

As yet eqn. (2) has not been completely verified because sufficient data for the calculation of β have not been available.

Recently Wall and Rouse¹ studied the association of benzoic acid in benzene and showed that the dissociation constant K for the dimer is subject to the following numerical equation

$$\log_{10} K = 3.790 - (1977/T) \quad (3)$$

Using K calculated from (3), it is possible to compute β and thus provide a check for (2). This

TABLE I

 $t = 6^\circ\text{C}.$

C_W	C_B	β	$C_W/\sqrt{C_B}$	$C_W(1-\alpha)/\sqrt{C_B}$	$C_W(1-\alpha)/\sqrt{C_B(1-\beta)}$
0.00329	0.0156	0.120	0.0263	0.0230	0.0245
.00435	.0275	.092	.0264	.0234	.0246
.00493	.0355	.081	.0262	.0235	.0245
.00579	.0495	.069	.0261	.0235	.0244
.00644	.0616	.063	.0260	.0236	.0244
.00749	.0835	.054	.0259	.0237	.0244
.00874	.1144	.046	.0258	.0237	.0243
.00993	.148	.041	.0258	.0238	.0243
.0114	.195	.036	.0258	.0240	.0244

(1) F. T. Wall and P. E. Rouse, Jr., *THIS JOURNAL*, **68**, 3002 (1941).

procedure has been applied to the results of Creighton,² the data being summarized in Table I.³ In this table the concentrations C_W and C_B are expressed in *normal* moles per liter. It will be observed that whereas $C_W/\sqrt{C_B}$ and $C_W(1-\alpha)/\sqrt{C_B}$ show definite trends with changing concentration, the values of $C_W(1-\alpha)/\sqrt{C_B(1-\beta)}$ leave little to be desired in the way of consistency. We thus have a check on the theory from which eqn. (2) was derived.

It should not be supposed that the above described agreement provides a rigorous check on eqn. (3). It so happens that the numbers in the last column of the table are not very sensitive to the value of K used. Ordinarily eqn. (3) could not be expected to be very reliable at 6° because that temperature corresponds to a fairly long extrapolation from the temperature range for which the equation was fitted.

(2) Creighton, *J. Franklin Inst.*, **180**, 63 (1915).

(3) With the exception of the columns involving β , the data of Table I were taken from Millard, "Physical Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1941, p. 361.

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COMMUNICATION TO THE EDITOR

THE LOCATION OF THE DOUBLE BOND IN CLIONASTEROL

Sir:

In a previous communication (F. R. Valentine and W. Bergmann, *J. Org. Chem.*, **6**, 452 (1941)) one of us has pointed out that the striking similarity existing between clionasterol and the sterol of the fresh-water sponge, *Spongilla lacustris*, strongly suggests the identity of the two sterols. Recently Mazur [*THIS JOURNAL*, **63**, 2442 (1941)] has presented evidence intended to prove that the spongilla sterol, and therefore in all probability also clionasterol, are 5,6-dihydrostigmasterol.¹ It can now be shown that clionasterol is different from this dihydrostigmasterol, and that it possesses a double bond in the 5,6-

(1) 5,6-Dihydrostigmasterol has already been prepared by Marker and Wittle [*THIS JOURNAL*, **59**, 2707 (1937)]. Its melting point is 50° higher than either of the two sponge sterols.

position. The presence of this linkage has been convincingly demonstrated by a number of oxidation reactions in which clionasterol shows the same behavior as cholesterol and steroids of similar constitution. Thus oxidation of clionasterol with aluminum isopropoxide yields clionastenone of m. p. 79° and $\alpha_D +80.0^\circ$ (Calcd. for $C_{29}H_{48}O$: C, 84.4; H, 11.8. Found: C, 84.2; H, 11.9); 3,5-dinitrophenylhydrazone, m. p. 230° (Calcd. for $C_{35}H_{52}O_4N_4$: C, 70.8; H, 8.9; N, 9.4. Found: C, 70.6; H, 8.9; N, 9.6). Clionastenone shows the typical absorption spectrum of an α,β -unsaturated ketone, and its strongly positive rotation indicates that the usual shift of the double bond from the 5,6- to the 4,5-position has taken place during the oxidation. The presence of a 5,6-double bond was further demonstrated by the oxidation of clionasterol with hydrogen peroxide to give clionastantriol-3,5,6; m. p. 238°

(Calcd. for $C_{29}H_{52}O_3$: C, 77.6; H, 11.6. Found: C, 77.2; H, 11.7) and by its oxidation with selenium dioxide to give cliostene-(4,5)-diol-3,6; m. p. 232° ; $\alpha_D + 8^\circ$ (Calcd. for $C_{29}H_{50}O_2$: C, 80.9; H, 11.6. Found: C, 81.1; H, 11.7). The

diol yields clionasthenone upon dehydration with acids.

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WERNER BERGMANN
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RECEIVED JANUARY 15, 1942

NEW BOOKS

The Theory of Organic Chemistry—An Advanced Course.

By GERALD E. K. BRANCH, Ph.D., Professor of Chemistry, and MELVIN CALVIN, Ph.D., Instructor in Chemistry, University of California. Prentice-Hall, Inc., New York, N. Y., 1941. xix + 523 pp. 49 figs., 55 tables. 15×23 cm. Price, \$4.00.

"The Theory of Organic Chemistry—An Advanced Course" is the most ambitious attempt yet made to describe the phenomena of organic chemistry in terms of the electronic structural theory as it has been enriched by modern quantum mechanics. It is written as a textbook for an advanced course implying a previous knowledge of physics, physical chemistry, mathematics, and some organic chemistry.

Three introductory chapters provide a generalized presentation of the development of the organic structure theory, of the theory of atomic structure, and of their meeting ground in the modern concepts of molecular structure. Chapter 4 considers the modes of interaction of groups in the molecule and introduces the concept of resonance. There follows a chapter on the interpretation of physical properties in relation to structure, including bond distances and angles, dipole moments, Raman spectra, and color. Chapters 6 and 7 deal with equilibrium and energy relationships in acid dissociation, tautomerism, addition reactions and free radicals. Chapter 8 derives and illustrates some general equations of kinetics. Chapter 9, entitled "Three-Center Reactions," discusses acid-base catalysis, the Walden inversion, solvolytic and displacement reactions. The final chapter deals with miscellaneous reactions of the double bond, culminating in aromatic substitution.

The presentation of the subject is deductive rather than inductive. Full expositions are given in generalized notation, followed by a descent to experimental illustrations. In this regard the style emphasizes the kinship of the authors' viewpoint with that of Professor C. K. Ingold, to whose leadership they pay appreciative tribute in the preface.

The strongest parts of the book are those dealing with structural problems. The various discussions of resonance and its implications for organic phenomena are the best yet written, and ought to be required reading for those writing casually on this subject for the Journal. Many pertinent examples are cited in these discussions, although fuller documentation would have been desirable. With

occasional exceptions, such as the bond angles of the halo-methanes (p. 135), the interpretation of the dissociation constants of the dibasic acids (pp. 226-228) and the structure of aliphatic diazo compounds (p. 411), the book is up to date. It is attractively set up and well bound. The authors have not neglected those important finishing touches, the proofreading and the index.

P. D. BARTLETT

Principles of General Chemistry.

By STUART R. BRINKLEY, Associate Professor of Chemistry, Yale University. Third Edition. The Macmillan Company, 60 Fifth Avenue, New York, N. Y., 1941. x + 703 pp. Illustrated. 16×24 cm. Price, \$4.00.

The third edition has been much enlarged and considerably altered. The chapters dealing with the physical properties and structure of matter have been brought to the first part of the book in order to give a better basis for the theoretical discussions occurring later. The structure of the atom has been used to a much greater extent than formerly as a basis for explaining chemical action. The conception of complete ionization and the use of the Brönsted definition of acids and bases are carried out logically throughout the book.

Considerable emphasis has been put on the idea of oxidation number. While the author has made it clear that this number takes no direct cognizance of the distinction between covalent and ionic union, the question arises as to whether or not the young student will understand its empirical quality. The ion-electron method of balancing oxidation equations is, however, presented for use in water solution.

In general the book is an excellent one and is recommended for students who have had considerable previous preparation in chemistry.

P. A. BOND

Catalysis, Inorganic and Organic.

By SOPHIA BERKMAN, JACQUE MORRELL and GUSTAV EGLOFF of Universal Oil Products Company Research Laboratories. Reinhold Publishing Corporation, 330 West 42nd St., New York, N. Y., 1940. 1130 pp. Price, \$18.00.

The first chapter of 57 pages is devoted to the historical development of the subject and a theoretical discussion.