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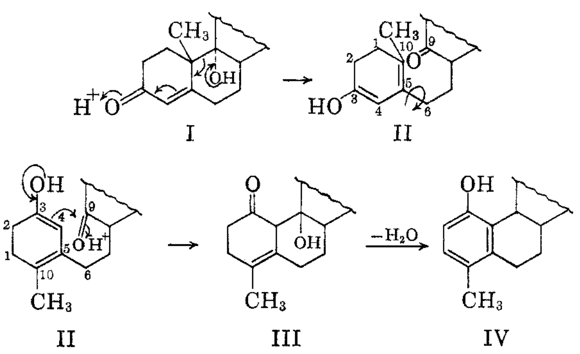
4-Androstene-3,17-dione was shown to be hydroxylated in the 9α-position with a species of Nocardia (A20-10) isolated from soil.[1] We have observed that treatment of the hydroxylated product (I) with pyridine hydrochloride at 218° resulted in a rearrangement to 1-hydroxy-4-methylestra-1,3,5(10)-trien-17-one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