The enhancement disappeared on standing for two to four days at room temperature, but could be restored by further irradiation. Feebly catalytic samples, prepared by annealing the standard preparation at 200° without further pumping, showed a several thousandfold increase in activity when irradiated, but the increase disappeared in a few hours, even at $-78°$. Irradiation during activity measurement on the assumption that short-lived states might play a role as in photosensitization gave results not greatly different from those irradiated *in vacuo* between measurements, indicating that short-lived states need not be invoked.

The reality of the radiation effect is attested by some 49 separate irradiations which produced in 38 cases appreciable increase in activity. Some instances of lack of change appear to indicate saturation of the effect, while some decreases are thought to have resulted from poisoning. No activity was induced by gamma rays in samples that had not been activated in the manner described above.

The high rate of change of activity with irradiation and the ready annealing of the change suggest that the effects observed may be attributable to electrons or positive holes trapped in special sites in the alumina lattice. Experiments intended to show more about the phenomena are in progress.

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RECEIVED NOVEMBER 9, 1956

THE STABILITY RELATIONSHIP OF 1-METHYLCYCLOPENTENE AND METHYLENECYCLOPENTANE

Sir:

Evidence bearing on the problem of stability differences that exist between isomers possessing exocyclic and endocyclic double bonds in 5- and 6-membered ring systems has been summarized by Brown, Brewster and Shechter.[1] The conclusions reached by these authors are expressed in the generalization that "reactions will proceed in such a manner as to favor the formation or retention of an exo double bond in the 5-ring and to avoid the formation or retention of the exo double bond in the 6-ring systems." Although the position adopted with respect to 6-membered ring compounds is well-supported,[2] evidence available concerning the 5-ring cases is less convincing.

In connection with a general study of heats of catalytic hydrogenation in solution, currently in progress in this Laboratory, we have had an opportunity to examine the heat changes accompanying hydrogenations of 1-methylcyclohexene, methylenecyclohexane, 1-methylcyclopentene, and methylenecyclopentane. The results obtained for these substances are listed in Table I. In each isomer pair the methylenecycloalkane shows a higher heat of hydrogenation than does the 1-methylcycloalkene, the differences being 2.1 kcal./mole for the 6-membered, and 3.8 kcal./mole for the 5-membered ring compounds. Since these values reflect differences in heat content rather than in free energy, we were prompted to investigate the equilibrium behavior of the methylene derivatives in the presence of acid. Our results for methylenecyclohexane are in complete accord with those of Wallach and his associates,[2] and it was further established that in acetic acid containing *p*-toluenesulfonic acid methylenecyclopentane is converted essentially quantitatively into 1-methylcyclopentene. The amounts of methylenecyclopentane present in the equilibrated product are too small to be detectable by infrared analysis, although trace contamination by acetate ester is indicated. The conclusion that 1-methylcyclopentene is *more* stable than methylenecyclopentane is therefore inescapable.

TABLE I

HEATS OF HYDROGENATION IN ACETIC ACID SOLUTION (25° C.)

Compound	$-\Delta H$, kcal./mole
1-Methylcyclohexene	25.70 ± 0.10
Methylenecyclohexane	27.82 ± 0.07
1-Methylcyclopentene	23.01 ± 0.04
Methylenecyclopentane	26.82 ± 0.08

A complete report of this work will be published shortly.

DEPARTMENT OF CHEMISTRY
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RECEIVED DECEMBER 6, 1956

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(1) H. C. Brown, J. H. Brewster and H. Shechter, THIS JOURNAL, **76**, 467 (1954).

(2) Of special relevance is the demonstration of O. Wallach, E. Evans, J. B. Churchill, M. Rentschler and H. Mallison, *Ann.*, **360**, 26 (1908), that various alkylidenecyclohexanes are converted into the corresponding 1-alkylcyclohexenes by the action of acid.

BOOK REVIEWS

Statistical Mechanics. Principles and Selected Applications. By TERRELL L. HILL, Naval Medical Research Institute, Bethesda, Maryland. McGraw-Hill Book Company, Inc., 330 West 42nd Street, New York 56, N. Y. 1956. xiii + 432 pp. 16 × 23.5 cm. Price, $9.00.

This book gives an excellent discussion of some of the recent advances which have been made in the applications of statistical mechanics. According to the author, "the primary aim of this volume is to provide a rather detailed account of a selected group of these developments, namely, fluctuation theory, imperfect gas and condensation theory, distribution functions, nearest neighbor (Ising) statistics, and free volume and hole theories of liquids and solids."

The book opens with introductory chapters on classical statistical mechanics, quantum statistical mechanics, and the relation of statistical mechanics to thermodynamics. The theory of statistical mechanics is developed on a postulational basis although brief mention is made of ergodic theory. In these chapters the author introduces a hierarchy of ensembles including generalized, grand canonical, isothermal-isobaric, canonical and microcanonical ensembles, and discusses the applications of each. These chapters are quite brief but serve to bring together the relations, notation and terminology which the author uses in later chapters.

Following the introductory chapters and a chapter devoted to fluctuation theory, there is a sequence of chapters on various aspects of the problem of the equation of state of gases, liquids and solids. Some of the material in these chapters is new and a great deal more has been available previously only in the original papers.

The discussions of the particular applications of statistical mechanics chosen by the author are quite complete and very readable. This book is certain to be highly useful as a ready source of information in these fields.

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Technique of Organic Chemistry. Volume II. Second Edition. Editor: ARNOLD WEISSBERGER, Research Laboratories, Eastman Kodak Co., Rochester, New York. Catalytic Reactions. By V. I. KOMAREWSKY, Illinois Institute of Technology, Chicago, Illinois, C. H. RIESZ, Armour Research Foundation of Illinois Institute of Technology, Chicago, Illinois, F. L. MORRITZ, Sinclair Research Laboratories, Inc., Chicago, Illinois. Photochemical Reactions. By C. R. MASSON, Atlantic Regional Laboratory, National Research Council of Canada Halifax, Nova Scotia, V. BOEKELHEIDE, and W. ALBERT NOYES, JR., University of Rochester, Rochester, New York. Electrolytic Reactions. By SHERLOCK SWANN JR., University of Illinois, Urbana, Illinois. Interscience Publishers, Inc., 250 Fifth Avenue, New York 1, N. Y. 1956. ix + 543 pp. 16 × 23.5 cm. Price, $11.50.

This second edition of "Technique of Organic Chemistry" Vol. II is so greatly expanded from the first edition that it could almost be called a new book. The increase in subject matter extends to all three sections of the volume, *viz.*, "Catalytic Reactions," "Photochemical Reactions" and "Electrolytic Reactions."

The first section, by V. I. Komarewsky, C. H. Riesz and F. L. Morritz, is introduced by a comprehensive and well illustrated coverage of the equipment and techniques required to handle the many experimental situations which the chemist is likely to encounter. Although the experienced worker in this field may prefer certain pet techniques which are not discussed, he should find the text highly rewarding as a source of new ideas and as a yardstick against which to measure the effectiveness of his own procedures. For those entering the field of catalysis the book should be invaluable. Techniques and equipment required to meet most experimental situations will be found. In this section the greatest difference between the first and second edition is the serious effort made to assemble examples of the catalytic reactions most likely to be encountered by the organic chemist. The inclusion in the appropriate text of detailed directions for preparing the catalyst of reference is a feature to be applauded.

The second section, "Photochemical Reactions," by C. R. Masson, V. Boekelheide and W. A. Noyes, Jr., and the third section, "Electrolytic Reactions" by Sherlock Swann, Jr., are particularly worth the attention of the organic chemist unfamiliar with the potentialities of these fields. In the field of photochemistry, especially, the reviewer was impressed by the wealth of new research which has been published since the appearance of the first edition of this work and a major part of this section is devoted to a survey of the aspects of these new developments of particular interest to the organic chemist. The reader will find specific directions for carrying out photochemical syntheses where this approach offers advantages over more conventional approaches. More often the extensive survey of organic syntheses by photo processes will suggest situations where the use of light may be seriously considered as the procedure of choice. Equally deserving of comment, the authors' obvious interest in photochemical reactions has not been allowed to cloud their recognition of the limitations of the technique.

Electrochemical techniques, as a facile solution to synthetic problems, also, probably receive less consideration than they deserve. Professor Swann adequately covers the subject for the person who is willing to survey and take advantage of the opportunities in this area, but who may not wish to become an expert. For this purpose the coverage of theory and practice is all that is intended. A wide variety of procedures and type reactions are described and illustrated with suitable examples. Although this section seems to have undergone the least revision from the first edition, there has been added an impressive compilation of electrolytic organic reactions and the pertinent literature references.

There are few typographical errors and the book is easily read. The reviewer was somewhat frustrated by his inability to uncover the original source, either in the book or in *Chemical Abstracts*, of an intriguing mention of the photooxidation of dihydropyran, but this is intended in no way to detract from the suggestion that this book has much to offer the organic chemist.

SHELL DEVELOPMENT COMPANY FREDERICK F. RUST
EMERYVILLE, CALIFORNIA

BOOKS RECEIVED

November 10, 1956—December 10, 1956

MELVIN J. ASTLE. "The Chemistry of Petrochemicals." Reinhold Publishing Corporation, 430 Park Avenue, New York 22, N. Y. 1956. 267 pp. $6.50.

C. H. BAMFORD, A. ELLIOTT, AND W. E. HANBY. "Synthetic Polypeptides. Preparation, Structure, and Properties." Volume V. Physical Chemistry. A Series of Monographs. Edited by Eric Hutchsinson. Academic Press, Inc., Publishers, 111 Fifth Avenue, New York 3, N. Y. 1956. 445 pp. $10.00.

FRANK M. BIFFEN AND WILLIAM SEAMAN. "Modern Instruments in Chemical Analysis." First Edition. McGraw-Hill Book Company, Inc., 330 West 42nd Street, New York 36, N. Y. 1956. 333 pp. $7.50.

RICHARD J. BLOCK AND KATHRYN W. WEISS. "Amino Acid Handbook. Methods and Results of Protein Analysis." Charles C. Thomas, Publisher, 301–327 East Lawrence Avenue, Springfield, Illinois. 1956. 386 pp. $10.50.

FREDERICK R. EIRICH (edited by). "Rheology. Theory and Applications." Volume I. Academic Press, Inc., Publishers, 111 Fifth Avenue, New York 3, N. Y. 1956. 761 pp. $20.00.

JESSE P. GREENSTEIN AND ALEXANDER HADDOW (edited by). "Advances in Cancer Research." Volume IV. Academic Press, Inc., Publishers, 111 Fifth Avenue, New York 3, N. Y. 1956. 416 pp. $10.00.

W. HEITLER. "Elementary Wave Mechanics with Applications to Quantum Chemistry." Second Edition. Oxford University Press, 114 Fifth Avenue, New York 11, N. Y. 1956. 193 pp. $2.90.

JOHN E. LEFFLER. "The Reactive Intermediates of Organic Chemistry." Interscience Publishers, Inc., 250 Fifth Avenue, New York 1, N. Y. 1956. 275 pp. $6.00.

N. J. LEONARD, Editor-in-Chief. "Organic Syntheses." Volume 36. John Wiley and Sons, Inc., 440 Fourth Avenue, New York 16, N. Y. 1956 120 pp. $3.75.

H. REMY. "Treatise on Inorganic Chemistry." Volume II. "Sub-Groups of the Periodic Table and General Topics." Translated by J. S. Anderson. Edited by J. Kleinberg. D. Van Nostrand Co., Inc., 126 Alexander Street, Princeton, New Jersey. 1956. 800 pp. $17.75.

SOCIETY OF CHEMICAL INDUSTRY. "Ion Exchange and its Applications." Papers Read at the Conference in the William Beveridge Hall, London University, 5th–7th April, 1954, with the discussions that followed. The Macmillan Company, 60 Fifth Avenue, New York 11, N. Y. 1956. 173 pp. $7.50.

MELVILLE L. WOLFROM, Editor, and R. STUART TIPSON, Associate Editor. "Advances in Carbohydrate Chemistry." Volume 11. Academic Press, Inc., Publishers, 111 Fisher Avenue, New York 3, N. Y. 1956. 465 pp. $11.00.