with aqueous-methanolic sodium hydroxide solution at 100° for 10 hours gave toluene and dextrorotatory II. The latter compound was obtained in 89% yield by distillation *in vacuo*. Its physical constants were found to be: m.p. 47–48° (reported[3a] 50°), $[\alpha]^{25}\text{D}$ +22.4 ± 1.0° (*c*, 2.184 in water) (reported[3b] +22.8°).

Anal. Calcd. for $C_9H_{13}PO$: C, 64.30; H, 7.73; P, 18.46. Found: C, 64.36; H, 7.84; P, 18.28.

Similar treatment of dextrorotatory I[2] with sodium hydroxide solution gave levorotatory II, $[\alpha]^{25}\text{D}$ −22.8 ± 1.0° (*c*, 2.168 in water), m.p. 48–49° (*Anal.* Found: C, 64.16; H, 7.90; P, 18.15).

Vapor phase chromatographic examination of the hydrocarbon fraction of a reaction mixture obtained by treatment of racemic I with sodium hydroxide solution revealed that toluene was the only compound present.

Although the reactions cited above are completely stereospecific, it is still an open question whether they proceed with inversion or retention of configuration. In nucleophilic displacement reactions on silicon in optically active silicon compounds, evidence has been provided for both inversion and retention of the configuration of the silicon atom, depending on the reagents.[4] However, it is not possible to draw too close a comparison between the reactions of silicon and phosphorus compounds. For example, whereas displacement of hydride ion by hydroxide ion in a silane is a second order reaction,[5] displacement of a hydrocarbon anion by hydroxide ion in a phosphonium salt is a third order reaction,[1] even though both reactions are presumed to proceed through a transition state in which the central atom (silicon or phosphorus) has a trigonal bipyramidal configuration.

Acknowledgment.—This investigation was supported in part by a research grant, RG-4215, from the National Institutes of Health, Public Health Service.

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[3] (a) J. Meisenheimer and L. Lichtenstadt, *Ber.*, **44**, 356 (1911); (b) J. Meisenheimer, J. Casper, M. Horing, W. Lauter, L. Lichtenstadt and W. Samuel, *Ann.*, **449**, 213 (1926).

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

[5] See L. H. Sommer, O. F. Bennett, P. G. Campbell and D. R. Weyenberg, *ibid.*, **79**, 3295 (1957), and earlier references cited there.

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RECEIVED MAY 25, 1959

KINETIC STUDY OF THE DECOMPOSITION OF QUATERNARY PHOSPHONIUM HYDROXIDES

Sir:

We wish to report the results of kinetic studies on the reaction of quaternary phosphonium halides with sodium hydroxide to produce phosphine oxides and hydrocarbons. These studies on methylethylphenylbenzylphosphonium iodide and on a series of *p*-Y-benzyltribenzylphosphonium halides (where Y = NO_2, Cl, H, CH_3, or CH_3O) revealed several facts: (1) all of the reactions were third order, with a first order dependence on the concentration of phosphonium cation and a second order dependence on the concentration of hydroxide ion; (2) the relative ease of elimination of the various groups parallels their stability as anions; and (3) the relative ease of the departure of a given group is definitely influenced by the nature of the non-departing groups (see partial rate factors for departure of benzyl group in Table I).

TABLE I

REACTIONS OF $p\text{-Y-}C_6H_4CH_2P(CH_2C_6H_5)_3^+$, I^- WITH NaOH

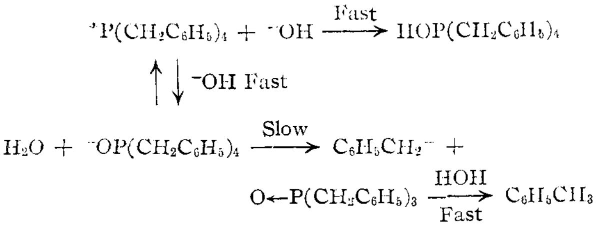
Y	k_2 (l./mole-min.)	Toluene, mole %	*p*-Y-Toluene, mole %	Yield, %	Partial rate factor for departure of benzyl group[b]
NO_2	. . .[a]	0.0	100.0	95	. .
Cl	13.80	64.1	35.9	90	2.95
H	2.72	75.0	25.0	90	0.68
CH_3	2.05	82.9	17.1	90	0.57
OCH_3	1.45	93.3	6.7	85	0.45

[a] Too rapid to be measured. [b] Partial rate factor = (k_2 × mole % toluene)/(3 × 100).

For the series *p*-Y-benzyltribenzylphosphonium halides, our kinetic studies were conducted in aqueous dimethoxyethane (1:1) at 38.9° with the phosphonium salt present in twenty-fold molar excess. The specific rate constants, k_2, shown in Table I represent pseudo-second-order constants. Product ratios were determined by vapor phase chromatographic analysis of the hydrocarbon fraction of each reaction mixture.

The kinetic measurements for methylethylphenylbenzylphosphonium iodide were carried out in 1.00 *N* potassium chloride solution at 99.4°. A total of four kinetic determinations were made, the first two with $[OH^-] = 2[R_4P^+]$ and the other two with $[OH^-] = [R_4P^+]$. The average specific rate constant, av. k_3, = 7.90 ± 0.24 $l.^2$/moles^2-hr. The data were completely inconsistent with a second order reaction.

A mechanism consistent with these observations, as applied to tetrabenzylphosphonium iodide, is as proposed[1]



$$\begin{tikzcd} {}^{+}P(CH_2C_6H_5)_4 + {}^{-}OH \arrow[r, "\text{Fast}"] \arrow[d, shift left, "{}^{-}OH\ \text{Fast}"] & HOP(CH_2C_6H_5)_4 & \\ H_2O + {}^{-}OP(CH_2C_6H_5)_4 \arrow[u, shift left] \arrow[r, "\text{Slow}"] & C_6H_5CH_2^{-} + & \\ & O\leftarrow P(CH_2C_6H_5)_3 & \end{tikzcd}$$

$$C_6H_5CH_2^{-} \xrightarrow[\text{Fast}]{\text{HOH}} C_6H_5CH_3$$

This mechanism is similar to that postulated by Ingold and co-workers[2] insofar as formation of a pentacovalent phosphorus intermediate (trigonal bipyramidal) is concerned, but differs in that Ingold considered the initial addition of hydroxide ion to phosphorus to be rate-determining. Ingold also supposed, on the basis of product ratio studies alone, that the relative ease of elimination of any specific group was independent of the other groups attached to phosphorus, which is contrary to our findings.

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[1] Conceivable variations of this general mechanism are (a) synchronous attack of the second hydroxide ion and departure of the benzyl anion and (b) the formation of a transition species with two hydroxide ions bonded to phosphorus (tetragonal bipyramidal structure).

[2] (a) C. W. Fenton and C. K. Ingold, *J. Chem. Soc.*, 2342 (1929); (b) L. Hey and C. K. Ingold, *ibid.*, 531 (1933).

It should be mentioned, also, that Horner, Hoffmann, Wippel and Hassel[3] have determined the major product in each of the reactions of a series of *p*-Y-phenyltriphenylphosphonium halides with sodium hydroxide, and they found that the relative ease of elimination of groups parallels the anionic stability.

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[3] L. Horner, H. Hoffman, H. G. Wippel and G. Hassel, *Chem. Ber.*, **91**, 52 (1958).

BOOK REVIEWS

Chemie der Azofarbstoffe. By HEINRICH ZOLLINGER, Privatdozent an der Universität Basel. Birkhäuser Verlag, Elizabethenstrasse 19, Basel 10, Switzerland. 1958. 308 pp. 17.5 × 24.5 cm. Price, sFr. 36.25.

This approach to the chemistry of azo dyes has been made from the physical-organic chemist's point of view, which has been subordinate in the various books published about dye chemistry since the last war.

The material employed in the book is completely up-to-date and thoroughly documented. In keeping with the purely scientific nature of the text, reference to patents is very meager. In at least one instance, reliance on patent information has been independently verified (see ref. 44 on p. 79). Twenty-eight references chosen at random were found to be entirely accurate.

The material is easily read and the presentation is straightforward. No mechanism or theory is put forward or developed without adequate definition of the terms used. The organization of the topics discussed is logical and orderly. The first chapter is devoted to the concepts, definitions and methods of studying reaction mechanisms. The next six are concerned with diazo and diazonium compounds. Methods and mechanisms of diazotization, equilibria and isomerisms, and decomposition reactions of diazo and diazoamino compounds are thoroughly discussed. Chapters 8 and 9 present methods of preparing azo compounds and the mechanisms of the most important method, the coupling reaction. Chapter 10 should prove fruitful to the organic dye chemist since it explains the application of coupling theories to the technology of azo dyes. The next chapter (11) is the only one in which the subject matter is treated from a strictly organic point of view. It explains the nomenclature and classification of azo dyes from the technical aspect, and contains seven sections in which the chemistry of the most important classes is concisely but clearly explained and illustrated. There is also an interesting table of the most important developments in the azo dye industry, presented in chronological order. Chapter 12 deals with the relation between constitution and properties of azo dyes. There is an excellent general summary on structure and light absorption of organic compounds, and a discourse on the relation of color as seen by the eye to the spectral absorption curve. The tautomerism and acid–base equilibria of azo dyes are also discussed. It is a disappointment to this reviewer that a section on correlation of structure to light fading of azo dyes, which would seem to belong to this chapter, was not included. It is true that this particular aspect of dye chemistry is quite confused, but emphasis of this fact might have given impetus to a truly scientific study of light fastness. A valuable aid to the industrial dyer would have been the inclusion of a section concerned with structure and ease of reduction, which is important in such applications as discharge printing. Chapter 13, which presents the chemistry of metallic complexes, is indeed timely because of the growing importance of the relatively new, so-called "neutral dyeing" complexes for nitrogenous fibers. The nature of the complex bonds, and the equilibrium, stability and stereochemistry of the complexes are nicely portrayed. No doubt, the last two chapters in the book will be considered by some as not properly belonging here because their scope is greater than the use of only azo dyes. These are concerned with the use of dyes on various fibers and the physical chemistry of the dyeing processes. However, certainly no harm is done and, if the book is to be used as a text, the condensed treatment employed will, for many purposes, eliminate references to more lengthy and cumbersome treatises.

A few minor criticisms, which do not detract seriously from the general usefulness of the book, are to be noted. The indexing appears to be incomplete; for example, structural formulas for triphenodioxazines appear twice in the text, but no reference to them is found in the index. Also, reference to reports based on captured German documents is rather loose; for example, reference 20 on page 115 is given simply as "FIAT-Report 1313." Since this latter is a three-volume work of about 1400 pages, the reader might find it annoying to ferret out the desired information without more specific instruction.

The printing, paper, and binding of the book are of high quality.

Dr. Zollinger's book is a must for the azo dye research chemist and is suitable as a text, especially at the graduate level. It is hoped that this treatise, together with the recent books of a more organic and technological nature, will stimulate American colleges to offer courses in dye chemistry.

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Outlines of Enzyme Chemistry. Second Edition, Revised and Enlarged. By J. B. NEILANDS, Department of Biochemistry, University of California, and PAUL K. STUMPF, Department of Agricultural Biochemistry, University of California. John Wiley and Sons, Inc., 440 Fourth Avenue, New York 16, N. Y. 1958. xii + 411 pp. 15.5 × 23.5 cm. Price, $8.50.

In view of the rapid accumulation of new information and continual modification of research trends in the field of enzymology, the prompt appearance of a new edition of even an elementary textbook of enzymology such as "Outlines of Enzyme Chemistry" is very welcome. The second edition retains the character and general organization of the first, but has been expanded approximately 30 per cent. Most chapters show judicious revision with only minor expansion, but greatly enlarged discussions or new chapters are offered in several areas of current research interest or rapid recent development.

The book, with 27 chapters, is organized into four sections, of which the first two are concerned with general principles and the physical chemistry of enzymes. The first section includes brief but valuable chapters of general and historical introduction, enzyme isolation methods, criteria of purity and characterization of enzymes. The physical chemical aspects of enzymology are given extended, lucid treatment at a fairly elementary level, with separate chapters devoted to chemical and hydrogen ion equilibria, metal-ion equilibria, kinetics, effects of substrate concentration, of *p*H, and of temperature, action of inhibitors, energetics-oxidation–reduction, specificity of enzymes, and mech,