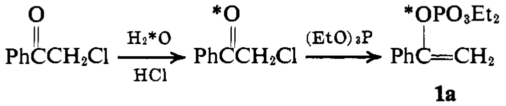
the present case to improve solubility and is not expected to affect the position of bond cleavage. The oxygen in the product acetophenone rapidly equilibrates with the solvent under these conditions and could not be used as a criterion of bond cleavage.[10]

Hydrolysis experiments were carried out using both normal ester in ^{18}O-labeled water and labeled ester (prepared by the sequence in eq 4) in normal water.



$$PhC(=O)CH_2Cl \xrightarrow[HCl]{H_2{*}O} PhC(={*}O)CH_2Cl \xrightarrow{(EtO)_3P} PhC({*}OPO_3Et_2)=CH_2 \qquad (4)$$

1a

The reaction product was made basic and extracted with $CHCl_3$, then the aqueous layer was acidified and extracted with ether, and the ether layer was evaporated and weighed. This residue was treated with ethereal diazomethane and the resultant methyl diethyl phosphate (**4**) from **3** was isolated by vpc (10 ft × $^3/_8$ in. SE-52 on Chromosorb W at 155° and 120 ml/min of He) and the ^{18}O content was calculated from the mass spectrum of **4** by the method of Swain.[11] Authentic samples of labeled and unlabeled **3** were prepared by the reaction of diethyl chlorophosphate ($(EtO)_2POCl$) with each batch of labeled water used and normal water, respectively. Acid prepared in this way was either esterified directly with diazomethane or subjected to the workup conditions and then esterified. The ^{18}O content was the same in both cases, showing that there was no exchange during work-up. The results of the labeling experiments are shown in Table I.

Table I. ^{18}O Content of $(EtO)_2P(O)OMe$ Obtained from Hydrolysis of $PhC(OPO_3Et_2)=CH_2$ (**1a**)

Excess ^{18}O content, $PhC(OPO_3Et_2)=CH_2$,[a] %	Excess ^{18}O content, solvent H_2O,[a,b] %	Excess ^{18}O content, product $(EtO)_2P(O)OMe$,[a] %
0.0 ± 0.3	3.3 ± 0.4	0.9 ± 0.3
6.9 ± 0.8	0.0 ± 0.1	7.4 ± 0.6
0.0 ± 0.3	7.4 ± 0.9	0.1 ± 0.3

[a] Obtained from the ratio of the mass spectral ions (M + 2)/M with natural abundance subtracted out. Deviations are averages of at least four determinations. [b] Determined from authentic $(EtO)_2P(O)OMe$ prepared from diethyl chlorophosphate and labeled water.

The results indicate predominant, and perhaps exclusive, acid-catalyzed hydrolysis of **1a** by C–O bond cleavage, corresponding to the scheme in eq 2. A similar mechanism probably holds for acid-catalyzed hydrolysis of other vinyl phosphates with close structural similarity to **1a**, but it is unsafe to extend this conclusion to more complicated structures where neighboring group participation may occur,[9] or ionized substrates may be involved.[12]

It has been noted before[2] that 4-coordinate phosphorus is reluctant to undergo substitution *via* 5-coordinate intermediates, as would be required for P–O cleavage. This barrier can be relieved in the hydrolysis of strained cyclic phosphates, where the reactions occur with Berry pseudorotation[13] or turnstile rotation.[14]

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Edward P. Lyznicki, Jr., Thomas T. Tidwell*
Department of Chemistry, University of South Carolina
Columbia, South Carolina 29208

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Book Reviews

Organosilicon Derivatives of Phosphorus and Sulfur. By S. N. Borisov, M. G. Voronkov, and E. Ya. Lukevits (Academy of Sciences of the Latvian SSR, Riga). Plenum Press, New York, N. Y. 1971. xiv + 343 pp. $25.00.

This volume is the latest in a series of monographs in inorganic chemistry edited by Eugene G. Rochow. Although it is a translation of the original Russian text published in 1968, it has been updated to include literature references up to June 1, 1969. The book is truly a comprehensive review to the international literature on the rapidly expanding field of organosilicon derivatives containing heteroatoms. In this respect, it fills many gaps and completes the international chain of contributions to this area of heteroorganic chemistry.

The text is equally divided between organosilicon derivatives of phosphorus and sulfur. The chapter subheadings are systematically divided into preparative methods, physical properties, chemical properties, and practical applications of the various bond grouping combinations (*i.e.*, Si–O–P, Si–N–P). There are also a sufficient number of tables of known members of each class of organosilicon compounds to make literature searching a lot easier.

The book contains sections on organosilicon ylides, derivatives of sulfur-containing heterocycles such as penicillin and thiophenes, and several other topics interesting to the synthetic chemist. In general, this volume would be most appealing and useful to the industrial chemists and a good number of academic researchers in this particular field. It is a "practical" reference book in the field of organosilicon derivatives of phosphorus and sulfur, and if for nothing else can be strongly recommended for its comprehensive literature in this area.

J. P. Marino, *University of Michigan*

Hydrides of the Elements of Main Groups I–IV. By E. Wiberg and E. Amberger. American Elsevier, New York, N. Y. 1971. 775 pp. $85.00.

It would be nice if a monumental effort like this (3800 references) could be on the shelves of everyone interested in the field of hydride chemistry. However, at the price, I doubt that many chemists can justify the expense. Unfortunately, the present-day strain on library budgets will undoubtedly even preclude the purchase of this book by many libraries. The reviewer can appreciate the expense of the translation of this work from the German but doubts that an $85.00 price tag is justified. Perhaps the publishers anticipated a greater devaluation of the American Dollar than actually occurred!

The book contains a short introductory chapter on the hydrides in general and nine additional chapters on the hydrides of the alkali metals, the alkaline-earth metals, boron, aluminum, gallium–indium–thallium, silicon, germanium, tin, and lead, respectively.

The majority of the text naturally dwells in those areas where the most has been reported, the boron hydrides (270 pp, 1400 references) and the silicon hydrides (160 pp, 950 references). A valuable feature of the organization of the book is the compilation of many data in tables and sections separate from the discussion. These sections provide quick reference for many physical properties and cite the types of spectral data which have been published for a given compound.

In an undertaking of this magnitude, it is understandable that there must be omissions and oversights. Because of some experience with the chemistry of the boron hydrides, I can be most critical of the oversights in that chapter. Perhaps my criticisms are symptomatic of similar features also to be found in other chapters, especially by one acquainted with that particular area.

Near the start of the chapter on the boron hydrides there is an informative discussion of mechanisms and type-reactions. Unfortunately, even though some of the mechanisms have been fairly well established, there is not a single reference to the original literature for any of the fifteen mechanisms. Another poorly referenced sections deals with borane–donor adducts; here the stability of the donor–acceptor bond is discussed primarily in terms of σ and π components with little regard to simpler explanations involving only the σ overlap. Later there is a discussion of the specific means by which various boranes may be prepared. The reader should realize that many convenient and well-tested laboratory preparations of the boron hydrides are found in the "Inorganic Syntheses" series which, by my observation, was not referenced anywhere in this entire work on the hydrides. Finally, although the authors purport to offer the chemist working with the hydrides reliable and detailed information on all important publications through 1970, they have overlooked numerous, carefully executed investigations of boron hydride chemistry published by S. Hermanek and his coworkers in the Czechoslovakian literature. All of the Czech literature was not overlooked, however, since it is cited in other chapters.

R. W. Rudolph, *University of Michigan*

Elements of Polymer Degradation. By LEO REICH (Picatinny Arsenal) and SALVATORE S. STIVALA (Stevens Institute of Technology). McGraw-Hill Book Co., New York, N. Y. 1971. xvi + 361 pp. $18.50.

Various types of polymer degradation, thermal oxidative, radiative, mechanochemical, chemical, and biological, are discussed in this book. The kinetics and mechanisms of thermal degradation and oxidative degradation of polymers are explained. Factors affecting polymer stability are also discussed. With respect to polymer degradation, the discussions are thorough and highly theoretical and mathematical. The book should serve as an excellent reference in the study or research of polymer degradation.

Theories and practices of various instrumental techniques used in studying polymer degradation are included in the book. Dynamic thermogravimetric analysis (TGA) and differential thermal analysis (DTA) are discussed in considerable detail. Individuals working in this area will find the book useful. Gel permeation chromatography (GPC), gas chromatography (GC), and infrared-absorption spectroscopy are explained in less detail. Oher techniques, such as viscometry and chemiluminescence, are briefly discussed.

Various polymers are discussed, but, as the authors point out, the polymers were selected mainly on the basis that they have been treated extensively in the literature with respect to kinetics and mechanisms and could be used to illustrate principles described in the book.

Paul J. Secrest, *Sherwin-Williams Research Center*

Essays in Chemistry. Volume 2. Edited by J. N. BRADLEY (University of Essex), R. D. GILLARD, and R. F. HUDSON (University of Kent at Canterbury). Academic Press, New York, N. Y. 1971. x + 124 pp. $4.25 (softbound).

This is the second volume in a proposed two volumes per year series designed to help the graduate chemist keep abreast of developments in other fields. Thus articles are illustrative rather than exhaustive, and references cited are few and general. This volume includes: Molecular Orbital Calculations in Organic Chemistry, by B. J. Duke; Electrode Processes, by G. J. Hills; The Jahn-Teller Effect in Transition Element Compounds, by J. A. Creighton; The Stereochemistry and Electronic Properties of Complexes of the Copper (II) Ion, by B. J. Hathaway; and Organic Photochemistry, by S. T. Reid. All are well written. Each provides the novice with both an appreciation of the importance of the subject and an understanding sufficient to attempt more comprehensive or specialized works.

George H. Wahl, Jr., *North Carolina State University*

Experimental Organic Chemistry. By RAYMOND B. SEYMOUR (University of Houston) and JERRY G. HIGGINS (Illinois State University). Barnes and Noble, Inc., New York, N. Y. 1971. x + 188 pp. $3.25 (soft vinyl binding).

This book is a collection of classical experiments for a one-semester survey course; highlights include an estimation of the efficiency of fractional distillation using vpc, extractive separation of a quaternary mixture, preparation of Nylon 6,10, paper chromatography of amino acids, preparation of a variety of dyes and application of these and others to various fibers, and preparation of molecular models using gumdrops and toothpicks. In mechanistic explanations, curved arrows are used inconsistently—sometimes they indicate a reasonable flow of electrons and sometimes they represent the movement of an atom.

George H. Wahl, Jr., *North Carolina State University*

Progress in the Chemistry of Organic Natural Products. Volume 28. Edited by W. HERZ (Florida State University), H. GRISEBACH (University of Freiburg), and A. I. SCOTT (Yale University). Springer-Verlag, Inc., New York, N. Y. 1970. xi + 503 pp. $44.10 ($40.10 by subscription).

This is the first volume of the familiar "Fortschritte" series to be published since the retirement of Professor Zechmeister. The new editors have carried on the high standards of the series. There are ten chapters on a variety of topics of interest to natural product chemists: Structural and Biogenetic Relationships of Isoflavonoids (E. Wong); Recent Advances in the Chemistry of Cyanogenic Glycosides (R. Eyjolfsson); Naturstoffe mit Pyridinstruktur und ihre Biosynthese (D. Gross); Peptide Alkaloids (E. W. Warnhoff); Insektensexuallockstoffe (K. Eiter); Arthropod Molting Hormones (H. Hikino and Y. Hikino); Total Synthesis of Prostoglandins (J. E. Pike); Chemistry of Cephalosporin Antibiotics (R. B. Morin and B. G. Jackson); Oligosaccharide der Frauenmilch (H. Weigandt und H. Egge); and Glucagon: Chemistry and Action (W. Bromer).

Michael M. Martin, *University of Michigan*