

acetylation, the conanine IV, m.p. 186–190°,  $[\alpha]_{\text{D}}^{25}$  +83°, found C, 74.12; H, 9.76, was obtained.<sup>3</sup>

Reduction of IV ( $\text{LiAlH}_4$ -THF) gave V, m.p. 174–177°,  $[\alpha]_{\text{D}}^{25}$  +70°, found: C, 75.79; H, 10.75; which formed the corresponding methiodide VI, m.p. 277–279°,  $[\alpha]_{\text{D}}^{25}$  +47°, found C, 56.14; H, 8.39. Heating the quaternary ammonium hydroxide form<sup>4</sup> of VI afforded VII as the hemimethanolate, m.p. 177–180°,  $[\alpha]_{\text{D}}^{25}$  +74°, found: C, 74.80; H, 10.78; which on treatment with methyl iodide furnished the methiodide, m.p. 260°,  $[\alpha]_{\text{D}}^{25}$  +25°, found: C, 57.04; H, 8.81. The latter was heated in DMF containing sodium methoxide to produce VIII, m.p. 145–146°,  $[\alpha]_{\text{D}}^{25}$  +45°, found: C, 79.65; H, 10.13; which was oxidized ( $\text{CrO}_3$ -acetone) to IX, m.p. 169–170.5,  $[\alpha]_{\text{D}}^{25}$  +77°, found: C, 79.98; H, 9.61. Hydroxylation ( $\text{OsO}_4$ ) of IX afforded X as the hemihydrate, m.p. 212–215°,  $[\alpha]_{\text{D}}^{25}$  +89.2°, found: C, 70.78; H, 9.46; which was acetylated ( $\text{Ac}_2\text{O}$ -Py) to form XI, m.p. 171–173.5,  $[\alpha]_{\text{D}}^{25}$  +72°, found: C, 69.25; H, 8.66. The latter was oxidized ( $\text{RuO}_4$  in  $\text{CCl}_4$ )<sup>5</sup> to produce XII, m.p. 242–246,  $[\alpha]_{\text{D}}^{25}$  +51°, found: C, 67.18; H, 7.88. By use of improved methods<sup>6</sup> for introducing the  $\Delta^4$  moiety into 3-keto allo steroids, XII was transformed into XIII, m.p. 197–201,  $[\alpha]_{\text{D}}^{25}$  +123°, found: C, 67.47; H, 7.48, which was hydrolyzed ( $\text{KHCO}_3$ ) to afford XIV, m.p. 149–151°, found C, 69.71; H, 7.84.

Tritylation of XIV ( $(\text{C}_6\text{H}_5)_3\text{CCl}$ -Py) gave XV as the hemihydrate, m.p. 225–229°,  $[\alpha]_{\text{D}}^{25}$  +104°, found: C, 78.24; H, 7.09, which was oxidized to XVI, obtained as the hemihydrate, m.p. 230–234°,  $[\alpha]_{\text{D}}^{25}$  +106°, found: C, 78.90; H, 6.88. Removal of the protecting group (80% HOAc) gave XVII, m.p. 211–220°,  $[\alpha]_{\text{D}}^{25}$  +183°, found: C, 69.96; H, 7.25, (lit<sup>7</sup> m.p. 212–216, 223–238  $[\alpha]_{\text{D}}^{25}$  +180  $\pm$  4°). Compound XVII has been converted to aldosterone.<sup>8,9</sup>

(3) E. J. Corey and W. R. Hertler, *THIS JOURNAL*, **80**, 2903 (1958); E. J. Corey and W. R. Hertler, *ibid.*, **81**, 5209 (1959); P. Buchschacher, J. Kalvoda, D. Arigoni and O. Jeger, *ibid.*, **80**, 2905 (1958).

(4) Cf. J. Weinstock and V. Boekelheide, *ibid.*, **75**, 2546 (1953).

(5) L. M. Berkowitz and P. N. Rylander, *ibid.*, **80**, 6682 (1958).

(6) R. M. Evans, J. C. Hamlet, J. S. Hunt, P. G. Jones, A. G. Long, J. F. Oughton, L. Stephenson, T. Walker and B. M. Wilson, *J. Chem. Soc.*, 4356 (1956).

(7) J. Schmidlin, G. Anner, J.-R. Billeter, K. Heusler, H. Ueberwasser, P. Wieland and A. Wettstein, *Helv. Chim. Acta*, **40**, 2291 (1957).

(8) J. von Euw, R. Neher and T. Reichstein, *ibid.*, **38**, 1423 (1955).

(9) It is a pleasure to thank Dr. T. A. Geissman and Dr. Joseph Weinstock for many helpful discussions.

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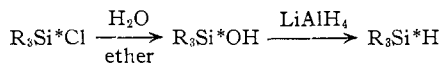
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STEREOCHEMISTRY OF CHLORIDE ION  
DISPLACEMENT FROM SILICON. HYDROLYSIS  
AND METHANOLYSIS OF AN OPTICALLY ACTIVE  
ORGANOCHLOROSILANE

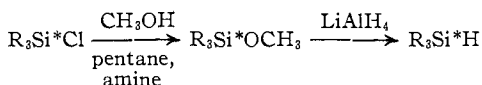
Sir:

We wish to record the first stereochemical study of the hydrolysis of an optically active triorgano-

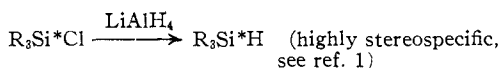
chlorosilane,  $\text{R}_3\text{Si}^*\text{Cl}$ . The results formulated below for optically active  $\alpha$ -naphthylphenylmethylchlorosilane,<sup>1</sup> taken in conjunction with the data obtained for the lithium aluminum hydride reductions, clearly indicate a high degree of stereospecificity for both hydrolysis and methanolysis reactions under the conditions specified.<sup>2</sup>



I,  $[\alpha]_{\text{D}} +6.4^\circ$  II,  $[\alpha]_{\text{D}} +20.5^\circ$  III,  $[\alpha]_{\text{D}} +30^\circ$



$[\alpha]_{\text{D}} +6.4^\circ$  IV,  $[\alpha]_{\text{D}} +17^\circ$   $[\alpha]_{\text{D}} +30^\circ$



$[\alpha]_{\text{D}} +6.3^\circ$   $[\alpha]_{\text{D}} +32^\circ$

A solution of 31 g. of I in 500 ml. of ether was added rapidly to 700 ml. of cold water in a 2-liter separatory funnel which was immediately stoppered and vigorously shaken for 1–2 minutes. The ether layer then was separated, washed four times with water, and dried over potassium carbonate. Evaporation of solvent gave 28.0 g. of II (found: Si, 10.6; infrared spectrum showed typical silanol absorption at 2.80 and 3.05 microns as well as the maxima characteristic of the  $\alpha$ -naphthylphenylmethylsilyl system). Reduction of II with lithium aluminum hydride at 140–145° using di-*n*-butyl ether as solvent gave a 72% yield of III (m.p. 62–63°; identical with III as previously reported<sup>1</sup> except for a somewhat smaller specific rotation).

A solution of 14 g. of I in 40 ml. of carbon tetrachloride (as prepared by chlorination of (–) III)<sup>1</sup> was diluted with 100 ml. of pentane and then added to a solution containing 10 ml. of methanol, 20 ml. of cyclohexylamine and 300 ml. of pentane. The reaction mixture was swirled for a moment in a separatory funnel, washed five times with cold water, dried over sodium sulfate and evacuated. Crystallization of the residue from pentane gave 89% yield of IV (m.p. 64.5–65°; found: Si, 10.2; mol. wt., 274). Reduction of IV with lithium aluminum hydride at room temperature in ethyl ether solution gave 68% yield of III.

The high degree of stereospecificity observed for both hydrolysis and methanolysis of optically active  $\alpha$ -naphthylphenylmethylchlorosilane in ether and pentane solvents, respectively, clearly rules out a planar siliconium ion intermediate for these reactions in the specified solvents.

Rapid hydrolysis of a chlorine function linked to bridgehead silicon in 1-chloro-1-silabicyclo[2.2.1]-heptane<sup>3</sup> using ether as the solvent shows that hydrolysis can occur with retention of configuration.

Nevertheless, evidence partially summarized below, which will be detailed in later publications, provides strong indications that inversion of con-

(1) L. H. Sommer and C. L. Frye, *THIS JOURNAL*, **81**, 1013 (1959).

(2) Conditions used were imposed by two factors: rapid racemization of the silanol or methoxysilane in the presence of acid; and rapid racemization of  $\text{R}_3\text{Si}^*\text{Cl}$  by chloride ion.

(3) L. H. Sommer and O. F. Bennett, *THIS JOURNAL*, **79**, 1008 (1957).

figuration is the stereochemical path followed by the hydrolysis and methanolysis reactions herein reported and by many other reactions of  $R_3Si^*Cl$  including the lithium aluminum hydride reduction which previously was given a tentative assignment of retention of configuration.<sup>1</sup>

(1) X-Ray studies show that  $(+)-R_3Si^*H$  and  $(-)-R_3Si^*Cl$  form mixed crystals which comprise perfect solid solutions of the two optically active substances—the component molecules are randomly mixed in the crystal. In sharp contrast,  $(+)-R_3Si^*H$  and  $(+)-R_3Si^*Cl$  form only eutectic mixtures—these molecules cannot mix randomly in the crystalline state.<sup>4</sup>

(2) Grignard reduction of  $(+)-R_3Si^*OCH_3$  gives  $(+)-R_3SiH$  and the olefin derived from the Grignard

reagent in a reaction which is most plausibly interpreted as proceeding through a quasi six-ring transition state whose geometry would demand retention of configuration as the preferred stereochemical path.

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

(4) For previous use of this difference in phase behavior for correlation of configuration see the review by J. Timmermans, *J. chim. phys.*, **49**, 162 (1952). Conclusions drawn on the basis of a difference in phase behavior have, without exception, proved accurate.

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RECEIVED MAY 17, 1960

## BOOK REVIEWS

**Transactions of the Royal Institute of Technology.** Stockholm, Sweden. Number 132. **A Precision Calorimeter for Enthalpy Titrations.** By KURT SCHLYTER. Royal Institute of Technology Library, Stockholm 70, Sweden. 1959. 41 pp. 17.5 × 24.5 cm. Price, Kr. 5:—.

The author describes an adiabatic calorimeter for measuring heat effects when one liquid is added to another. The first liquid was kept in a buret immersed in the water of the constant temperature bath in which the Dewar flask of the calorimeter also was immersed. The temperature of the calorimeter and contents was maintained within 0.1° of 25.00° which was the temperature of the bath. Such temperature regulation was made possible by a cooling coil through which cold air flowed as well as by the usual electrical heaters. Thus when the first liquid was added to the second they were both initially at 25.00 ± 0.019°. Quantities of heat measured varied between 0.2 to 21 cal. with an estimated uncertainty of ±0.03 cal. After each addition of reagent and temperature measurement, the temperature of the calorimeter was brought back to that of the constant temperature bath. Two consecutive additions of reagents with temperature measurements could be carried out in about 35 minutes.

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**General Crystallography. A Brief Compendium.** By W. F. DE JONG, Lecturer at the Technical University of Delft, with the collaboration of J. BOUMAN. W. H. Freeman and Company, 660 Market Street, San Francisco 4, California. 1959. ix + 281 pp. 14.5 × 22 cm. Price, \$6.00.

This interesting little book is an American edition of the original Dutch version which appeared in 1951. It is stated that some revision has accompanied the translation: the classification of symmetry now follows the International Tables for X-Ray Crystallography, new illustrations have been added and the section of Physical Crystallography rewritten.

The treatment is designed for the beginning student. The author does not consider his compendium primarily as a textbook but rather as a guide for self study. The material presented is divided into four general categories. Part I (92 pp.), entitled Geometric Crystallography, begins with a presentation of geometric relationships, followed by a section on analytical relations for various lattices and projections, and concludes with a brief discussion of crystal drawing, problems in Geometric Crystallography and Geometric Crystal determination. This section is well-illus-

trated and gives considerably more detail on these subjects than is found in most treatments.

Part II (43 pp.) is concerned with Structural Crystallography. A brief historical introduction is followed by discussion of structure theory (symmetry elements, space groups, lattices, etc.) and the determination of structure. The latter includes rather brief presentation of basic diffraction principles, experimental methods, intensities, Fourier analysis, Patterson diagrams and the general procedure for structure analysis. The treatment should be most helpful for general orientation of the beginning student.

Part III, Chemical Crystallography (52 pp.) presents a rather elementary outline of basic chemical features of bonding which are of importance in determining the nature of the structural units in the crystal. A survey of typical structures for the elements is presented, followed by description of representative structures of substances composed of two different kinds of atoms and, very briefly, a sampling of structures of more complex substances.

Part IV, Physical Crystallography (75 pp.), consists of a "phenomenological" (descriptive) section, and an "explanatory" (atomistic) section. In the former a mathematical background in vectors and tensors is presented, followed by consideration of dielectric properties of crystals, the propagation of light, magnetic induction, thermal conduction, electronic conduction, pyro- and piezo-electric properties and elasticity. In the explanatory part, structure, imperfections, and their relation to crystal energy and various physical characteristics are considered briefly.

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**Mechanism and Structure in Organic Chemistry.** By EDWIN S. GOULD, Stanford Research Institute. Henry Holt and Company, 383 Madison Avenue, New York 17, N. Y. 1959. x + 790 pp. 16.5 × 24 cm. Price, \$12.50.

There are many differences between this text and all others in the field of theoretical organic. It is quite clear that the author has concentrated his efforts on producing a book which will be both comprehensive and easily consumed by students at an intermediate level. I feel that both of these objectives have been accomplished to an impressive extent. As would be expected, achievement of such aims has cost something in rigor and penetrating analysis. On the other hand, Gould has kept his discussions basically sound which is more than can be said of any other author who has set out to present physical organic to the man in the street.