sesses the A, B, C, E, F, G, K, L and M bands of the ordinary Δ^4-3-ketone spectrum. Such differences might be understandable if III has the same A-ring conformation as the ordinary Δ^4-3-ketones while that of I and II is different. The spectra of all three compounds have been compared as Nujol mulls and of I and II also in carbon disulfide solution.

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The Reaction of Lead Tetraacetate with Progesterone and Testosterone

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From the reaction of two or three moles of lead tetraacetate with one of progesterone were isolated 2α-hydroxyprogesterone acetate, 2α,21-dihydroxyprogesterone diacetate, and 1,4-pregnadien-21-ol-3,20-dione acetate. From the reaction of lead tetraacetate with testosterone acetate were isolated 2α-hydroxytestosterone diacetate, 2β-hydroxytestosterone diacetate and 1,4-androstadien-17β-ol-3-one acetate. Some reactions of these compounds are described. The rearrangement of 6-bromotestosterone acetate to 2-hydroxytestosterone diacetate was observed with isolation of the 2β-epimer rather than the previously reported 2α-epimer.

Several studies have been made of the mole for mole reaction of lead tetraacetate (LTA) with progesterone.[2-4] The products isolated were 2α-hydroxyprogesterone acetate, 2α,21-dihydroxyprogesterone diacetate, desoxycorticosterone acetate and an unidentified monohydroxyprogesterone.[2c]

Reichstein and Montigel[3] treated 1 mole of allopregnan-3-ol-20-one acetate with 1.8 moles of LTA to produce 53% acetoxylation at C-21 and 2% diacetoxylation at C-17, 21. 5-Pregnen-3-ol-20-one acetate with 3.2 moles of LTA gave a 19% yield of a 21-acetoxylated product. Mancera[5] acetoxylated 5-pregnen-3-ol-20-one benzoate at C-21 in 39% yield (1 mole LTA, if 100% pure), whereas Giral,[6] using this benzoate and more than a fourfold excess of LTA, obtained a 22% yield of an unknown[5] monoacetoxylated product, the only compound isolated. Thus, there are few cases of polyacetoxylation on record, even with excess LTA.

In this Laboratory the reaction of one mole of progesterone with two moles of LTA produced a complex mixture containing at least ten components as evidenced by infrared spectra. Diacetoxylated progesterones appear to constitute a rather large portion of the reaction products, but extensive work with solvents on the original oily product gave only a 2.5% yield of pure 2α,21-dihydroxyprogesterone diacetate. Chromatography on silica gel, which was only moderately effective, gave a mixture of diacetoxylated progesterones, a center cut of which (15% yield) showed an infrared spectrum very similar to that of the pure 2,21-diacetoxy compound; the purification of this mixture was so difficult that it was abandoned. 2α-Hydroxyprogesterone acetate[2c,4] (8%) and a new compound (I), $C_{23}H_{30}O_4$ (8%), were separated chromatographically and isolated in a pure state. I apparently results from the introduction of one acetoxy group and one double bond into the progesterone molecule.

Hydrogenation of I yielded allopregnan-21-ol-3,20-dione acetate,[7] pregnan-21-ol-3,20-dione acetate[8] and a trace of allopregnan-21-ol-20-one acetate[9] which were identical with the products obtained by the hydrogenation of desoxycorticosterone acetate under the same conditions. Thus the position of the acetoxyl group was fixed at C-21.

The hydrogenation experiment indicates that both unsaturated linkages in the molecule are conjugated with a carbonyl group, but the position and height of the ultraviolet absorption maximum rules out positions 6 or 16 for the second bond. Its location at position 1 is in accord with the data, a 1,4-dien-3-one showing the same absorption pattern as a 4-ene-3-one.[10] This was confirmed by a dienone–phenol rearrangement[11] of I to form a

(1) Deceased.

(2) (a) G. Ehrhart, H. Ruschig and W. Aumüller, *Angew. Chem.*, **52**, 363 (1939); (b) British Patent 502,474; (c) *Chem. Ber.*, **72**, 2035 (1939).

(3) T. Reichstein and C. Montigel, *Helv. Chim. Acta*, **22**, 1212 (1939).

(4) F. Sondheimer, St. Kaufmann, J. Romo, H. Martinez and G. Rosenkranz, THIS JOURNAL, **75**, 4712 (1953).

(5) O. Mancera, *ibid.*, **72**, 5752 (1950).

(6) F. Giral, *ibid.*, **72**, 1913 (1950).

(7) T. Reichstein and J. von Euw, *Helv. Chim. Acta*, **22**, 1209 (1939).

(8) T. Reichstein and H. Fuchs, *ibid.*, **23**, 658 (1940).

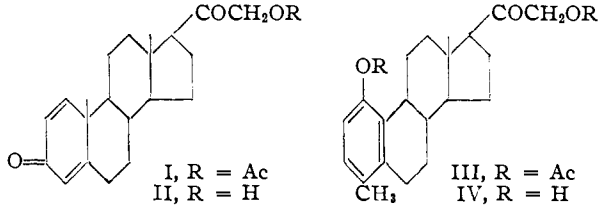
(9) R. E. Marker, THIS JOURNAL, **62**, 2543 (1940).

(10) Louis F. and Mary Fieser, "Natural Products Related to Phenanthrene," Reinhold Publishing Corp., New York, N. Y., 1949, pp. 191 and 193.

(11) R. B. Woodward and Tara Singh, THIS JOURNAL, **72**, 494 (1950).

phenolic diacetate, 1-hydroxy-4-methyl-17β-hydroxyacetyl-1,3,5 (10)-estratriene diacetate (III), with accompanying loss of the 3-keto group. III was hydrolyzed to the corresponding diol IV. Thus, I may be assigned the structure 1,4-pregnadien-21-ol-3,20-dione acetate.

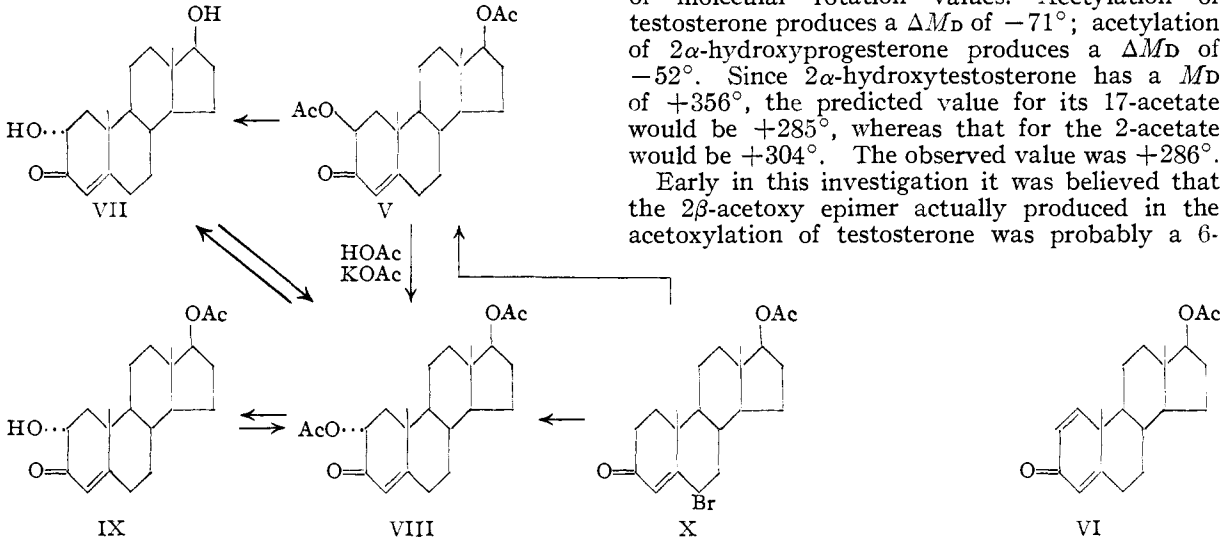
The separation of I was done sufficiently carefully to conclude that 7 to 8% represents its total formation under the conditions described. This yield was not affected appreciably by increasing the reaction time fivefold, running the reaction at 118°, or using three molecules of LTA; with five molecules of LTA, no I was isolated. I was not produced by pyrolysis of 2,21-dihydroxyprogesterone diacetate at temperatures up to 300°; therefore, this 2,21-diacetoxy compound does not appear to be an intermediate in its formation.



The reaction of desoxycorticosterone acetate with LTA, which would be expected to give a better yield of I than progesterone, gave approximately the same yield.

Hydrolysis of I gave 1,4-pregnadien-21-ol-3,20-dione (II) which is different from the "oxyprogesterone" reported by Ehrhart, *et al.*[2c]; the latter compound remains unidentified.

Because of the complexity of these mixtures,[12] we next studied a more simple acetoxylation reaction, that of testosterone acetate and LTA.



We obtained the same mixture of 2β-(unstable configuration) and 2α-(stable configuration) hydroxytestosterone diacetates (V and VIII), reported by Sondheimer and co-workers[4] and, in addition, a 1.5% yield of 1,4-androstadien-17β-ol-3-one acetate (VI).[13] This is in contrast to the 7.5% yield of dienone from progesterone. We had anticipated a higher rather than a lower yield of dienone from testosterone acetate into which only a double bond need be introduced. 2β-Hydroxytestosterone diacetate (V) crystallized from the mixture of products as reported,[4] but chromatography on silica gel (in contrast to alumina[4]) failed to separate the 2α-epimer. However, by the epimerization technique described below we isolated an 8.5% yield of this stable epimer VIII without resorting to chromatography (17% reported[4]).

2β-Hydroxytestosterone diacetate (V) was epimerized to 2α-hydroxytestosterone diacetate (VIII) by refluxing the former in potassium acetate–acetic acid solution.[14] This result, in addition to the fact that hydrolysis of both epimeric acetates produces 2α-hydroxytestosterone (VII), give complete substantiation to the system described.

When the mixture remaining after separation of 2β-hydroxytestosterone diacetate was subjected to brief hydrolysis with potassium bicarbonate, 2α-hydroxytestosterone 17-acetate (IX) separated. The assignment of the acetate group to the C-17 position is based on infrared absorption data. The band representing the 17β-OH group of testosterone appears at 2.81 μ, whereas 2α-hydroxytestosterone shows bands at 2.81 and 2.91 μ, and 2α-hydroxyprogesterone shows a band at 2.91 μ. As the monoacetate IX shows only a 2.91 μ band, it is the 2α-hydroxy-17β-acetoxy compound. IX was then acetylated to 2α-hydroxytestosterone diacetate to rule out any gross rearrangements.

The identification of IX as the 2α-hydroxy-17β-acetoxy compound was confirmed by a comparison of molecular rotation values. Acetylation of testosterone produces a ΔM_D of −71°; acetylation of 2α-hydroxyprogesterone produces a ΔM_D of −52°. Since 2α-hydroxytestosterone has a M_D of +356°, the predicted value for its 17-acetate would be +285°, whereas that for the 2-acetate would be +304°. The observed value was +286°.

Early in this investigation it was believed that the 2β-acetoxy epimer actually produced in the acetoxylation of testosterone was probably a 6-hydroxytestosterone diacetate. As confirmation, 6-bromotestosterone acetate (X)[15] was prepared and refluxed with potassium acetate in acetic acid.

(12) Our results indicate that mixtures of 2α- and 2β-acetoxylated compounds were present and that the isolation procedure would have been greatly simplified had the 2β-epimers been converted to the stable 2α-configuration prior to work-up.

(13) H. H. Inhoffen, G. Zühlsdorff and Huang-Minlon, *Ber.*, **73**, 451 (1940).

(14) Epimerization with sodium methoxide in boiling benzene (1 hr.) was unsuccessful.

(15) Ch. Meystre and A. Wettstein, *Experientia*, **2**, 408 (1946); C. Djerassi, G. Rosenkranz, J. Romo, St. Kaufmann and J. Pataki, THIS JOURNAL, **72**, 4534 (1950).

The product was 2β-hydroxytestosterone diacetate (V). This is the same rearrangement reported recently by Sondheimer, *et al.*,[4] for this series (12% yield) and by Fieser and Romero[16] (17% yield) for the cholestenone series; however, these workers obtained the stable 2α-epimer. Seeds of the unstable 2β-epimer were probably more abundant in this Laboratory for 2β-hydroxytestosterone diacetate crystallized from our mixture in 21% yield and we missed the other isomer. It must be concluded that either a mixture of epimers is produced in this reaction or that the 2β-epimer is the primary rearrangement product which then partially isomerizes to the stable α-configuration under favorable reaction conditions.

The authors thank Mr. M. E. Auerbach, Mr. K. D. Fleischer and their associates for their microanalytical work.

Experimental[17-19]

Acetoxylation of Progesterone.—To a solution of 170 g. of 85% pure LTA (0.33 mole) in 1800 ml. of glacial acetic acid at 70°[20] was added, all at once and with stirring, a solution of 50 g. (0.16 mole) of progesterone in 200 ml. of glacial acetic acid at approximately 70°. Titration of an aliquot for oxidizing power ten minutes after mixing indicated that less than 1% reaction had occurred. The reaction was complete (starch–iodide test negative) after six hours heating at 85–90°.[21] Most of the solvent was removed under vacuum with warming, 1 l. of water was added, and the mixture extracted three times with ether. The extracts were washed five times with water and then with sodium bicarbonate solution until alkaline; they were dried briefly over sodium sulfate and overnight over anhydrous calcium sulfate (Drierite).

The ether solution was made up to 1 l., 1 l. of Skellysolve A added, and the liquid decanted from the precipitated gum onto a chromatographic column containing 1 kg. of silica gel. The residual gum was dissolved in ether and the process repeated until all material was on the column, 10 l. of the solvent mixture being required. The column was developed with an additional 10 l. of this mixture and thereafter a mixture of 60% ether and 40% Skellysolve A was used for elution. From liters of eluate 29–36 was isolated, after one recrystallization from ether and three from methanol, 4.9 g. (8%) of 2α-hydroxyprogesterone acetate,[2c,4] m.p. 198.1–199.6°, $[\alpha]^{25}D$ +158° (1% in $CHCl_3$).

Liters of eluate 37–64 gave 33 g. of a white solid, the infrared spectrum of which indicated it to be largely 2α,-21-dihydroxyprogesterone diacetate.[2c,4]. After three recrystallizations from methanol, it melted at 165–180°, $[\alpha]^{26}D$ +156° (0.5% in EtOH); yield 11 g. (16%) and showed an infrared spectrum similar to that of the pure diacetoxylated compound described below.

Anal. Calcd. for $C_{25}H_{34}O_6$: C, 69.72; H, 7.96. Found: C, 69.30; H, 8.11.

The combined solid from fractions 79–85 and 113–116 was washed with a small quantity of ether and added to fractions 86–112. This solid was recrystallized from acetone–ether to give 3.0 g. (5.1%) of colorless, heavy rods and prisms of 1,4-pregnadien-21-ol-3,20-dione acetate (I), m.p. 202.6–204.0°, $[\alpha]^{25}D$ +125.6° (1% in EtOH), λ_{max}^{EtOH} 243 mμ, log ε 4.19, $\lambda_{max}^{CS_2}$ 5.71 and 5.79 μ (21-acetoxy-20-ketone); 6.00 μ and $\lambda_{max}^{CHCl_3}$ 6.17 and 6.24 μ (1,4-dien-3-one). The yield could be raised to 7.5% by careful reworking of residues.

Anal. Calcd. for $C_{23}H_{30}O_4$: C, 74.55; H, 8.16. Found: C, 74.40; H, 8.25.

When the ether extracts from the acetoxylation reaction mixture (three moles of LTA were used), instead of being chromatographed, were concentrated to 500 ml. and Skellysolve A added to cloudiness, 5.0 g. of solid was obtained; repetition of the process three times furnished 0.8 g. more, m.p. 120–170°. Five recrystallizations from benzene–ether yielded 1.30 g. (2.5%) of 2α,21-dihydroxyprogesterone diacetate,[2c,4] m.p. 195–197°, $[\alpha]^{20}D$ +156° (0.47% in EtOH).

Anal. Calcd. for $C_{25}H_{34}O_6$: C, 69.72; H, 7.96; acetyl, 20.0. Found: C, 69.74; H, 8.08; acetyl, 20.2.

Hydrogenation of 1,4-Pregnadien-21-ol-3,20-dione Acetate (I).—Compound I (1 g.) was added to a prereduced suspension of 1.0 g. of 2% palladium-on-calcium carbonate[22] in 20 ml. of absolute alcohol and the mixture hydrogenated at 52 lb. pressure and 25°. In seven hours 2.04 moles of hydrogen per mole of I had been absorbed and the reaction had stopped. The mixture was heated to boiling, filtered, and the catalyst extracted once with hot alcohol. The combined filtrate was freed from solvent, and the solid residue treated with 8 ml. of pyridine and 5 ml. of acetic anhydride. After 20 hours at 25°, excess pyridine and acetic anhydride were removed, the residue was dissolved in 35 ml. of ethyl acetate and 65 ml. of ether added. This solution was washed once with 10% potassium carbonate, once with 2 *N* sulfuric acid, twice with water, and dried (sodium sulfate). The white solid obtained by evaporation of the solvents was dissolved in 20% ether–80% Skellysolve A and chromatographed on 100 g. of silica gel.

20% ether–80% Skellysolve A washed off 28 mg. of **allopregnan-21-ol-20-one acetate.** Recrystallization from 2.5 ml. of acetone afforded 13 mg. of rods and elongated prisms, m.p. 196–199°.[23] There was no depression in melting point upon admixture with the corresponding compound from the hydrogenation of desoxycorticosterone acetate as described below; the infrared spectra were identical.

35% ether–65% Skellysolve A washed off 60 mg. of pregnan-21-ol-3,20-dione acetate which was recrystallized from methanol; m.p. 148–151°.[24] This showed no depression in melting point when mixed with the corresponding material from the hydrogenation of desoxycorticosterone acetate; the infrared spectra were identical.

Elution with 50% ether–50% Skellysolve A gave allopregnan-21-ol-3,20-dione acetate which was recrystallized from ether–Skellysolve A; yield 538 mg., m.p. 194–198°. Upon recrystallization from methanol, it melted at 197–199°[25] and showed no depression when melted with the corresponding product from the hydrogenation of desoxycorticosterone acetate; the infrared spectra were identical.

Hydrogenation of Desoxycorticosterone Acetate.—Desoxycorticosterone acetate (6.6 g.) was hydrogenated as described above. Three compounds were isolated by silica gel chromatography in the following order: allopregnan-21-ol-20-one acetate[23] (yield 106 mg., 1.6%), m.p. 200–201°, $[\alpha]^{25}D$ +98.5° (1% in $CHCl_3$), pregnan-21-ol-3,20-dione acetate[24] (yield 756 mg.) (12%), m.p. 150.5–152° and allopregnan-21-ol-3,20-dione acetate,[25] m.p. 194–198°,[25] yield 2.95 g. (44%). The analysis given is for the first of these compounds.

Anal. Calcd. for $C_{23}H_{36}O_3$: C, 76.62; H, 10.07; acetyl, 11.9. Found: C, 76.70; H, 9.88; acetyl, 12.0.

1-Hydroxy-4-methyl-17β-hydroxyacetyl-1,3,5(10)-estratriene Diacetate (III).—To a solution of 900 mg. of 1,4-pregnadien-21-ol-3,20-dione acetate (I) in 60 ml. of acetic anhydride was added, all at once, a solution to 60 mg. of concentrated sulfuric acid in 18 ml. of acetic anhydride. After standing for three hours, this mixture was poured into 250 ml. of ice-water. The solid was filtered, air-dried, dissolved in 50% ether–50% Skellysolve A and chromatographed on 80 g. of silica gel; the same solvent mixture was used for elution. Two liters of eluate removed the triene which was then recrystallized from 12 ml. of acetone to give III; yield 523 mg., m.p. 188.4–189.6°, $[\alpha]^{22}D$ +232°

(16) Louis F. Fieser and M. A. Romero, *ibid.*, **75**, 4716 (1953).

(17) All melting points are corrected.

(18) Chromatograms were run on 100–200 mesh silica gel, the Davison Chemical Corp., Baltimore, Md.

(19) The infrared spectra were determined with a Perkin-Elmer model 21 double beam recording spectrophotometer equipped with a sodium chloride prism.

(20) The elevated temperature was necessary to keep the lead tetraacetate in solution.

(21) On a 10-g. run of progesterone at 90°, the reaction was 37% complete in one hour and complete in three hours.

(22) M. Busch and H. Stöve, *Ber.*, **49**, 1063 (1916).

(23) Reference 9 gave m.p. 197–200°, no rotation given.

(24) Reference 8 gave m.p. 150–151°.

(25) Refereuce 7 gave m.p. 197–199°.

(1.77% in $CHCl_3$), λ_{max}^{EtOH} 267 mμ, log ε 2.54. Evaporation of the filtrate to 3 ml. and addition of 3 ml. of Skellysolve A afforded a further 129 mg., m.p. 187.4–189.6°, total yield 65%.

Anal. Calcd. for $C_{25}H_{32}O_5$: C, 72.79; H, 7.82; acetyl, 20.85. Found: C, 72.95; H, 7.70; acetyl, 20.65.

1-Hydroxy-4-methyl-17β-hydroxyacetyl-1,3,5(10)-estratriene (IV).—A mixture of 200 mg. of III, 250 mg. of potassium bicarbonate, 20 ml. of methanol and 4.5 ml. of water was refluxed for two hours. The methanol was removed, the product extracted with ether, and the dried extract freed from solvent. The resulting solid was recrystallized once from acetone–Skellysolve A and once from benzene–Skellysolve B to give 88 mg. of IV, m.p. 215–218°, $[\alpha]^{24}D$ +269 ±10° (2.65% in EtOH).

Anal. Calcd. for $C_{21}H_{28}O_3$: C, 76.80; H, 8.59. Found: C, 76.70; H, 8.46.

Reaction of Desoxycorticosterone Acetate with LTA.—Desoxycorticosterone acetate (8 g., 0.022 mole) in 50 ml. of glacial acetic acid at 70° was added to 11.3 g. (0.022 mole + 10%) of 92% LTA in 150 ml. of glacial acetic acid at 70°. This mixture was heated at 90–95° for 100 minutes (LTA exhausted), and worked up as described for acetoxylated progesterone. One recrystallization of the chromatographed product from ether afforded 520 mg. (6.5%) of 1,4-pregnadien-21-ol-3,20-dione acetate (I), m.p. 201–204°.

1,4-Pregnadien-21-ol-3,20-dione (II).—One gram of 1,4-pregnadien-21-ol-3,20-dione acetate (I) was refluxed with potassium bicarbonate in aqueous methanol for two hours. Chromatography of the product in 1:1 ether–Skellysolve A on 60 g. of silica gel, with gradually increasing ether concentrations in the eluant, gave 223 mg. (25%) of II, m.p. 187–190°, $[\alpha]^{25}D$ +129° (1% in EtOH) after one recrystallization from ether.

Anal. Calcd. for $C_{21}H_{28}O_3$: C, 76.80; H, 8.59. Found: C, 76.53; H, 8.61.

Acetoxylation of Testosterone.—To a solution of 58 g. (0.117 mole pure) of 89% LTA in 700 ml. of glacial acetic acid at 50° was added, all at once, a solution of 35.1 g. (0.106 mole) of testosterone acetate in 250 ml. of acetic acid at 25°. The mixture was heated at 85–90° for three hours (starch–iodide test negative), the volume reduced to 300 ml. by warming *in vacuo*, and the resulting oil poured into 700 ml. of cold water. After the addition of 800 ml. of ether, the mixture was shaken vigorously and filtered to remove 6.35 g. of crude 2β-hydroxytestosterone diacetate[4] (V) which was recrystallized twice from ethanol; yield 4.97 g. (12%), m.p. 201–204°, $[\alpha]^{25}D$ −65° (1% in $CHCl_3$); λ_{max}^{EtOH} 243 mμ, log ε 4.2.

The ethereal and aqueous layers of the filtrate were separated and the latter extracted with ether. The combined, dried (Na_2SO_4) ether solution was adjusted to a 15% ether–85% Skellysolve A composition and chromatographed on 600 g. of silica gel. The ether concentration was raised slowly to 35% in the course of elution with 30 l. of solvent, whereupon 4.1 g. (12%) of unchanged testosterone acetate was recovered. This was followed immediately by the elution of a mixture of 2α- and 2β-acetoxylated testosterones, which after one crystallization from ether and a second from ethanol, melted at 172–198°, yield 14.5 g. (35%) (**mixture A**); further recrystallization did not raise the melting point. The infrared spectrum of the mixture confirmed the composition given.

From liters of eluate 64–70 (35% ether solvent) was recovered 1.1 g. of 1,4-androstadien-17β-ol-3-one acetate (VI) which, after one recrystallization from Skellysolve B and two from ether, afforded 0.60 g. (1.5%) of relatively pure material, m.p. 152.5–155.2°, $[\alpha]^{24}D$ +26° (1% in $CHCl_3$); reported[13] m.p. 151–152°, $[\alpha]^{22}D$ +28.1° ($CHCl_3$).

Anal. Calcd. for $C_{21}H_{28}O_3$: C, 76.80; H, 8.59. Found: C, 76.70; H, 8.46.

Mixture A, with 10 g. of potassium acetate and 200 ml. of acetic acid, was refluxed for 29 hours, the acetic acid largely removed under reduced pressure, the residue extracted with ether, and the extract washed free of acid. Upon removal of the solvent, the dried (Na_2SO_4) solution yielded a semi-solid mass which was triturated with 20 ml. of ether and filtered. The solid (6.9 g.) was recrystallized three times from methanol to give 3.15 g. (8.5%) of prisms of 2α-hydroxytestosterone diacetate (VIII), m.p. 210–213°.

Epimerization of 2β-Hydroxytestosterone Diacetate (V).—A mixture of 400 mg. of V, 1 g. of potassium acetate and 15 ml. of glacial acetic acid was refluxed for 15 hours, cooled, and poured into 50 ml. of water. This mixture was extracted three times with ether and the combined extract washed three times with water, once with 10% aqueous potassium bicarbonate, and once with water. The dried solution was freed from solvent and the residual solid recrystallized twice from methanol to give 150 mg. (37%) of 2α-hydroxytestosterone diacetate (VIII), m.p. 210–213°, which showed no melting point depression upon admixture with an authentic sample. The infrared spectrum of the product confirmed its identity.

Hydrolysis of Mixture A.—A solution of 3.00 g. of mixture A, 100 ml. of methanol and 5 g. of potassium bicarbonate in 50 ml. of water was refluxed for two hours and chilled; 0.9 g. of colorless plates separated, m.p. 200–214°, which were recrystallized from methanol and then sublimed at 180° (0.4 mm.) to give 2α-hydroxytestosterone 17-acetate (IX), m.p. 221–226°, $[\alpha]^{23}D$ +83° (1% in $CHCl_3$), $\lambda_{max}^{CS_2}$ at 2.91, 5.77 and 5.97 μ.

Anal. Calcd. for $C_{21}H_{30}O_4$: C, 72.79; H, 8.73. Found: C, 72.94; H, 8.20.

Acetylation of 2α-Hydroxytestosterone 17-Acetate (IX).—Acetylation of 263 mg. of IX with acetic anhydride and pyridine at 95° followed by recrystallization from methanol gave 195 mg. (58%) of 2α-hydroxytestosterone diacetate (VIII), m.p. 208–211°. This compound was identified by a mixed melting point determination and comparison of its infrared spectrum with that of an authentic sample.

Rearrangement of 6-Bromotestosterone Acetate (X).—A mixture of 1.50 g. of X,[15] 3.9 g. of potassium acetate and 25 ml. of glacial acetic acid was refluxed for 4 hours, cooled and poured into 75 ml. of water. The mixture was extracted twice with ether and the combined extract washed twice with water, three times with 10% aqueous potassium carbonate, and once with water. The solution was dried (Na_2SO_4), concentrated to 25 ml., chilled, and the precipitate filtered; further concentration produced a small additional amount. The combined precipitate, after one recrystallization from methanol, melted at 190–196°, yield 420 mg. A second recrystallization gave 294 mg. (21%) of 2β-hydroxytestosterone diacetate (V), m.p. 198–201.5°, $[\alpha]^{23}D$ −64° (1% in $CHCl_3$). This showed the same infrared absorption spectrum as the 2β,17β-diol diacetate prepared from testosterone and LTA. A mixed melting point of these diacetates showed no depression, whereas a mixture with the 2α,17β-diol diacetate VIII, melted at 176–201°.

Anal. Calcd. for $C_{23}H_{32}O_5$: C, 71.10; H, 8.30. Found: C, 70.92; H, 8.00.

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