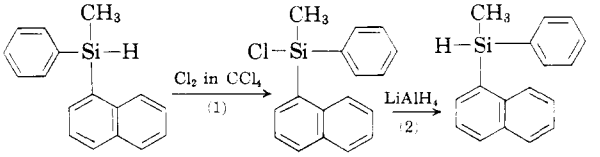
OPTICALLY ACTIVE ORGANOSILICON COMPOUNDS HAVING REACTIVE GROUPS BONDED TO ASYMMETRIC SILICON. DISPLACEMENT REACTIONS AT SILICON WITH PURE RETENTION AND PURE INVERSION OF CONFIGURATION

Sir:

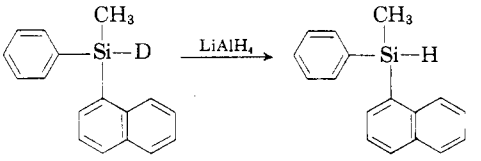
As the start of a new phase in organosilicon chemistry, which may prove as significant for silicon chemistry as was the discovery of the Walden inversion in 1895 for carbon chemistry, we wish to record these advances: (a) practical synthetic routes to optically active organosilicon compounds having reactive 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.

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(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