The apparatus used for the pyrolysis of the acetates consisted of a Pyrex reaction tube having a reaction zone of 1.5 cm. outside diameter and packed with 15 ml. of about $^{1}/_{8}$ inch quartz chips or $^{1}/_{8}$ inch glass beads. The tube was heated by a thermostatically controlled vertical furnace. The acetates were introduced by means of a motor driven syringe.

The butenes were analyzed by vapor phase chromatography using a column described previously.[1]

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Preparation of Pyrrole

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The requirement for relatively large quantities of pyrrole in this laboratory prompted an investigation for a rapid inexpensive synthesis of this material. Of the methods reported in the literature, the dehydrogenation of pyrrolidine using a flow system offered the greatest promise.

Catalysts which have been used in the dehydrogenation of cyclic amines include platinum or palladium on asbestos,[1] oxides of magnesium, calcium or zinc or mixtures of these,[2] and nickel-nickel chromite.[3] Although the catalysts most frequently employed in the dehydrogenation of pyrrolidine or substituted pyrrolidines have been platinum or palladium on asbestos, the effectiveness of rhodium on alumina in reducing nitrogen heterocyclic systems,[4] suggested that it might be a superior dehydrogenation catalyst for cyclic amines. Accordingly, this was the catalyst investigated in these experiments.

The optimum conditions for the dehydrogenation of pyrrolidine using rhodium on alumina were 650° with an HLSV[5] of 8–10. Shorter contract times resulted in lower yields of pyrrole while longer contact times produced more decomposition. It is interesting to note that the dehydrogenation using platinum or palladium on asbestos is reported to occur at 300°.[1]

Two other potential catalysts were investigated: Berl saddles were ineffective; activated alumina pellets were about half as effective as rhodium on alumina at optimum conditions.

In addition to pyrrole and unreacted pyrrolidine in the dehydrogenated product, there was obtained some of the 2-(2-pyrrolidyl)pyrrole reported by Fuhlhage and Vander Werf.[6] It appears that 1-pyrroline is an intermediate in dehydrogenation reactions in which rhodium on alumina is the catalyst.

The slightly better yield of pyrrole obtained in the distillation procedure is probably due to the dissociation of the 2-(2-pyrrolidyl)pyrrole present in the crude dehydrogenation mixture.

Bell[7] reports that diethylamine can be converted into pyrrole when introduced into a hot tube. Using the optimum conditions of the pyrrolidine experiments and a rhodium on alumina catalyst, pyrrole was produced in less than 1% yield.

EXPERIMENTAL[8]

Materials. The pyrrolidine used in these experiments was the practical grade supplied by the Matheson, Coleman and Bell Co. The rhodium catalyst, 0.5% rhodium on $^{1}/_{8}''$ activated alumina pellets, was obtained from Baker and Co., Inc. and the Puralox catalyst, $^{1}/_{8}''$ activated alumina pellets, from the Harshaw Scientific Co.

Apparatus. The apparatus consisted of a vertically arranged vycor reactor tube (2.5 × 30 cm.) in a continuous flow system. The reactor contained 30 ml. of the catalyst and an upper layer (30 ml.) of Berl saddles. A vycor preheater tube containing 30-ml. Berl saddles was used to volatilize the sample which was introduced into the preheater from a buret and flushed through the system by a stream of dry nitrogen.

Preparation of pyrrole. Eighty-five grams of pyrrolidine was introduced into the flow type apparatus at an HLSV of 8–10 and nitrogen flow rate of 440 ml./min. The temperature of the reactor, containing 30 ml. of 0.5% rhodium on alumina was maintained at 650° and the preheater temperature was maintained at 300°. The weight of the condensed pyrolysis product was 70 g. The crude product was added to 200 ml. of water, saturated with Dry Ice and then separated from the carbonic acid solution. After a second treatment, the combined aqueous portions were extracted with three 100-ml. portions of ether, the ether extract combined with the carbonic acid insoluble layer and dried over sodium sulfate. Distillation of the residue after removal of the drying agent and the ether yielded 35.6 g. (45%) of pyrrole, b.p. 127–129°, n_D^{20} 1.5040. Analysis by gas chromatography indicated the pyrrole to be 99.5% pure. In addition to the pyrrole, a tarry residue (5.1 g.) was obtained.

The crude product could also be purified by distillation in a Podbielniak High-Temperature Fractional Distillation Apparatus to give pyrrole in 50% yield. Columns of lesser efficiency were ineffective.

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(1) N. D. Zelinsky and Y. K. Yur'ev, *Ber.*, **62**, 2589 (1929).

(2) I. G. Farben Ind., Brit. Patent **515,865**, Dec. 15, 1939.

(3) H. Adkins and L. G. Lundsted, *J. Am. Chem. Soc.*, **71**, 2964 (1949).

(4) Brochure, *The Role of Platinum Group Metal as Catalysts*, Baker and Co., Newark, N. J.

(5) Hourly liquid space velocity = volume of reactant/volume of catalyst/hour.

(6) D. W. Fuhlhage and C. A. Vander Werf, *J. Am. Chem. Soc.*, **80**, 6249 (1958).

(7) C. A. Bell, *Ber.*, **10**, 1868 (1877).

(8) Melting points were taken on a Fisher-Johns melting point apparatus and are corrected. Boiling points are uncorrected. Microanalyses were by Weiler and Strauss, Oxford, England.

Investigation of the carbonic acid soluble portion. The carbonic acid extract of the pyrolysis product was made strongly alkaline with sodium hydroxide, extracted with three 100-ml. portions of ether and the ether extract dried over potassium carbonate. Distillation of the ether extract, after removal of the ether, gave 16.3 g. of a water-pyrrolidine mixture, b.p. 78–98°, 4.8 g. of a semi-solid liquid, b.p. 122–169° (1 mm.) and 9.7 g. of tarry residue.

2-(2-Pyrrolidyl)pyrrole (I). The semi-solid liquid, b.p. 122–169° (1 mm.) on several recrystallizations from Skellysolve B gave 3.6 g. of a white crystalline solid, melting at 85.5–86.5°. The solid was basic and gave a positive Ehrlich test for pyrrole.

Anal. Calcd. for $C_8H_{12}N_2$: Neut. equiv., 136. Found: Neut. equiv., 134, 138.

Literature[6] b.p. 94° (0.5 mm.); m.p. 86.3–87.8°.

Picrate of I. Treatment of a solution of I in 95% ethanol with a saturated ethanolic picric acid solution produced a picrate which melted at 170–171° after several recrystallizations from 95% ethanol. Literature[6] m.p. 164–165.5° (uncorrected).

Anal. Calcd. for $C_{14}H_{15}N_5O_7$: C, 46.0; H, 4.2; N, 19.2 Found: C, 46.7; H, 4.2; N, 18.8.

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Rearrangement of 9α-Hydroxy-4-androstene-3,17-dione

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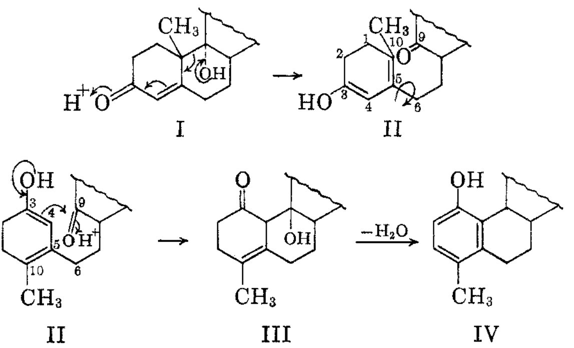
4-Androstene-3,17-dione was shown to be hydroxylated in the 9α-position with a species of Nocardia (A20-10) isolated from soil.[1] We have observed that treatment of the hydroxylated product (I) with pyridine hydrochloride at 218° resulted in a rearrangement to 1-hydroxy-4-methylestra-1,3,5(10)-trien-17-one (IV).[2]

A possible mechanism for this transformation is outlined in the partial formulas (I–IV). The initial step involves a reverse aldol type of reaction, which parallels that previously postulated for the microbiological conversion of 4-androstene-3,17-dione to 9,10-seco-3-hydroxy-1,3,5(10)-androstatriene-9,17-dione,[3] except in the present case the reaction is facilitated by acid. Rotation about the C_5—C_6 bond of II places C_4 in a favorable position to undergo an aldol condensation with the carbonyl group at C_9. Dehydration of the aldol product (III) followed by migration of the resulting double bond into ring A and enolization complete the transformation.



EXPERIMENTAL

A mixture of 1.00 g. of 9α-hydroxy-4-androstene-3,17-dione, m.p. 222–223.5°, and 10 g. of pyridine hydrochloride was maintained at 218° for 50 min. in an atmosphere of nitrogen. The reaction then was cooled, diluted with water, and chilled in an ice bath. The precipitate, which was collected by filtration, washed well with water, and dried, could not be induced to crystallize from ether–petroleum ether (60–68°). The residue remaining after the organic solvents had been removed was chromatographed on 70 g. of silica gel. The column was eluted with varying proportions of benzene–ethyl acetate. Elution with 5% ethyl acetate in benzene gave 404 mg. of a mixture of oil and solid. Two hundred sixty-seven mg. of this mixture was washed free of oil with ether. The solid, which remained, was recrystallized from ether–petroleum ether (60–68°) to afford 57 mg. of colorless massive rods, m.p. 239–248°. Repeated crystallization from ether–petroleum ether (60–68°) raised the m.p. to 251–254°, undepressed by an authentic sample of 1-hydroxy-4-methylestra-1,3,5(10)-trien-17-one (IV).[2,4]

Its infrared spectrum determined in KBr was identical with that of the authentic sample of IV. λ_{max}^{MeOH} 281–286 mμ (ε 2250), λ_{min}^{MeOH} 249.5 mμ (ε 182); λ_{max}^{KBr} 3.07, 5.82, 6.28, 12.28μ.

Other fractions obtained from the column proved to be intractable tars and resins.

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(1) R. M. Dodson and R. D. Muir, *J. Am. Chem. Soc.*, **80**, 6148 (1958).

(2) (a) A. S. Dreiding, W. J. Plummer, and A. J. Tomasewski, *J. Am. Chem. Soc.*, **75**, 3159 (1953). (b) A. S. Dreiding and A. Voltman, *J. Am. Chem. Soc.*, **76**, 537 (1954).

(3) R. M. Dodson and R. D. Muir, *J. Am. Chem. Soc.*, **80**, 5004 (1958).

(4) We are indebted to Drs. Willard M. Hoehn and Richard A. Mikulec of our laboratory for providing us with a sample of 1-hydroxy-4-methyl-estra-1,3,5(10)-trien-17-one prepared according to ref. 2.

Method for Preparing 2-Aryl-3-aroylpropionitriles

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An attempt was made to prepare 2-phenyl-3-benzoylpropionitrile by treating benzaldehyde with acetophenone and sodium cyanide.[1] The major

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(1) R. B. Davis, *J. Org. Chem.*, **24**, 880 (1959).