

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.

Acknowledgment.—The authors are grateful for support of this work by the Directorate of Chemical Sciences, Air Force Office of Scientific Research, Grant No. AF-AFOSR-502-64.

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RECEIVED MAY 16, 1964

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

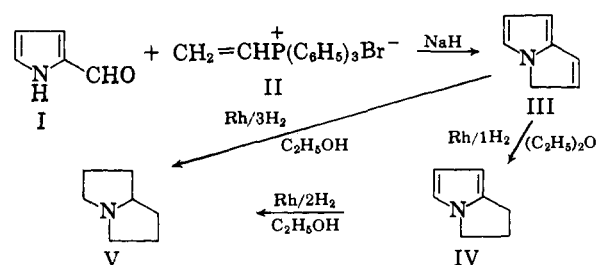
When 2-pyrrolaldehyde⁴ (I, 0.210 mole) was allowed to react with sodium hydride (0.183 mole) in anhydrous ether (200 ml., 4 hr.) followed by the addition of the salt II (0.215 mole) an exothermic reaction was observed. The resulting mixture was stirred under reflux for 24 hr. followed by filtration, 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 C_7H_7N : 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^{20} 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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RECEIVED MAY 27, 1964

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