

A comprehensive study of the reaction of phenyl-(trihalomethyl)mercurials with various functional alcohols and organic acids, with oxyacids of other elements, and with other element-hydrogen compounds is in progress. The mechanisms of these reactions are under investigation.

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Reactions of Phosphorus Compounds. IV. Preparation of 3H-Pyrrolizine, 1,2-Dihydro-3-H-pyrrolizine, and Pyrrolizidine

Sir:

We wish to report the first synthesis of the parent 3H-pyrrolizine (III) and its reduction to 1,2-dihydro-3H-pyrrolizine (IV) and the fully saturated pyrrolizidine (V). This technique provides a superior method for the preparation in high yield of these bridgehead nitrogen heterocycles from readily available starting materials. The interest in this fused-ring system stems from the appearance of saturated and partially saturated pyrrolizine rings in many alkaloids.¹

This synthesis was accomplished by employing the new general method developed in our laboratory for the preparation of heterocyclic and carbocyclic ring systems² from vinyltriphenylphosphonium bromide (II).³

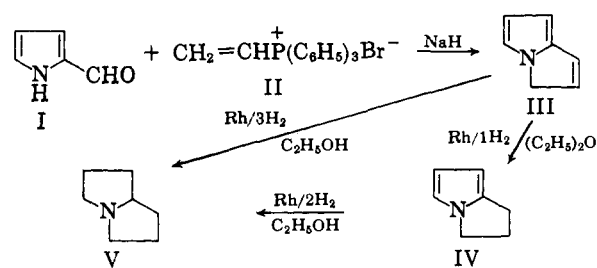
When 2-pyrrolaldehyde⁴ (I, 0.210 mole) was allowed to react with sodium hydride (0.183 mole) in anhydrous ether (200 ml., 4 hr.) followed by the addition of the salt II (0.215 mole) an exothermic reaction was observed. The resulting mixture was stirred under reflux for 24 hr. followed by filtration, concentration, and distillation. Pyrrolizine (III, 16.6 g., 87% yield) was obtained, b.p. 68–70° (15 mm.), n_D^{27} 1.5745.

(1) W. L. Mosby, "Heterocyclic Compounds," Vol. 15, Interscience Publishers, Inc., New York, N. Y. 1961, Chapter III, and references cited therein.

(2) Previous paper in this series: E. E. Schweizer, *J. Am. Chem. Soc.*, **86**, 2744 (1964).

(3) E. E. Schweizer and R. D. Bach, *J. Org. Chem.*, **29**, 1746 (1964).

(4) Eastman Kodak Chemicals, Rochester 3, N. Y.



Redistillation on an 18-in. spinning band column gave an analytically pure sample, b.p. 65° (7.5 mm.), n_D^{27} 1.5751. *Anal.* Calcd. for C₇H₇N: C, 79.97; H, 6.71; N, 13.32. Found: C, 79.85; H, 6.60; N, 13.29. The infrared and n.m.r. spectra were consistent with the structure assigned.

Hydrogenation of pyrrolizine (III, 0.035 mole) with 5% rhodium on carbon in diethyl ether showed a rapid uptake of a quantitative amount of 1 mole of hydrogen per mole of III, and, on distillation, gave 3.04 g. (81%)⁵ of 1,2-dihydro-3H-pyrrolizine (IV), b.p. 70° (20 mm.), n_D^{25} 1.5267 (lit.⁶ b.p. 63° (10 mm.), n_D^{25} 1.5264). The infrared and n.m.r. spectra were consistent with the structure assigned.

Reduction of 1.41 mmoles of III over 5% rhodium on carbon in ethanol showed a ready absorption of 99% of 3 moles of hydrogen per mole of III. The pyrrolizine picrate (VI) was obtained directly from the filtered hydrogenation mixture, m.p. 258–260° dec. (lit.⁷ m.p. 256–258° dec.). Similarly 0.05 mole of III gave 4.54 g. of pyrrolizidine, b.p. 77–84° (87 mm.), n_D^{27} 1.4596, shown to be 83% V by gas phase chromatography, for an over-all yield of 68%. A pure sample (better than 99% by g.p.c.) had b.p. 79° (70 mm.), n_D^{30} 1.4628 (lit.⁷ b.p. 140–143° (748 mm.), n_D^{30} 1.4561). A similar reduction of 1.29 mmoles of IV showed a quantitative uptake of 2 moles of hydrogen and yielded 91% VI, m.p. 260–262° dec.

Further studies on the preparation of substituted pyrrolizine systems and on the preparation of the parent pyrrolizinium salts are underway and will be reported in a future publication.

(5) Shown to be better than 99% pure by gas phase chromatography on a Carbowax 20 M on Haloport column from Wilkins Instrument Co.

(6) J. M. Patterson, J. Brasch, and P. Drenchko, *J. Org. Chem.*, **27**, 1652 (1962).

(7) N. J. Leonard and W. E. Goode, *J. Am. Chem. Soc.*, **72**, 5404 (1950).

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BOOK REVIEWS

Advances in Photochemistry, Volume 1. By W. ALBERT NOYES, JR., Department of Chemistry, University of Rochester, Rochester, N. Y., GEORGE S. HAMMOND, Department of Chemistry, California Institute of Technology, Pasadena, Calif., and J. N. PITTS, JR., Department of Chemistry, University of California, Riverside, Calif. John Wiley and Sons, Inc., 605 Third Ave., New York 16, N. Y. 1963. ix + 443 pp. 15.5 × 23.5 cm. Price, \$16.50.

The first volume of "Advances in Photochemistry" contains nine chapters contributed by thirteen authors of different dis-

ciplinary backgrounds. All authors are well known for their contributions in the respective fields. Recent developments of new experimental techniques, such as spectroscopy and magnetic resonance spectrometry for the identification of intermediates and products, flash photolytic spectrometry for the detection of short-lived intermediates, and chromatography for the isolation of products, promoted a mutual interest among various groups of investigators. In view of the recent interest in photochemistry, the book is a timely addition to the field.

The first chapter on "The 'Vocabulary' of Photochemistry" by J. N. Pitts, F. Wilkinson, and G. S. Hammond provides

valuable information for those of us who had been confused by the multitude of terminologies. The next eight chapters, "The Photochemistry of Aromatic Hydrocarbon Solutions" by E. J. Bowen, "Photochemical Gas Phase Reactions in the Hydrogen-Oxygen System" by D. H. Volman, "Photochemistry of Cyclic Ketones" by R. Srinivasan, "Addition of Atoms to Olefins in the Gas Phase" by R. J. Cvetanovic, "A New Approach to Mechanistic Organic Photochemistry" by H. E. Zimmerman, "Isotopic Effects and the Mechanism of Energy Transfer in Mercury Photosensitization" by H. E. Gunning and O. P. Strausz, "Photochromism" by R. Dessauer and J. P. Paris, and "Photochemical Rearrangements of Organic Molecules" by O. L. Chapman, are reviews on topics of current interests. The reviewer enjoyed reading the chapters by Bowen, by Cvetanovic, by Dessauer and Paris, and by Chapman, although this is in no way reflecting the quality and thoroughness of the contribution from the other authors. As stated by the editors in the introduction, "...Frontiers in photochemistry are at times full of confusion and for this reason they are fascinating. The editors have in no sense acted as censors. . . .", some of us may find certain difference of opinions in the mechanistic aspects of photochemistry in this volume, but the reviewer found this to be particularly stimulating.

On the whole, the book provides not only informations about the recent advances in photochemistry, but also a broader perspective for photochemists of different backgrounds. The reviewer is eagerly looking forward to the next volume of the series.

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Polyethers. Part I. Polyalkylene Oxides and Other Polyethers. Edited by NORMAN G. GAYLORD, Gaylord Associates, Newark, N. J. Interscience Publishers, John Wiley and Sons, Inc., 605 Third Ave., New York 16, N. Y. 1963. xiv + 491 pp. 16 × 23.5 cm. Price, \$16.00.

The broad title "Polyethers" covers three parts and constitutes Volume XIII of the series of monographs on high polymers published by Interscience Publishers. This review concerns itself only with Part I, which covers polyalkylene oxides, polymers derived from 1,2-, 1,3-, and higher epoxides and polyacetals. Epoxy resins are discussed in Part II and polyalkylene sulfides (and other polythioethers) are described in Part III of Volume XIII. Polyethers which do not fall into these categories are those derived from cellulose, starch, and other carbohydrate polymers occurring in nature as well as homo- and copolymers of vinyl alkyl ethers. In other words, the term "polyether" is meant to cover those polymeric ethers in which the carbon-oxygen linkage occurs in the polymer backbone rather than in a pendant side chain. Thus, although a number of valuable, commercial, polymeric ethers are not discussed in this volume, they may be found in other volumes of this series.

In general, Part I of this Volume XIII will be appreciated by chemists concerned with technical applications for polymeric ethers as well as the research man more interested in theoretical studies and implications. The collected references alone in any publication on polymer chemistry are of considerable value since many of them are scattered in the patent literature. These collected references at the end of each chapter cover the literature up to 1961, with an occasional reference to 1962.

The chapter on polymers derived from carbonyl compounds, by J. C. Bevington, is well organized in regard to content and covers both cyclic and linear polymers obtained from formaldehyde, acetaldehyde, and higher aldehydes. The polymerization of chlorinated and unsaturated aldehydes, dialdehydes, ketones, and ketene is also discussed briefly. The descriptive matter is not limited to information regarding preparation and physical properties of the polymers. Structural features, polymerization mechanisms, and molecular weight data are also considered.

The commercially important polymers derived from 1,2-epoxides (chiefly ethylene oxide and propylene oxide) are discussed in two chapters. The chemistry of the monomers and polymers is reviewed by L. E. St. Pierre in considerable detail and includes the preparation, properties, and hazards of the monomers, the synthesis of the polymers and copolymers, and their structure and physical properties. Molecular weight information (including molecular weight distributions) on the polymers is also presented, as well as current views of polymerization mechanisms. The chapter on the applications and technology of these polymers, by Anita S. Kastens, is very comprehensive in scope. A compilation of nearly 600 references, drawn almost exclusively from the patent literature and technical data sheets, will be greatly appreciated by the industrial chemist concerned with applications of this class of polymer. Technical data presented in the form of charts and tables are extensive, and a discussion of the fields of applications includes textiles, agriculture, cosmetics, pharmaceuticals, paper, paints, household cleaners and polishes, etc. Numerous formulations are given which are typical of products used in these applications.

The chemistry of the epoxides is extended to 1,3- and 1,4-epoxides by A. C. Farthing, and the discussion, in general, is similar to that already described.

The chapter on polyurethanes derived from polyalkylene oxides, by K. C. Frisch and S. Davies, combines a description of the chemistry of these materials, including that of the isocyanate function and of diisocyanates in particular, with the applications and technology of polyurethanes.

The final chapter, by the editor, reviews polymeric acetals, including linear, cyclic polyacetals and polyspiroacetals, and the various synthetic routes whereby they may be prepared. Other miscellaneous syntheses which afford polymeric ethers are briefly described.

In addition to the author and subject indexes, there is also a list of trademarks whereby commercial products mentioned in the book can be associated with their manufacturers.

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