

acid and stirred for two hours at 0°, after which it was saturated with sodium chloride. The precipitated product was dried *in vacuo* after washing until free of the chloride ion. The mono-sodium salt was obtained as a dark-red powder, soluble in cold alkali, sparingly soluble in hot concentrated hydrochloric acid, and very little soluble in cold or hot dilute hydrochloric acid. The yield was 93.5%.

Anal. Calcd. for $C_{32}H_{28}O_6N_6P_2Na$: P, 9.2. Found: P, 9.31.

Preparation of the Arsonic Analog of Congo Red (VII).—4-Nitronaphthalenearsonic acid was prepared according to Saunders and Hamilton⁷ in 80% yield and the product was reduced with ferrous hydroxide as described above. The product, purified by reprecipitation from 10% sodium hydroxide with 3 *N* hydrochloric acid, formed light yellow plates, which decomposed at 215°; yield 69.5%. Coupling of the amino acid with benzidine was carried out as described under VI and the product was isolated in 69% yield as a dark-red mono-sodium salt, whose properties were similar to those of VI.

Anal. Calcd. for $C_{32}H_{28}O_6N_6As_2Na$: As, 19.65. Found: As, 19.7.

Determination of Indicator Properties.—The various substances were dissolved in 0.01 *N* hydrochloric acid and the colors of the solutions were observed while either 0.1 *N* sodium hydroxide or 0.1 *N* hydrochloric acid was added to the system. Upon establishment of color the *pH* of the system was determined with a *pH* meter. An average of four determinations was made on each compound, with reproducibility of 0.1 *pH* unit. It must be noted that VII failed to develop its full purple color until the solution was very strongly acid.

Dyeing Experiments.—The Indian Head cotton cloth used for the tests was desized by boiling with sodium alkyl sulfonate detergent and the thoroughly washed strips were treated with the various dyes (I–VII) in saturated solutions which were adjusted to *pH* 8 with stirring for 30 minutes at 80–90°. The specimens were then removed, immersed in 1% hydrochloric acid, thoroughly rinsed and air-dried. The dyeing of silk and wool fabrics was done directly by immersion into a saturated solution of each dye for five minutes at 95°, followed by stirring at this temperature for 25 minutes. A drop of hydrochloric acid was placed into the dye solution (100 ml. of water) to facilitate solution. After washing, the specimens were air-dried.

Absorption Measurements.—Saturated solutions of the dyes in water at the various *pH* levels were examined by means of a Beckman DU model quartz spectrophotometer. The congo red analogs were examined in absolute alcohol solution owing to their low solubility in aqueous medium within *pH* ranges employed. Readings of optical density were taken at 2- μ intervals from the low-frequency side until the first maximum was passed.

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Reduction of 3-(2-Pyridyl)-propionaldehyde

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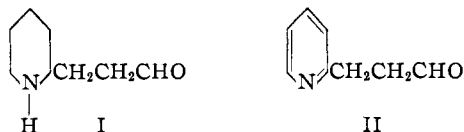
Previous attempts at preparation of the highly unstable pomegranate alkaloid pelletierine (I) have been made by hydrolysis of its acetal,^{1,2} available from the corresponding pyridine compound by hydrogenation, and by lithium aluminum hydride reduction of 3-ketooctahydropyrrocoline.³ These methods failed, presumably due to aldolization catalyzed by the basic piperidine nitrogen atom.

(1) J. P. Wibaut and M. G. J. Beets, *Rec. trav. chim.*, **60**, 905 (1941); M. G. J. Beets, *ibid.*, **62**, 553 (1943).

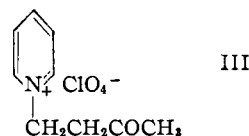
(2) M. A. Spielman, S. Swadesh and C. W. Mortensen, *J. Org. Chem.*, **6**, 780 (1941).

(3) J. A. King, V. Hofman and F. H. McMillan, *ibid.*, **16**, 1100 (1951); F. Galinovsky, O. Vogel and R. Weiser, *Monatsh.*, **83**, 114 (1952).

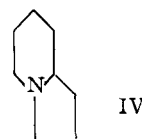
It was reasoned that if the sequence of the two reactions of the first method be reversed, *i.e.*, hydrolysis of the acetal of the pyridylpropionaldehyde (II, dehydropelletierine) followed by reduction of the pyridine ring, that the lower basicity of the nitrogen function of II, particularly in the form of a salt, such as the hydrochloride, might permit the direct formation of I.



Dehydropelletierine has been reported as an unstable base,¹ but in this work it has been found to be quite stable as the hydrochloride. Hope for reduction of the pyridine ring of II without affecting the carbonyl group was based on the previously observed⁴ selective reduction of the pyridine ring of the quaternary ketone III.



Reduction of dehydropelletierine hydrochloride in alcohol⁵ gave only octahydropyrrocoline (IV). Similar behavior has been observed in reduction of the acetal of II in both hydrochloric and acetic



acids, although it was found that increasing the concentration of the acetic acid solution of the acetal gave pelletierine acetal as the major product rather than IV.¹

Attempts to control the reduction of II hydrochloride by increasing its concentration in alcohol were without effect. When reduction was carried out in glacial acetic acid at high concentrations the solution became dark, even during the reaction, and from the tarry product the only crystalline derivatives obtainable were those of small amounts of octahydropyrrocoline. Although crystalline derivatives of I could not be isolated, the occurrence of tars in the manner observed indicates the probable formation and subsequent polymerization of pelletierine during the course of the reduction.

Acknowledgment.—The author wishes to acknowledge the technical assistance of Mr. Frank Vasington.

Experimental⁶

Dehydropelletierine (II).—A solution of 10 g. of 3-(2-pyridyl)-propionaldehyde diethyl acetal² in 10 ml. of 10% hydrochloric acid and 15 ml. of alcohol was refluxed for three hours. The alcohol was removed under vacuum and the solution was made basic with 10% sodium carbonate and extracted with ether. The ether extracts were dried over sodium sulfate, evaporated and the residue distilled. The fraction boiling at 106–108° at 9 mm. was collected as a

(4) F. M. Miller, unpublished results.

(5) T. S. Hamilton and R. Adams, *THIS JOURNAL*, **50**, 2260 (1928).

(6) Melting points observed on a Fisher-Johns melting point block. Analyses by Oakwold Laboratories, Alexandria, Virginia.

colorless oil which was dissolved in ether and treated with dry hydrogen chloride. The separated dehydropelletierine hydrochloride was recrystallized from alcohol-ether, m.p. 136–138°.

Anal. Calcd. for $C_8H_{10}NOCl$: N, 8.23. Found: N, 8.22.

The picrate was prepared from the hydrochloride in alcohol.

Anal. Calcd. for $C_{14}H_{12}N_4O_8$: N, 15.38. Found: N, 15.47.

Reduction of II.—A solution of 0.51 g. of dehydropelletierine hydrochloride in 25 ml. of absolute alcohol was stirred in an atmosphere of hydrogen in the presence of 0.05 g. of platinum oxide catalyst. Absorption of three molecular equivalents of hydrogen occurred within 45 minutes and the reduction was stopped even though hydrogen up-take had not ceased. The catalyst was filtered off and the alcohol removed under vacuum. The addition of anhydrous ether caused crystallization of a very hygroscopic hydrochloride, which was dissolved in alcohol and converted into the picrate, m.p. 231–232°. Octahydropyrococline picrate is reported to melt at 232°. ¹

Anal. Calcd. for $C_{14}H_{18}N_4O_7$: N, 15.82. Found: N, 16.13.

The aurochloride was prepared from the hydrochloride in water, m.p. 190°. ⁷

Carrying out the reduction in alcohol at higher concentrations (up to 1.0 g. per 8 ml.) gave identical results. When either the hydrochloride or the free base was reduced in the same manner in glacial acetic acid at high concentrations (1.0 g. of the hydrochloride per 4.0 ml.) the solution began to darken shortly after the reduction was begun. All attempts to obtain a crystalline picrate from the reaction mixture gave only small amounts of octahydropyrococline picrate.

(7) K. Löffler and H. Kaim, *Ber.*, **42**, 94 (1909).

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The Preparation of $NaC^{14}N$ and $NaCN^{15}$

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1. Preparation of $NaC^{14}N$.—Many methods of preparation of $NaC^{14}N$ from $BaC^{14}O_3$ have been described during recent years^{2–10}; however, nearly all of them require special apparatus which is often not immediately available in most laboratories. The original method of Adamson,⁴ in which barium carbonate is heated with sodium azide, has been found by most workers to give erratic results. The essential feature of the following modification of Adamson's method is that only ordinary laboratory apparatus is used, and no special pumping or heating arrangements are necessary. Although the yields are not quite as high as those obtained in some of the methods involving more complicated

(1) This note is based on a portion of a thesis to be submitted by Alan G. MacDiarmid in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Graduate School of the University of Wisconsin.

(2) R. D. Cramer and G. B. Kistiakowsky, *J. Biol. Chem.*, **137**, 549 (1941).

(3) R. B. Loftfield, *Nucleonics*, **1**, No. 3, 54 (1947).

(4) A. W. Adamson, *THIS JOURNAL*, **69**, 2564 (1947).

(5) R. Abrams, *ibid.*, **71**, 3835 (1949).

(6) B. Belleau and R. D. H. Heard, *ibid.*, **72**, 4268 (1950).

(7) G. O. Henneberry and B. E. Baker, *Can. J. Research*, **26B**, 345 (1950).

(8) G. O. Henneberry, W. F. Oliver and B. E. Baker, *ibid.*, **29**, 229 (1951).

(9) J. A. McCarter, *THIS JOURNAL*, **73**, 483 (1951).

(10) J. W. Spyker and A. C. Neish, *Can. J. Chem.*, **30**, 461 (1952).

apparatus, e.g., that of Henneberry and Baker,⁷ the simple procedure below is excellent for the rapid preparation.

The apparatus consists of a length of glass tubing (approximately $2\frac{1}{2}$ by $\frac{1}{4}$ in.) sealed at one end, connected to one arm of a T-joint by rubber tubing. The stem of the T projects down into the first (B) of two vertical test-tubes (about 1×6 in., stoppered). The other arm leads through a right angle to the bottom of the second test-tube (C) from the top of which glass tubing leads to a nitrogen inlet and a 50-ml. reservoir bulb (D). The test-tubes are slipped snugly through 4-in. squares of asbestos.

The $BaC^{14}O_3$ is placed on a small watch glass and sufficient inert barium carbonate is added to it to give a total weight of approximately 0.1 g. This is then mixed into a paste with a little ethyl alcohol, using a small glass rod, and is allowed to dry in a desiccator. It is scraped from the watch glass on to black glazed paper and any lumps are gently broken up by pressing with a spatula. The barium carbonate is then mixed well, while still on the glazed paper, with 1.5 g. of sodium azide which has been finely powdered, in small amounts, in a mortar.

The apparatus is flushed out with dry nitrogen and a slow stream kept up throughout the experiment. The carbonate-azide mixture is introduced into A. Bunsen burners are then placed under the test-tubes so that the inner blue cone of the flame just impinges on the bottom of the test-tubes. The asbestos shields are placed approximately 1.5 inches above the bottoms of the test-tubes, which should now glow with a dull red heat. The tube A is raised and is tapped gently so that its contents are slowly emptied into the test-tube B. This should take about 15 minutes. As the powder reaches the bottom of B minute explosions occur and some of the undecomposed powder is blown over into C where it finally reacts. Metallic sodium collects on the sides of the tubes and remains there throughout the course of the experiment since no air enters the tube after the miniature explosions because of the nitrogen reservoir, D. The asbestos shields are now removed and the base and walls of both test-tubes are heated to a dull red heat for ten minutes by movement of the Bunsen burners. They are then allowed to cool, the nitrogen supply is turned off, and water is carefully added drop by drop to B and C to decompose the sodium. The contents of C are transferred with boiling water to B so that there is approximately 20 ml. of liquid in B. About 5 ml. of 0.1 N barium hydroxide is added to remove any carbonate formed; the solution is brought to boiling and filtered. The filtrate is placed in a distillation apparatus with boiling chips, acidified with 50% sulfuric acid and the $HC^{14}N$ distilled into approximately 10 ml. of 0.1 N sodium hydroxide. The strength, and also the specific activity of the resulting sodium radiocyanide solution, may be adjusted by the addition of inert sodium cyanide.

In the above manner of preparation, many of the experimental variables in Adamson's original method are eliminated. Consistent yields of 70% or more were obtained in blank runs with inert barium carbonate. Using the written directions above, yields of over 70% were obtained in the Department of Biochemistry at this University.¹¹

2. Preparation of $NaCN^{15}$.— $NaCN^{15}$ was prepared from potassium phthalimide¹² containing N^{15} in the following manner.

A small steel "bomb" is made by drilling a hole ($2\frac{1}{2} \times \frac{3}{8}$ inch) in a hexagonal steel bar. This can be sealed by a bolt which screws into the hole for a distance of about half an inch. The joint is made gas tight by means of a soft copper washer. The bomb is then thoroughly washed inside with hot soap and water, rinsed with water and acetone and dried. Traces of rust in the bomb cause the formation of small amounts of hexacyanoferrate(II) impurity in the sodium cyanide.

0.3 g. of potassium phthalimide and 1.5 g. of sodium slices are placed in the bomb which is then heated in a furnace for 20 minutes at 700° in an upright position. After cooling, water is carefully added drop by drop to the contents of the bomb to decompose any remaining sodium. The carbonized mass is then extracted with hot water, and

(11) D. Wilson, Department of Biochemistry, University of Wisconsin, private communication, Nov., 1952.

(12) Potassium phthalimide containing N^{15} obtained from Eastman Kodak Co., Rochester 4, N. Y.