

The assay method we employed was as follows: Day old chicks were placed on a vitamin K free diet and kept on this diet for fourteen to seventeen days. When a preliminary determination of clotting time showed that at least 90% of the chicks had clotting times above thirty minutes, the samples, dissolved in 0.1 cc. of peanut oil, were administered orally. Eighteen hours later, the clotting times on the dosed birds were determined. Usually ten chicks were used at each dose level.

In the course of six weeks, nine assays were run on 2-methylnaphthoquinone. Following is a typical protocol of our results:

Substance	Dose	No. birds	Clotting time in min.				Per cent. under 10 min.
			0-5	6-10	11-30	>30	
2-Methyl-naphthoquinone	1 $\gamma$	10	5	4	1	0	90
2-Methyl-naphthoquinone	0.75 $\gamma$	9	4	3	1	1	77
2-Methyl-naphthoquinone	0.5 $\gamma$	9	3	1	3	2	44
Alfalfa extract	$\approx$ 75 mg.	9	3	3	2	1	67
Negative controls	0	10	0	0	0	10	0

In all over 120 chicks were used in testing 2-methyl-1,4-naphthoquinone at levels of 0.5 to 1.0  $\gamma$  and the results in every case were essentially the same as above.

From the results of Ansbacher and Fernholz and from ours, it would appear that, in the chick at least, 2-methylnaphthoquinone possesses anti-hemorrhagic activity of the same order of magnitude as the vitamin K<sub>1</sub> reported by Thayer, *et al.*<sup>3</sup> These results are particularly striking inasmuch as hitherto no simple compounds corresponding in chemical structure to the chemically identified vitamins exhibit the same order of activity as the vitamins themselves. It is also noteworthy that 2-ethylnaphthoquinone (activity above 200  $\gamma$ ) and 2-*n*-propylnaphthoquinone<sup>4</sup> (inactive at 400  $\gamma$ ) are decidedly less effective than the methyl homolog. While 2,3-dimethylnaphthoquinone has some anti-hemorrhagic activity (effective at 50  $\gamma$ ), 2,6- and 2,7-dimethyl-1,4-naphthoquinone<sup>1</sup> exhibit little, if any (inactive at 400  $\gamma$ ), notwithstanding the fact that the substituents about the quinone systems of the latter two compounds are similar to 2-methylnaphthoquinone.

RESEARCH LABORATORIES  
MERCK & Co., INC.  
RAHWAY, NEW JERSEY, AND THE  
MERCK INSTITUTE OF  
THERAPEUTIC RESEARCH

M. TISHLER  
W. L. SAMPSON

RECEIVED AUGUST 18, 1939

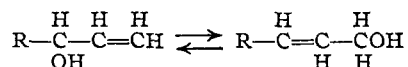
(3) Thayer, *et al.*, *Proc. Soc. Exp. Biol. Med.*, **41**, 194 (1939).

(4) Prepared by Professor Fieser and his collaborators.

## THE INTERCONVERSION OF CROTYL ALCOHOL AND METHYLVINYLCARBINOL IN AQUEOUS SULFURIC ACID

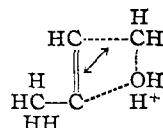
Sir:

According to the generally accepted ideas [Burton and Ingold, *J. Chem. Soc.*, 1907 (1928); J. W. Baker, "Tautomerism," pages 241-7, Routledge, London, 1934], carbinol systems of the type



are the least mobile of the allylic systems, exhibiting little or no tendency to isomerize. Although the system has been reported to be mobile when R = phenyl [Valeur and Luce, *Bull. soc. chim.*, **27**, 611 (1920)], Burton and Ingold [*loc. cit.*] were unable to verify the observation. Another example of isomerization was reported by Prévost [*Ann. chim.*, [10] **10**, 147 (1928)], who found that crotyl alcohol was formed during the dehydration of methylvinylcarbinol over alumina at high temperatures.

However, work on the mechanism of the reaction of the butenols with solutions of hydrogen bromide [Young and Lane, *THIS JOURNAL*, **60**, 847 (1938)] convinced us that crotyl alcohol and methylvinylcarbinol should be interconvertible in the presence of acids to form equilibrium mixtures even at room temperatures. This predicted interconversion was based on a postulate that activation of the oxonium ion of either crotyl alcohol or methylvinylcarbinol might lead to the same resonating molecule



in which the oxygen is bonded weakly to both carbons 1 and 3 [Young and Nozaki, paper in process of publication]. Consequently 50-ml. portions of crotyl alcohol and methylvinylcarbinol are being treated with mixtures of water and sulfuric acid adjusted so that the normality of acid in 228 ml. of reaction mixture is 7.4, 3.7, and 1.9. With methylvinylcarbinol after one week at room temperature the 7.4 *N* acid had caused the production of 4.5 g. of crotyl alcohol and 5 g. of a fraction which appears to be a mixture of crotyl and methylvinylcarbinyl ethers. With crotyl alcohol after two weeks the 7.4 *N* acid had produced 22 g. of the ether fraction and equal quantities, 4 g., of methylvinylcarbinol and

crotyl alcohol, while the 3.7 *N* acid had produced less ether and more alcohol, 7 g. of each. Since the problem requires a careful study of the effect of the acid concentration on the proportion of hydration, ether formation and alcohol rearrangement, we wish to record the fact that mobility may be induced in this supposedly stable allylic

system even at low temperatures. The possibility that butenyl sulfates are involved in the rearrangement is being investigated.

DEPARTMENT OF CHEMISTRY  
UNIVERSITY OF CALIFORNIA AT  
LOS ANGELES  
LOS ANGELES, CALIFORNIA

WILLIAM G. YOUNG  
KENZIE NOZAKI  
RUTH WARNER

RECEIVED JULY 31, 1939

---

## NEW BOOKS

---

**Lehrbuch der organischen Chemie.** (Textbook of Organic Chemistry.) By PAUL KARRER, Professor in the University of Zurich. Sixth, revised and enlarged edition. Georg Thieme Verlag, Rossplatz 12, Leipzig C 1, Germany, 1939. xxiii + 689 pp. 6 figs. 17.5 × 24 cm. Price, RM. 34; bound, RM. 36.

The sixth German edition is practically identical with the English edition recently reviewed in these pages [THIS JOURNAL, 61, 756 (1939)]. The new subject matter in the sixth edition (which is also incorporated in the English translation) includes only the section on organic deuterium compounds (five pages), a page on ergot alkaloids and half a page on phthalocyanins. Other topics have been brought up to date, especially in the active fields of natural products. In the preface the author calls attention to a greater inquiry into reaction mechanisms than in previous editions. The change in this regard seems slight, the text retaining its almost purely descriptive character.

PAUL D. BARTLETT

**The Oxidation States of the Elements and their Potentials in Aqueous Solutions.** By WENDELL M. LATIMER, Ph.D., Professor of Chemistry, University of California. Prentice-Hall, Inc., 70 Fifth Avenue, New York, N. Y., 1938. xiv + 352 pp. 16 × 24 cm. Price, \$3.00.

The usefulness of thermodynamic data is determined by the carefulness with which they have been obtained, the clearness with which they are presented and the convenience with which they may be used. Judged by these criteria Latimer has achieved a remarkably successful volume. The author has endeavored to include references to all works published up to 1938. The results of these investigations are presented concisely in a series of tables in the appendix. The first two give  $E^0$  values for several hundred half cell reactions, one for acid solutions and one for alkaline solutions. Then follows a table of free energies of formation and one giving equilibrium constants, arranged alphabetically by the elements. The next table gives values for the activity coefficients of strong electrolytes and the last gives values for the entropy of elements, compounds and ions. If the volume contained only these thirty pages of tables it would be invaluable.

For the convenience of students who are not working in the field of physical chemistry, the first two chapters give an introduction to the use of the tables. These chapters discuss the subject of units, conventions, general methods employed in the determination of oxidation-reduction potentials, ionization potentials, electron affinities, lattice energies, and their relation to standard oxidation-reduction potentials. A section of the appendix serves as a guide in the use of activity coefficients and the concept of the ionic strength. Although these chapters of a general nature are designed to make the remainder of the volume useful they will also serve as a convenient review of the most often used portions of thermodynamics for students of organic and inorganic chemistry.

Nineteen chapters follow these first two general sections, taking up in detail the chemistry of the elements arranged by families. Here an investigator interested in any particular element will find gathered together the available thermodynamic data and references to the literature. These data are interpreted and applied to the chemical behavior of the element. Where no data are available the author frequently has given estimates, which will be useful guides to those without a background of long experience in this field.

This volume will not only constitute an essential part of every chemist's reference library but will also introduce students who wish to use physico-chemical data to the elements of thermodynamics.

HENRY E. BENT

**Inorganic Quantitative Analysis.** By HAROLD A. FALES, Ph.D., Columbia University, and FREDERIC KENNY, Ph.D., St. Francis College. Second edition. D. Appleton-Century Company, Inc., 35 West 32nd Street. New York, N. Y., 1939. xiii + 713 pp. 132 figs. 15 × 22.5 cm. Price, \$4.00.

The educational philosophy of this excellent book is contained in the following sentences from the preface: "It has been the aim of the authors, in preparing this work, to apply the principles of Physical Chemistry to the theory of Quantitative Analysis in a detailed and thorough manner. In stressing this point of view, it has not been forgotten, however, that the two other