatment to give the corresponding 1,4-oxides. The photolysis of hypo-

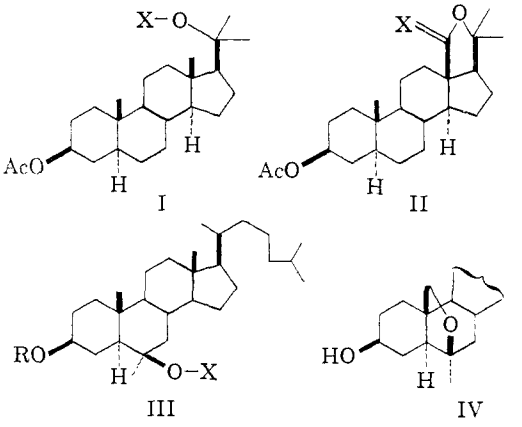


(A) (B)

chlorites to give alkoxy radicals and atomic chlorine is, of course, well known.[3]

3β-Acetoxy-20-methylallopregnan-20-ol (I, X = H)[4] was converted to the hypochlorite (I, X = Cl), m.p. 145–147°, $[\alpha]_D$ 0° (in CCl_4), $\lambda_{max.}^{CCl_4}$ 258 and 318 mμ (ε = 107 and 9.5, respectively) using chlorine monoxide.[5] This hypochlorite was photolyzed in dry benzene using a mercury lamp (200 watt, Pyrex filter)[1,6] with water cooling. The product, refluxed with 5% methanolic potassium hydroxide for 2 hr., gave, on reacetylation and chromatography, 20-methyl-18,20-oxidoallopregnan-3β-yl acetate (II, X = H_2) (20%), m.p. 152–154°, $[\alpha]_D$ +17° (in $CHCl_3$) as well as starting material (I, X = H). The constitution of the product was shown by its n.m.r. spectrum[7] (loss of C_{18} methyl group) and by vigorous chromic acid oxidation to the γ-lactone (II, X = O),[8] m.p. 209–210°, $[\alpha]_D$ 0° (in $CHCl_3$), $\nu_{max.}^{KBr}$ 1757 and 1745 cm.$^{-1}$. The ether (II, X = H_2) and its derived lactone (II, X = O) have been prepared independently by Cainelli, *et al.*[8]

Similarly 3β-acetoxy-6α-methylcholestan-6β-ol (III, R = Ac, X = H)[9] was converted to its hypochlorite (III, R = Ac, X = Cl) and photolyzed. Base treatment of the product as above afforded 6α-methyl-6,19-oxidocholestan-3β-ol (IV) (50%), m.p. 179–181°, $[\alpha]_D$ +19° (in $CHCl_3$) as well as the diol (III, R = X = H). The constitution of (IV) was confirmed by its n.m.r. spectrum[10,11] (loss of C_{19} methyl group).



I II

III IV

Acknowledgments.—We thank Dr. M. M. Pechet for his encouragement and the Misses C. Pantuck and L. Gendron for able experimental assistance.

(2) We thank Professor Walling (Columbia University) for his kind personal communication and for helpful advice.

(3) Cheves Walling, "Free Radicals in Solution," J. Wiley and Sons, Inc., New York, N. Y., 1957, p. 386.

(4) A. Butenandt and H. Cobler, *Z. physiol. Chem.*, **234**, 218 (1935); B. Koechlin and T. Reichstein, *Helv. Chim. Acta*, **27**, 549 (1944).

(5) M. Anbar and I. Dostrovsky, *J. Chem. Soc.*, 1105 (1954).

(6) D. H. R. Barton and J. M. Beaton, *J. Am. Chem. Soc.*, **82**, 2641 (1960).

(7) We thank Dr. J. W. Lown for kindly determining these n.m.r. spectra.

(8) G. Cainelli, B. Kamber, J. Keller, M. L. Mihailović, D. Arigoni and O. Jeger, *Helv. Chim. Acta*, **44**, 518 (1961).

(9) L. F. Fieser and J. Rigaudy, *J. Am. Chem. Soc.*, **73**, 4661 (1951); R. A. Sneen, *ibid.*, **80**, 3982 (1958).

(10) Satisfactory analytical data have been secured for all new compounds except that the hypochlorites were characterized through iodimetry (being thereby reduced to the parent alcohol).

(11) The substance of this Communication was given in a lecture by D. H. R. B. at the Annual General Meeting of the Chem. Soc. at Liverpool, U. K., on April 12th, 1961. At that time Dr. V. A. Petrov (B.D.H.) informed us by personal communication that he had observed similar results in steroids.

RESEARCH INSTITUTE FOR
MEDICINE AND CHEMISTRY M. AKHTAR
CAMBRIDGE 42, MASS. D. H. R. BARTON

RECEIVED APRIL 19, 1961

BOOK REVIEWS

The Surface Chemistry of Metals and Semiconductors. A Symposium Sponsored by the Office of Naval Research and the Electrochemical Society, Columbus, Ohio, 1959. Edited by HARRY C. GATOS. With the assistance of J. W. FAUST, Jr., and W. J. LAFLEUR. John Wiley and Sons, Inc., 440 Fourth Avenue, New York 16, N. Y. 1960. xi + 526 pp. 16 × 23.5 cm. Price, $12.50.

This volume is the record of a symposium on the surface chemistry of metals and semiconductors held under the auspices of the Electrochemical Society and the Office of Naval Research in October, 1959. It contains twenty-two papers which are presented in five sections entitled The Chemistry and Physics of Surfaces, Imperfections and Surface Behavior, Electrode Behavior of Metals and Semiconductors, Surface Reactions in Liquid Media, and Surface Reactions in Gaseous Media, respectively. The character of the individual contributions varies considerably. There is, for example, a short (11 page) general introduction to the physics and chemistry of surfaces by W. H. Brattain, a report on some recent experimental investigations of oxidation–reduction reactions at the germanium electrode by H. Gerischer, and lengthy and fairly detailed review articles on the oxidation of metals by K. Hauffe and by Gwathmey and Lawless.

This volume is perhaps best described as a collection of elementary review papers and, as such, should be of value to chemists and physicists seeking an introduction to recent research in the areas enumerated above. It is possible that a surface chemist or electrochemist may find some of the contributions superficial, insufficiently detailed or similar to reviews previously published in the periodical literature. However, the papers are carefully and economi-

cally written, the list of contributors is a distinguished one, and it is likely that most physical chemists will find at least one of the contributions to be of interest and value.

The text, which is reproduced by an offset process, does not make a good appearance, but it is quite legible and the reproduction of the figures is good. The reviewer is not convinced that this book will be a permanently valuable work of reference and believes that it might have been more suitably published in soft covers with greater dispatch and at a considerably lower price.

DEPARTMENT OF CHEMISTRY
THE UNIVERSITY OF TEXAS LEON J. SLUTSKY
AUSTIN 12, TEXAS

Advances in Catalysis and Related Subjects. Volume XII. Edited by D. D. ELEY, Nottingham, England, P. W. SELWOOD, Evanston, Illinois, and PAUL B. WEISZ, Paulsboro, New Jersey. Academic Press Inc., 111 Fifth Avenue, New York 3, N. Y. 1960. x + 324 pp. 16 × 23.5 cm. Price, $11.00.

This volume includes six reviews: 1. The Wave Mechanics of the Surface Bond in Chemisorption, T. B. Grimley; 2. Magnetic Resonance Techniques in Catalytic Research, D. E. O'Reilly; 3. Base-Catalyzed Reactions of Hydrocarbons, Herman Pines and Luke A. Schaap; 4. The Use of X-ray K-Absorption Edges in the Study of Catalytically Active Solids, Robert A. Van Nordstrand; 5. The Electron Theory of Catalysis on Semiconductors, Th. Wolkenstein; 6. Molecular Specificity in Physical Adsorption, D. J. C. Yates.

Only a handful of aging chemists share this reviewer's memories of the remote era in which chemical bonds were described in pre-quantum mechanical language. Progress is always not merely painful, but painfully slow. The gay hope that all chemistry would flow without effort from the solution of wave equations has been utterly shattered, and there is no indication that the fastest computers now contemplated can put it together again. Even as a language, quantum mechanics brought no easy millenium. Lewis was able to express profound truth without it, as Kekulé had done long before; yet other distinguished chemists have always been able to write complete nonsense about chemical bonds in the most advanced language available to them. No one would consider that these qualifications contradict the transcendent importance of wave mechanics in shaping our concept of the chemical bond.

The application of quantum mechanics to the electronic structure of semiconductors has now reached a stage where it can contribute importantly to the understanding of many phenomena in catalysis by solids. Chemists will not learn this new language easily. They are handicapped not only by its intrinsic difficulty, but by the absence of cases in which simple, familiar statements can be translated into the new language. In these circumstances, all catalytic chemists should welcome the review by Grimley of Liverpool, and especially that by Wolkenstein of Moscow, who has played a major role in these developments. I shall make no attempt here to provide an easy two-sentence summary. It is my function merely to urge your attention.

Pines and Schaap have written a brief but fascinating account of a new chapter in hydrocarbon chemistry. These things could have been done fifty years ago, somewhat more painfully for the lack of modern analytical techniques. I have no doubt that fifty years from now this kind of work will still be rewarding. The frontiers are not all on the moon.

The other three reviews share the common characteristic that I could learn nothing by reading them at home in the absence of a complete scholarly library, which is the only reading opportunity I have. The problem is illustrated by the Yates review, in which the first half rests squarely on the concept that solids have a surface *tension*, an actual force which resists stretching of the surface, which is numerically distinct from the surface energy. I do not believe this. I consulted the reference to Gibbs, and found it irrelevant. The other references I could not consult, and the review contained no hint of their content. I may well be wrong in this matter, and some reader of these remarks may take the trouble to enlighten me. I expect, however, that a review will educate me directly, and not by such a devious and ironical process.

These remarks lay on my desk for days while I struggled with the feeling that they missed the real point. It comes to me now, from Isak Dinesen's "Out of Africa." You cannot capture the colors, she found, by shooting the Iguana. "It was the live impetuous blood pulsating within the animal, which had radiated out all that glow and splendor." And so you cannot, I believe, capture the spirit of a catalyst in magnetic resonance or absorption edges. Grimley, Pines and Wolkenstein, in their diverse ways, have dealt with live impetuous catalysts, and the other reviewers, however skillfully, with gray corpses.

UNIVERSAL OIL PRODUCTS COMPANY
30 ALGONQUIN ROAD LOUIS S. KASSEL
DES PLAINES, ILLINOIS

Advances in Enzymology and Related Subjects of Biochemistry. Volume XXII. Edited by F. F. NORD, Fordham University, New York, N. Y. Interscience Publishers, Inc., 250 Fifth Avenue, New York 1, N. Y. 1960. v + 567 pp. 16.5 × 23.5 cm. Price, $14.00.

"Advances in Enzymology" has long been established as a standard biochemical reference, and as a series has maintained a broad coverage of subjects of biochemical interest by means of authoritative articles. The present volume is a tribute to the editor, who has succeeded again in organizing a work of significance to workers and students in many areas of current activity. The range of topics extends from biologically-oriented articles on Genetic Control of Enzyme Activity (Fincham) and Induced Synthesis of Proteins (Halvorson) through descriptive biochemistry, including Synthesis and Hydrolysis of Sulfate Esters (Roy), Biosynthesis of Cholesterol (Popják and Cornforth) and Biochemistry of Sulfonium Compounds (Shapiro and Schlenk), to theoretical analysis of The Active Site and Enzyme Action (Koshland) and Coenzyme Binding (Shifrin and Kaplan) and also includes a non-enzymatic description of Synthesis of Nucleotide Coenzymes (Baddiley and Hughes) and an article on the technique of Column Chromatography of Enzymes (Turba).

The variation in subject matter is accompanied by differences in the state of development of the topics considered, and these differences are reflected in the manners in which the authors have treated their articles. The two discussions by Fincham and Halvorson consider two aspects of the question of protein synthesis. The intimate relation between gene and enzyme has been clearly established in the numerous examples cited by Fincham of single mutations causing modifications of the properties of individual enzymes. These studies demonstrate the mutual contributions of genetics and enzymology. The expression of gene action through qualitative and quantitative changes in enzymes is seen as a major (if not exclusive) property of mutations, and one that is increasingly susceptible of analysis. The altered enzymes and the components of enzymes obtained from appropriate mutant organisms offer novel materials for studying the relationship between enzyme structure and function. Halvorson's discussion of enzyme induction considers this phenomenon only in microörganisms, but the wealth of material available from this source permits a very complete analysis of the properties of induction and the current hypotheses of protein synthesis. These two articles are excellent summaries of very active fields of research. Both are organized to illuminate the questions that are of great interest at this time; they both summarize the literature thoroughly and carefully distinguish between observations and hypothesis.

The articles on sulfate esters and sulfonium compounds are comprehensive reviews of these aspects of sulfur biochemistry. They are unsatisfying only to the extent that they treat subjects that have not been cleared up adequately. The recent demonstrations of sulfate activation and transfer and the pluripotential properties of active methionine offer hope that some of the other reactions mentioned in these articles may be the subjects of successful investigation: that enzymes will be obtained in purer form, that anomalous kinetics will be explained, and that over-all conversions will be resolved into discrete enzymatic reactions. The elucidation of the biosynthesis of cholesterol is one of the dramatic developments of recent years, and the review by Popják and Cornforth, both major contributors to this development, beautifully outlines the evolution of the problem and de-