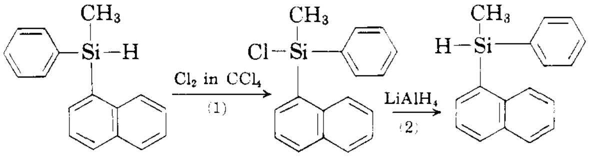
OPTICALLY ACTIVE ORGANOSILICON COMPOUNDS HAVING REACTIVE GROUPS BONDED TO ASYMMETRIC SILICON. DISPLACEMENT REACTIONS AT SILICON WITH PURE RETENTION AND PURE INVERSION OF CONFIGURATION

Sir:

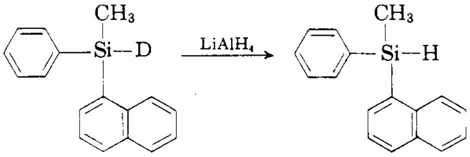
As the start of a new phase in organosilicon chemistry, which may prove as significant for silicon chemistry as was the discovery of the Walden inversion in 1895 for carbon chemistry, we wish to record these advances: (a) practical synthetic routes to optically active organosilicon compounds having reactive groups bonded to asymmetric silicon[1]; (b) the first proven examples of substitution reactions at asymmetric silicon proceeding with pure retention and pure inversion of configuration; (c) the first example of a Walden cycle in substitution reactions at a silicon atom.[2]

The pure optical isomers of α-naphthylphenylmethylsilane (I and II) were obtained by separation through fractional crystallization of diastereomeric alkoxysilanes ($R_3Si^*OR^*$),[3] and then stereospecific reduction with lithium aluminum hydride. The dextrorotatory isomer I (m.p. 63°; found: Si, 11.2; H (attached to Si), 0.415; mol. wt., 250) was converted to its optical isomer by a Walden cycle which involved chlorination to give a 90% yield of the optically pure levorotatory chlorosilane III (m.p. 64°; found: Si, 9.8; Cl, 12.4) with subsequent reduction with lithium aluminum hydride which gave (95% yield) the optically pure levorotatory silane II (m.p. 63°; identical with I in all respects (infrared spectrum, analyses, etc.) except for direction of rotation). Since both reactions (1 and 2) are completely stereospecific, one of these must proceed with pure retention and the other with pure inversion of configuration. These changes are represented with an arbitrary assignment of configuration for I and a tentative choice of reaction (1) as proceeding with inversion of configuration.



$[\alpha]_D + 32°$ (I) $[\alpha]_D - 6.3°$ (III) $[\alpha]_D - 32°$ (II)

The (+)-deuterosilane IV (m.p. 63°; found: Si, 11.2; D, 0.823; mol. wt., 251) gave optically pure I, thus providing unequivocal proof for pure retention of configuration in this reaction.



$[\alpha]_D + 32°$ (IV) $[\alpha]_D + 32°$ (I)

Experiments now in progress have yielded optically active R_3Si^*Br, R_3Si^*OH and $R_3Si^*OCH_3$. Thus, it seems virtually certain that a large new field of stereochemistry is in the offing.

We thank Dow Corning Corporation for generous support of this investigation.

College of Chemistry and Physics
The Pennsylvania State University
University Park, Pennsylvania
Leo H. Sommer
Cecil L. Frye

Received December 31, 1958

---

[1] Resolutions of three organosilicon compounds, only two of which contained (relatively unreactive) functions bonded to silicon were carried out by the pioneer of organosilicon chemistry, F. S. Kipping (*J. Chem. Soc.*, 209 (1907); 2090 (1908); 755 (1910)) but the routes to the optically active compounds were so tedious and lengthy, the amounts obtained so small, and the rotations so feeble, that studies of stereochemistry were not possible with these substances.

[2] In 1895, P. Walden (*Ber.*, **28**, 1287, 2766 (1895)) carried out a cycle of reactions by which an optically active organic compound was converted to its isomer of opposite rotation, and thereby provided the beginnings of our now extensive knowledge of the stereochemistry of substitution at a carbon atom.

[3] Synthesis and separation of these diastereoisomers will be detailed in a subsequent publication.

BOOK REVIEWS

Introduction to Enzymology. By Alan H. Mehler, National Institutes of Health, Bethesda, Md. Academic Press, Inc., 111 Fifth Avenue, New York 3, N. Y. 1957 viii + 425 pp. 15.5 × 23 cm. Price, $10.80.

"Introduction to Enzymology" evolved from a course presented by the author at the National Institutes of Health to an audience composed largely of investigators trained in areas peripheral to biochemistry. The text is primarily a descriptive treatment of the action of enzymes, especially in metabolic context. The introduction includes a discussion of the principles of enzyme assay and elementary kinetic relationships. The following chapters (II, Hydrolysis of Peptides and Proteins; III, Fermentation and Oxidation of Major Metabolic Fuels; IV, Biological Oxidation: Transfer of Oxygen, Hydrogen, and Electrons; V, Sugars and Sugar Derivatives; VI, Polynucleotides and Their Components; VII, Amino Acids; VIII, Acids and Acid Derivatives; summarize the state of knowledge (including mechanistic interpretations of the catalytic action) of nearly 200 specific enzymes and implicate the action of several hundred more in the various metabolic sequences presented. The structure and properties of coenzymes and prosthetic groups and some general concepts (*e.g.*, Free Energy and the Concept of Bond Energy, and Oxidation Reduction Potentials) are also reviewed. The final chapter (IX, Organization of Structure and Function) concerns the integration of enzymes within cells, adaptive enzymes and the synthesis of proteins.

In general, the information presented is accurate. The text includes approximately 1400 particularly significant reviews and articles (to early 1957). The precision of expression, however, often leaves something to be desired.

In addition to presenting considerable information the author succeeds in conveying to the reader a feeling of the manner in which new enzymes have been discovered and metabolic pathways have been elucidated. Several weaknesses have arisen along with, and perhaps as a result of, this virtue. The most severe in the reviewers opinion concerns the (lack of) translation of observations to meaning. Many of the principles and outstanding problems in enzyme chemistry and metabolic processes are not emphasized with clarity or derived with convincing accumulation of evidence. In the absence of such synthesis many of the facts presented appear to be unimportant and even superfluous to the uninitiated reader. It is suggested that this book would be most appreciated if studied in conjunction with a more theoretical treatment of enzyme chemistry or of metabolism. Under these circumstances the text would be recommended to students or to interested investigators trained in areas peripheral to biochemistry.

DIVISION OF BIOCHEMISTRY
DEPARTMENT OF CHEMISTRY
UNIVERSITY OF ILLINOIS
URBANA, ILLINOIS
WILLIAM J. RUTTER

Correlation between Physical Constants and Chemical Structure. Graphical Statistical Methods of Identification of Mineral and Fatty Oils, Glass, Silicones, and Catalysts. BY H. I. WATERMAN, Professor of Chemical Technology, Technical University, Delft (The Netherlands), in collaboration with C. BOELHOUWER and J. CORNELISSEN, Research Associates, Delft, Technical University. D. Van Nostrand Company, Inc., 120 Alexander Street, Princeton, N. J. 1958. v + 120 pp. 17 × 24.5 cm. Price, $5.25.

The authors show how they have used simple graphic methods to correlate physical properties of a complex organic or inorganic material with the elementary composition or chemical structure of the material. Specific examples are given for mineral oils and related hydrocarbon mixtures, fatty acids, glasses and silicones, and coal.

Physical properties studied by the authors include density, refractive index, molecular weight, surface tension, kinematic viscosity, magneto-optical rotation and the Faraday effect. Chemical structure is in terms of ring number per average molecule (naphthenic, aromatic or paraffinic), percentage of carbon in ring structure (naphthenic, aromatic or paraffinic), or degree of branching in saturated molecules.

Each graph takes the form of a family of curves showing the relationship between two physical properties for each of several elementary compositions or chemical structures.

The formula $\log v = (A/T^x) + B$ (A, B, X = constants) for the temperature dependence of kinematic viscosity is shown to be useful for investigating such materials as mineral oils, silicones and glasses.

In the final chapter, triangular graphs are used to study the effects of catalysts in kinetic studies of the hydrogenation and the chlorination of organic compounds.

The entire book appeared in *Anal. Chem. Acta*, **18**, No. 5 (1958).

COLOR PRINT AND PROCESSING
EASTMAN KODAK COMPANY
ROCHESTER 4, NEW YORK
GRANT WERNIMONT

Nuclear Reactor Experiments. By the staff of Argonne National Laboratory, Operated by the University of Chicago for the United States Atomic Energy Commission. J. BARTON HOAG, Editor and Contributor. D. Van Nostrand Company, Inc., 126 Alexander Street, Princeton N. J. 1958. xv + 480 pp. 16 × 23.5 cm. Price, $6.75.

The international reactor school at Argonne National Laboratory has been in existence for several years and its graduates are now putting their training to practical use in setting up atomic energy programs in dozens of countries. "Nuclear Reactor Experiments" shows clearly the high level of the equipment used in their training—a first class high-flux research reactor with all its complex facilities. It is stated that the purpose of the course, lasting 7 months, is "to give the rough knowledge needed of the whole reactor field to enable work in teams." Obviously this aim implies a skimming over many subjects in cursory fashion. One may argue with this objective of a reactor training course, but the experiments here described show that the participants get at least brief acquaintance with a wealth of neutron physics and reactor techniques.

The material covered includes radiation detectors, measurements of diffusion lengths and neutron "age," "exponential" experiments, measurement of neutron cross sections, operational characteristics of a reactor, heat transfer, metallurgical treatment of fuel, corrosion and radiation effects on materials, "hot" laboratory techniques, and chemical processing. The book is actually a laboratory manual only, describing specific experiments, and including a small account of the physical facts behind each technique. The description of each experiment is detailed, complete with precise instructions for various manipulations, and reproduction of neat "data sheets" for calculation of results.

The material other than description of experiments is not of sufficient value to render the book useful as a text or reference. Furthermore, the experiments are built around the particular equipment in use at Argonne. Similar facilities are available at other reactors, but much of the manual is so closely linked with Argonne that it would not be applicable at other reactors. Other than its obvious value for students at the Argonne school, it would seem most useful as a guide to those setting up training centers with other reactors. They could not easily procure all the complex instrumentation of the Argonne school—this reviewer well knows the time scale involved, having designed some of the Argonne experiments a decade ago—but the book would be an excellent guide to the techniques now in use at a modern reactor laboratory.

PHYSICS DEPARTMENT
BROOKHAVEN NATIONAL LABORATORY
UPTON, LONG ISLAND, N. Y.
DONALD J. HUGHES