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$\Delta^{5,7}$-STEROIDS. X.[1,2] TRANSFORMATION PRODUCTS OF $\Delta^{5,7}$-ANDROSTADIENE-3β,17β-DIOL

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In Paper VI (1) of this series, the preparation of a number of $\Delta^{5,7}$-steroidal hormones, among others, $\Delta^{5,7}$-androstadiene-3β,17β-diol (I) and its diacetate (II), was reported. In this publication, we wish to present some results of exploratory studies on $\Delta^{5,7}$-androstadiene-3β,17β-diol diacetate (II) which are directed to the development of a transformation of a $\Delta^{5,7}$-steroid to a compound containing an oxygen substituent at the C-11 position.[3]

We have studied the hydrogenation of the $\Delta^{5,7}$-diacetate (II) under a variety of conditions, which either do or do not favor bond migration. Reduction of I with sodium and alcohol (2) gave Δ^{7}-androstene-3β,17β-diol (III) which was found to be contaminated to a minor degree with $\Delta^{5,7}$-androstadiene-3β,17β-diol (I). Recrystallization from methanol removed the impurity, and pure III was obtained. Acetylation gave the diacetate (IV) whose properties were unaltered by treatment with potassium permanganate in acetone. The diol (III) was also characterized by its conversion to the dibenzoate (V) (Flowsheet I).

Hydrogenation of II in neutral ethyl acetate with Adams platinum oxide catalyst (3) gave the diacetate (IV) which was most probably contaminated with $\Delta^{8(14)}$-diacetate (VII). Recrystallization did not remove the impurity. However, conversion of the product to the free steroid (III) or dibenzoate (V), followed by recrystallization, gave pure products. The catalytic hydrogenation may also be carried out with Adams platinum oxide catalyst in alcohol. These conditions, apparently, do not favor bond migration.

The samples of the Δ^{7}-androstene-3β,17β-diol (III) prepared by the several methods (20–25% yields) were identical.

Hydrogenation of II in glacial acetic acid with Adams platinum oxide catalyst (4, 5) gave in excellent yield $\Delta^{8(14)}$-androstene-3β,17β-diol diacetate (VII). Hydrolysis gave VI, which on acetylation gave back VII, and on benzoylation gave VIII (Flowsheet I).

Attempts to rearrange $\Delta^{8(14)}$-androstene-3β,17β-diol diacetate (VII) and $\Delta^{8(14)}$-androstene-3β,17β-diol dibenzoate (VIII) with hydrogen chloride to obtain the corresponding Δ^{14}-diacetate (IX) and Δ^{14}-dibenzoate (X) were unsuccessful. This unforeseen fact is of some interest in view of the relative ease with which the bond migrates in sterols (6). The conclusion to be drawn from this observation

[1] Paper IX. Antonucci, Bernstein, Giancola, and Sax, *J. Org. Chem.*, **16**, 1453 (1951).

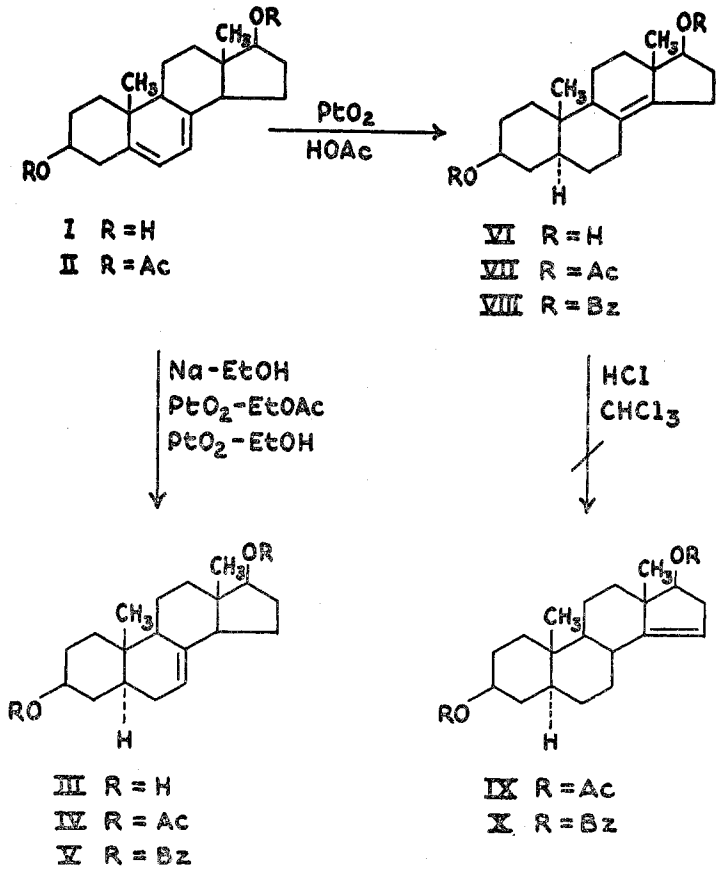
[2] Presented in part before the Organic Group at the third annual meeting of the North Jersey Section, American Chemical Society, Newark, N. J., January 8, 1951.

[3] Chamberlin, Ruyle, Erickson, Chemerda, Aliminosa, Erickson, Sita, and Tishler, *J. Am. Chem. Soc.*, **73**, 2396 (1951), and Fieser, Herz, and Huang, *J. Am. Chem. Soc.*, **73**, 2397 (1951), have recently announced a solution of this problem.

is that the C-17 substituent may display a considerable influence on reactions involving Rings C and D (?).

Moreover, the reaction between $\Delta^{8(14)}$-diacetate (VII) in ether with monoperphthalic acid was "normal", and gave the 8,14-oxido compound (XI), which was converted with dilute sulfuric acid in alcohol to $\Delta^{8,14}$-androstadiene-3β,17β-diol diacetate (XIII) (7, 8) (Flowsheet II). The structure assigned to the diene (XIII) was supported by its ultraviolet absorption spectrum, $\lambda_{max}^{abs.\ alc.}$ 247 mμ.[4]

FLOWSHEET I



Dehydrogenation of Δ^{7}-androstene-3β,17β-diol (III) with mercuric acetate gave $\Delta^{7,9(11)}$-androstadiene-3β,17β-diol (XV). Acetylation gave the diacetate (XVI), which, on hydrolysis, gave back XV. The dibenzoate (XVII) was also prepared (Flowsheet II). The structures assigned to the $\Delta^{7,9(11)}$-steroids (XV–XVII) were supported by their ultraviolet absorption spectra. In this connection,

[4] Windaus and Lüttringhaus (7); $\Delta^{8,14}$-ergostadiene-3β-ol: λ_{max} 248 mμ. Heath-Brown, Heilbron, and Jones, *J. Chem. Soc.*, 1482 (1940); $\Delta^{8,14}$-cholestadiene-3β-ol: λ_{max} 247.5 mμ.

we have determined the ultraviolet absorption spectra of $\Delta^{7,9(11)}$-cholestadiene-3β-ol, its acetate, and benzoate, and also the spectrum of $\Delta^{7,9(11)}$-ergostadiene-3β-ol. In Table I, are listed the ultraviolet absorption maxima of these $\Delta^{7,9(11)}$-steroids. It is to be noted that the free steroids and acetates exhibit three characteristic maxima, namely, at 235–236, 242–243, and 250–252 mμ (range of five compounds). The presence of three maxima for this conjugated double bond system has been noted previously by others (9). In the case of the benzoate derivatives, the two major maxima of the $\Delta^{7,9(11)}$-system have merged with the

FLOWSHEET II

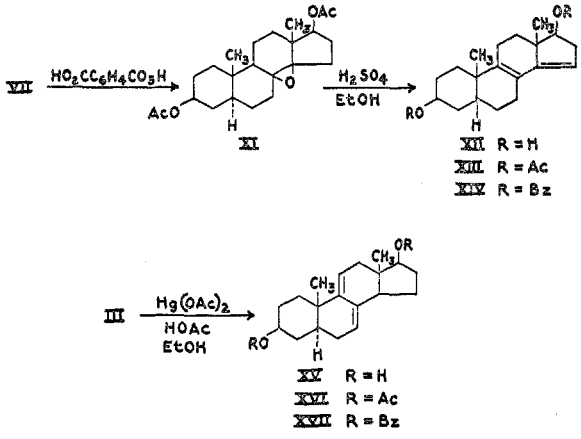


TABLE I

ULTRAVIOLET ABSORPTION MAXIMA OF $\Delta^{7,9(11)}$-STEROIDS

COMPOUND	ULTRAVIOLET ABSORPTION MAXIMA WITH MOLECULAR EXTINCTION COEFFICIENTS (solvent: absolute alcohol).
$\Delta^{7,9(11)}$-Cholestadiene-3β-ol	$\epsilon_{235.5\text{-}236}$ 14,100, ϵ_{243} 16,100, $\epsilon_{251\text{-}251.5}$ 10,600
$\Delta^{7,9(11)}$-Cholestadiene-3β-ol acetate	$\epsilon_{235.5}$ 15,400, ϵ_{243} 17,000, $\epsilon_{250.5\text{-}251}$ 11,400
$\Delta^{7,9(11)}$-Cholestadiene-3β-ol benzoate	$\epsilon_{234\text{-}234.5}$ 26,600, ϵ_{250} 12,500, ϵ_{278} 1,100, ϵ_{281} 900
$\Delta^{7,9(11)}$-Ergostadiene-3β-ol	$\epsilon_{235.5}$ 14,200, ϵ_{243} 15,700, $\epsilon_{251\text{-}251.5}$ 10,600
$\Delta^{7,9(11)}$-Androstadiene-3β,17β-diol	ϵ_{236} 12,100, $\epsilon_{242\text{-}243}$ 13,800, ϵ_{250} 9,000
$\Delta^{7,9(11)}$-Androstadiene-3β,17β-diacetate	ϵ_{235} 13,100, ϵ_{242} 14,900, ϵ_{250} 9,600
$\Delta^{7,9(11)}$-Androstadiene-3β,17β-dibenzoate	ϵ_{232} 36,200, $\epsilon_{249.5\text{-}50}$ 10,300 (inflection), ϵ_{278} 4150, ϵ_{280} 3,300

principal maximum of a benzoate (λ max 229 mμ) to reveal only a single maximum (monobenzoate: λ_{max} 234–234.5 mμ; dibenzoate: λ_{max} 232 mμ).

EXPERIMENTAL

Melting points. All melting points are uncorrected, and were determined with uncalibrated Anschütz thermometers (total immersion).

Ultraviolet absorption spectra. All spectra were determined with a Beckman quartz spectrophotometer (Model DU, mfg'd by the National Technical Laboratories, South Pasadena, California), and were determined in absolute alcohol spectroscopically free of benzene.

Optical rotations. The sample was dissolved in the stated solvent to make a 2-ml. solution, and the rotation was determined in a 1-dm. semi-micro tube. Generally, the rotation was determined for two wavelengths, 5893Å (D) and 5461Å (Hg).

$\Delta^{7,9(11)}$-Cholestadiene-3β-ol acetate. A solution of mercuric acetate (4.54 g.) in glacial acetic acid (85 ml.) was added to a solution of Δ^7-cholestene-3β-ol acetate (2.1 g.) in carbon tetrachloride (50 ml.). The mixture was shaken at room temperature for 18 hours, filtered, and the product was worked up in carbon tetrachloride. Evaporation gave a crystalline residue which was recrystallized once from dilute methanol-acetone, and three times from acetone-methanol, wt. 0.53 g., m.p. 117–119°; $[\alpha]_D^{29}$ +57.5°, $[\alpha]_{Hg}^{29}$ +69.6° (21.55 mg., chloroform, α_D +0.62°, α_{Hg} +0.75°) $\alpha_{Hg}/\alpha_D = 1.21$; $[M]_D$ +245°.

Anal. Calc'd for $C_{29}H_{46}O_2$ (426.66): C, 81.63; H, 10.87.
Found: C, 81.36; H, 10.87.

$\Delta^{7,9(11)}$-Cholestadiene-3β-ol.[5] Alkaline hydrolysis of $\Delta^{7,9(11)}$-cholestadiene-3β-ol acetate (0.40 g.) gave (recrystallization from acetone) 0.20 g. of the free sterol, m.p. 115–117°, $[\alpha]_D^{29}$ +57.3°, $[\alpha]_{Hg}^{29}$ +68.1° (18.5 mg., chloroform, α_D +0.53°, α_{Hg} +0.63°) $\alpha_{Hg}/\alpha_D = 1.19$; $[M]_D$ +220°.

Anal. Calc'd for $C_{27}H_{44}O$ (384.62): C, 84.31; H, 11.53.
Found:[6] C, 82.96; H, 11.60.

$\Delta^{7,9(11)}$-Cholestadiene-3β-ol benzoate.[7] $\Delta^{7,9(11)}$-Cholestadiene-3β-ol (130 mg.) on benzoylation and recrystallization from acetone gave 0.12 g., m.p. 137.5–139°, 151°. Two further recrystallizations from acetone gave 59 mg., m.p. 138–139.5°, 152.5°; $[\alpha]_D^{32}$ +52.4°, $[\alpha]_{Hg}^{32}$ +65.9° (25.2 mg., chloroform, α_D +0.66°, α_{Hg} +0.83°) $\alpha_{Hg}/\alpha_D = 1.26$; $[M]_D$ +256° ($CHCl_3$). $[\alpha]_D^{31}$ +61.5°, $[\alpha]_{Hg}^{31}$ +77.1° (17.9 mg., dioxane, α_D +0.55°, α_{Hg} +0.69°) $\alpha_{Hg}/\alpha_D = 1.25$; $[M]_D$ +300° (dioxane).

Anal. Calc'd for $C_{34}H_{48}O_2$ (488.72): C, 83.55; H, 9.90.
Found: C, 83.07; H, 9.81.

$\Delta^{7,9(11)}$-Ergostadiene-3β-ol.[8] Δ^7-Ergostenol (2.62 g.) was dehydrogenated in the manner described above. Crystallization of the crude product from acetone-methanol gave 1.04 g., m.p. 137–141°. Two recrystallizations from acetone-methanol gave 0.83 g., m.p. 138–141° $[\alpha]_D^{32}$ +42°, $[\alpha]_{Hg}^{32}$ +52° (20.0 mg., chloroform, α_D +0.42°, α_{Hg} +0.52°) $\alpha_{Hg}/\alpha_D = 1.24$; $[M]_D$ +167°.

Hydrogenation of $\Delta^{5,7}$-androstadiene-3β,17β-diol diacetate. A. Sodium and alcohol method. A refluxing solution of 2 g. of $\Delta^{5,7}$-androstadiene-3β,17β-diol diacetate (II) in 50 ml. of absolute alcohol was treated over a period of 9 hours with 70 g. of sodium; intermittently 75-ml. portions of absolute alcohol were added for a total of 1100 ml. Water was added, and the mixture was allowed to stand overnight. The precipitate was collected on Celite, and subsequently removed from it by solution in hot methanol. The solution was treated with water, and the crude product was collected. Recrystallization from methanol gave 1.13 g. of III, m.p. 192–193.5°. An ultraviolet absorption analysis of this material indicated a very slight contamination with starting material, *i.e.*, $\Delta^{5,7}$-diol (I). Two recrystallizations from methanol removed the impurity, and gave 0.53 g. of pure diol (III), m.p. 193–195°. From the mother liquors an additional quantity (0.32 g.) of III was isolated, m.p. 192–194°. $[\alpha]_D^{29}$ −25.2°, $[\alpha]_{Hg}^{29}$ −32.8° (23.8 mg., absolute alcohol, α_D −0.30°, α_{Hg} −0.39°) $\alpha_{Hg}/\alpha_D = 1.30$; $[M]_D$ +73°.

Anal. Calc'd for $C_{19}H_{30}O_2$ (290.43): C, 78.57; H, 10.41.
$C_{19}H_{30}O_2 \cdot \frac{1}{2}H_2O$ (299.44): C, 76.21; H, 10.44.
Found: C, 76.26; H, 10.58.

Δ^7-Androstene-3β,17β-diol diacetate (IV). Δ^7-Androstene-3β,17β-diol (III) (0.4 g.) on

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[5] Fieser, Herz, and Huang, *loc. cit.*: λ_{max} 243 mμ, ϵ = 10,000.

[6] The analysis indicated solvation or hydration of the product (dried at 78°, 0.05 mm. pressure for several hours).

[7] Fieser, Herz, and Huang, *loc. cit.*: m.p. 134°, $[\alpha]_D$ +32° (dioxane).

[8] Barton and Cox, *J. Chem. Soc.*, 219 (1949): m.p. 139.5–140.5°, $[\alpha]_D$ +31° ($CHCl_3$).

acetylation and recrystallization from methanol gave 0.35 g., m.p. 120–122°. The product (50 mg.) was dissolved in acetone, treated with a small amount of potassium permanganate, and was allowed to stand overnight at room temperature. The product was worked up in ether, and the extract was washed with dilute potassium hydroxide, and water. Evaporation of the dried ether solution, and two recrystallizations from dilute methanol gave IV, m.p. 121–122.5°, $[\alpha]_D^{27}$ —55°, $[\alpha]_{Hg}^{27}$ —61.2° (32.7 mg., chloroform, α_D —0.90°, α_{Hg} —1.00°) α_{Hg}/α_D = 1.11 $[M]_D$ —206°.

Anal. Calc'd for $C_{23}H_{34}O_4$ (374.50): C, 73.76; H, 9.15.
Found: C, 73.85; H, 9.40.

Δ^7-*Androstene-3β,17β-diol dibenzoate* (V). Δ^7-Androstene-3β,17β-diol (III) (0.32 g.) on benzoylation and recrystallization from acetone gave 0.38 g. of V, m.p. 210.5–212.5°; λ_{max} 229, 273, and 279–281 (inflection) mμ, ε = 28,000, ε = 2000, ε = 1600 resp., $[\alpha]_D^{28}$ —9.6° (27 mg., chloroform, α_D —0.13°); $[M]_D$ —48°.

Anal. Calc'd for $C_{33}H_{38}O_4$ (498.63): C, 79.48; H, 7.68.
Found: C, 79.46; H, 7.85.

B. Catalytic hydrogenation method 1. A mixture of 10 g. of $\Delta^{5,7}$-androstadiene-3β,17β-diol diacetate (II) in 200 ml. of neutral ethyl acetate, and 1 g. of Adams platinum oxide catalyst was shaken in an hydrogen atmosphere until the uptake of hydrogen was constant (35 minutes) when the reaction was interrupted. The catalyst was removed and the ethyl acetate was evaporated *in vacuo*. The solid residue was recrystallized three times from dilute methanol, wt. 8.17 g., m.p. 117–119°; $[\alpha]_D^{30}$ —33.1° (36.9 mg., chloroform, α_D —0.61°); λ_{max} none. However, the material was not pure probably due to contamination with $\Delta^{8(14)}$-diacetate (VII).

The hydrogenation product (4.09 g.) was refluxed for ½ hour with 125 ml. of 5% alcoholic potassium hydroxide, treated with 75 ml. of water, and the crystals were collected after a long period of standing; wt. 1.54 g., m.p. 185–192°. Recrystallization from methanol to constant melting point gave 1.1 g. of pure III, m.p. 193–195.5°, $[\alpha]_D^{25}$ —28.3°, $[\alpha]_{Hg}^{25}$ —37.2° (24.7 mg., absolute alcohol, α_D —0.35°, α_{Hg} —0.46°) α_{Hg}/α_D = 1.31; $[M]_D$ —82°.

The mother liquors from the above purification of the diol were concentrated, and gave 1.85 g. of solid which was dissolved in 5 ml. of pyridine, and was benzoylated with 2.5 ml. of benzoyl chloride. The crude dibenzoate was recrystallized from acetone, and gave 0.57 g. of pure V, m.p. 210–212.5°, $[\alpha]_D^{28}$ —10.4° (27 mg., chloroform, α_D —0.14°); $[M]_D$ —52°.

2. In another hydrogenation with 1.0 g. of I, 0.10 g. of Adams platinum oxide catalyst, and 100 ml. of alcohol there was obtained 0.74 g. of impure IV, m.p. 117.5–120°, which on hydrolysis gave 0.24 g. of pure III, m.p. 194–196° (with softening at 192.5°).

$\Delta^{8(14)}$-*Androstene-3β,17β-diol diacetate* (VII). *A.* Adams platinum oxide catalyst (11.955 mg.) in 5 ml. of glacial acetic acid was reduced in a hydrogen atmosphere. Then 73.765 mg. of $\Delta^{5,7}$-androstadiene-3β,17β-diol diacetate (II) was introduced, and the mixture was shaken in a hydrogen atmosphere. After ½ hour a constant uptake of hydrogen was reached. However the hydrogenation was interrupted after a total time of 1¼ hours; 4.62 ml. (S.T.P.) (1.02 mole-equivalents) of hydrogen was consumed as compared with the theoretical value of 4.53 ml. (S.T.P.) for 1 double bond.

The catalyst was removed by filtration, and the filtrate upon treatment with water gave crystals, m.p. 134–136°. Two recrystallizations from dilute methanol gave pure VII. m.p. 136.5–138°; λ_{max} none.

Anal. Calc'd for $C_{23}H_{34}O_4$ (374.50): C, 73.76; H, 9.15.
Found: C, 73.62; H, 9.34.

In another run with 2 g. of II, 150 ml. of glacial acetic acid, and 0.2 g. of Adams platinum oxide catalyst there was obtained 1.96 g. of VII, m.p. 137–138°; $[\alpha]_D^{30}$ —23.8°, $[\alpha]_{Hg}^{30}$ —29.5° (35.3 mg., chloroform, α_D —0.42°, α_{Hg} —0.52°) α_{Hg}/α_D =1.24; $[M]_D$ —89°.

B. $\Delta^{8(14)}$-Diol (VI) (10 mg.) in 0.8 ml. of pyridine was acetylated with 0.1 ml. of acetic anhydride; wt. 7.5 mg., m.p. 137–138°. A mixture m.p. determination with the $\Delta^{8(14)}$-diacetate prepared above showed no depression.

$\Delta^{8(14)}$-*Androstene-3β,17β-diol* (VI). $\Delta^{8(14)}$-Diacetate (VII) (0.15 g.) in 55 ml. of 5% alco-

holic potassium hydroxide was refluxed for 45 minutes; water was added, and the precipitate was collected, m.p. 161–163°. Recrystallization from dilute methanol gave 42.7 mg. of pure VI; m.p. 166.5–168° (dried in hi-vacuum at 100°); $[\alpha]_D^{20}$ +8.1°, $[\alpha]_{Hg}^{20}$ +8.5° (42.2 mg., absolute alcohol, α_D +0.17°, α_{Hg} +0.18°) $\alpha_{Hg}/\alpha_D = 1.06$; $[M]_D$ +23°.

Anal. Calc'd for $C_{19}H_{30}O_2$ (290.43): C, 78.57; H, 10.41.

Found: C, 78.50; H, 10.68.

$\Delta^{8(14)}$-*Androstene-3β,17β-diol dibenzoate* (VIII). An ice-cold solution of 30 mg. of the $\Delta^{8(14)}$-diol (VI) in 1.2 ml. of pyridine was benzoylated with 0.3 ml. of benzoyl chloride. The product was worked up in benzene, and an oil was obtained which crystallized on the addition of methanol, wt. 30 mg., m.p. 164–166°, with previous softening. Two recrystallizations from acetone-methanol gave 21.2 mg. of VIII, m.p. 170.5–171.5°; $[\alpha]_D^{8.0}$ +19.3° (33.1 mg., chloroform, α_D^{30} +0.32°); $[M]_D$ +96°.

Anal. Calc'd for $C_{33}H_{38}O_4$ (498.63): C, 79.48; H, 7.68.

Found: C, 79.52; H, 8.07.

Hydrogen chloride treatment of $\Delta^{8(14)}$-*androstene-3β,17β-diol diesters. A.* A vigorous stream of hydrogen chloride was bubbled for 1 hour into a solution of 0.73 g. of $\Delta^{8(14)}$-androstene-3β,17β-diol diacetate (VII), m.p. 137–138°, in 75 ml. of chloroform maintained at 0°. The solution was evaporated *in vacuo*, and the residue was crystallized from dilute methanol, wt. 0.72 g., m.p. 132–135°. Recrystallization from dilute methanol gave 0.63 g., m.p. 135–137°. A mixture m.p. determination with a sample of the starting material showed no depression.

Hydrolysis of the above material with 5% alcoholic potassium hydroxide, and recrystallization of the product from ethyl acetate-petroleum ether (b.p. 64–66°) gave $\Delta^{8(14)}$-androstene-3β,17β-diol (VI), m.p. 165–167°. Its infrared spectrum showed it to be identical in all respects with an authentic sample.

B. Similarly, 270 mg. of the dibenzoate (VIII) in 50 ml. of chloroform was treated with hydrogen chloride for 3 hours at 0°. Evaporation gave an oil which was crystallized from acetone-methanol, wt. 230 mg., m.p. 166–169°. Recrystallization from acetone-methanol gave 150 mg., m.p. 171–173°. A mixture m.p. determination with a sample of the starting material showed no depression.

$\Delta^{8(14)}$-*Oxidoandrostane-3β,17β-diol diacetate* (XI). To a solution of 150 mg. (0.0004 mole) of the $\Delta^{8(14)}$-diacetate (VII) in 15 ml. of anhydrous ether was added 0.146 g. (0.0008 mole) (2.3 ml. of stock ether solution; 1 ml. was equivalent to 0.0635 g.) of monoperphthalic acid. The mixture was refluxed for 6.5 hours. The ether was removed *in vacuo*, and the residue was digested with anhydrous chloroform. The solid was collected, wt. 0.129 g. (97% recovery of phthalic acid). The filtrate was evaporated *in vacuo*, and the residue was recrystallized six times from dilute acetone, and dilute methanol, wt. 18.7 mg., 187–188°.

Anal. Calc'd for $C_{23}H_{34}O_5$ (390.50): C, 70.74; H, 8.78.

Found: C, 71.07; H, 9.02.

In another run with 1 g. of VII, 100 ml. of ether, and 4.9 g. of monoperphthalic acid there was obtained 0.39 g. of XI, m.p. 187–190°.

$\Delta^{8(14)}$-*Androstadiene-3β,17β-diol diacetate* (XII). A refluxing solution of 300 mg. of XI in 20 ml. of alcohol was treated dropwise with dilute sulfuric acid (2–3 ml.); the resulting mixture was refluxed for 15 minutes, treated with water, and was worked up in ether. Evaporation gave an oil which was refluxed with 5 ml. of acetic anhydride for ½ hour. This product was worked up in ether. Evaporation gave an oil which was crystallized from dilute methanol, wt. 0.22 g., m.p. 106–108°. Recrystallization from dilute methanol did not change the m.p.; λ_{max} 247 mμ, $\epsilon = 16{,}100$; $[\alpha]_D^{25}$ —107°, $[\alpha]_{Hg}^{25}$ —133° (24.2 mg., chloroform, α_D —1.29°, α_{Hg} —1.61°) $\alpha_{Hg}/\alpha_D = 1.25$; $[M]_D$ —398°.

Anal. Calc'd for $C_{23}H_{32}O_4$ (372.49): C, 74.16; H, 8.66.

Found: C, 74.26; H, 8.90.

$\Delta^{5(14)}$-*Androstadiene-3β,17β-diol* (XII). A solution of 220 mg. of $\Delta^{8(14)}$-diacetate (XIII) in 50 ml. of 5% alcoholic potassium hydroxide was refluxed for 40 minutes, cooled, and was neutralized with cold very dilute hydrochloric acid. The product was worked up in ethyl acetate, and the extract was washed with water, and dried. Evaporation gave a glass which was dissolved in acetone. Addition of petroleum ether (b.p. 64–66°), and working of the

mixture gave a solid (?), wt. 100 mg., m.p. *ca.* 120° (bubbles at m.p.) (sample for analysis was dried for several hours at 80° and 0.05 mm. pressure). Analysis indicated solvation.

Anal. Calc'd for $C_{19}H_{28}O_2$ (288.41): C, 79.12; H, 9.78.

Found: C, 77.37; H, 10.05.

$\Delta^{8(14)}$-*Androstadiene-3β,17β-diol dibenzoate* (XIV). $\Delta^{8(14)}$-Diol (XI) (90 mg.) was benzoylated and recrystallized from methanol, 80 mg., m.p. 181–183° (with previous discoloration), λ_{max} 232, 280 mμ, $\epsilon = 34{,}400$, $\epsilon = 1{,}820$ resp., $[\alpha]_D^{23}$ —15.5°, $[\alpha]_{Hg}^{25}$ —21.2° (28.3 mg., chloroform, α_D —0.22°, α_{Hg} —0.30°) $\alpha_{Hg}/\alpha_D = 1.36$; $[M]_D$ —77°.

Anal. Calc'd for $C_{33}H_{36}O_4$ (496.62): C, 79.81; H, 7.31.

Found: C, 79.26; H, 7.59.

$\Delta^{7,9(11)}$-*Androstadiene-3β,17β-diol* (XV). *A.* A refluxing solution of 1.95 g. (0.0071 mole) of Δ^7-androstene-3β,17β-diol (III) in alcohol and 5 ml. of chloroform was treated with a hot solution of 6.77 g. (0.0213 mole) of mercuric acetate in alcohol acidified with 1 ml. of glacial acetic acid. The total volume of alcohol used for both solutions was 100 ml. The mixture was refluxed for 1 hour, cooled, and filtered. The filtrate was diluted with water, and the product was worked up in ethyl acetate. The extract was washed with dilute acetic acid, and water, and was dried with magnesium sulfate. The residue obtained on evaporation of the ethyl acetate was fractionally recrystallized from dilute methanol, acetone-petroleum ether (b.p. 64–66°), acetone, and dilute acetone. Two fractions were obtained, 0.24 g., m.p. 202.5–209°, λ_{max} 236, 243, and 251 mμ, ϵ = 13,100, 14,750, 9,750 resp., and 0.18 g., m.p. 198–204.5°.

In another run by essentially the method given above (chloroform omitted) there was obtained from 0.9 g. of III, 0.2 g. of XV (methanol recrystallization), m.p. 202–205°, ϵ_{242} 14,400, $[\alpha]_D^{30}$ +16.7°, $[\alpha]_{Hg}^{30}$ +21.7° (12 mg., chloroform, α_D +0.10°, α_{Hg} +0.13°) α_{Hg}/α_D =1.30; $[M]_D$+28°.

B. A solution of 0.17 g. of potassium hydroxide in 0.5 ml. of water, and 20 ml. of alcohol was added to 0.30 g. of the $\Delta^{7,9(11)}$-diacetate (XVI), and the mixture was refluxed for ½ hour. Cooling and addition of water gave crystals, wt. 0.23 g., m.p. 201.5–206°. Recrystallization from acetone gave 0.15 g. of pure XV, m.p. 198–204°.[9] From the mother liquor, an additional 65 mg. of XV was obtained. $[\alpha]_D^{29}$ —14.9°, $[\alpha]_{Hg}^{29}$ —17.2° (17.4 mg., pyridine, α_D —0.13°, α_{Hg} —0.15°) $\alpha_{Hg}/\alpha_D = 1.15$; $[M]_D$ —43°.

Anal. Calc'd for $C_{19}H_{28}O_2$ (288.41): C, 79.12; H, 9.78.

Found: C, 79.23; H, 10.24.

$\Delta^{7,9(11)}$-*Androstadiene-3β,17β-diol diacetate* (XVI). $\Delta^{7,9(11)}$-Diol (0.43 g.) (XV) was acetylated, and the crude product was recrystallized from dilute acetone, wt. 0.40 g., m.p. 126.5–128°. $[\alpha]_D^{27}$ +6.3°, $[\alpha]_{Hg}^{27}$ +10.1° (23.75 mg., chloroform, α_D + 0.075°, α_{Hg} +0.12°) α_{Hg}/α_D = 1.60; $[M]_D$ +23°.

Anal. Calc'd for $C_{23}H_{32}O_4$ (372.49): C, 74.16; H, 8.66.

Found: C, 73.99; H, 8.91.

$\Delta^{7,9(11)}$-*Androstadiene-3β,17β-diol dibenzoate* (XVII). Benzoylation of the diol (XV) and several recrystallizations from acetone gave XVII, m.p. 210–213.5°. $[\alpha]_D^{30}$ +6.4°,$[\alpha]_{Hg}^{30}$ +8.4° (19 mg., chloroform, α_D +0.06°, α_{Hg} +0.08°) $\alpha_{Hg}/\alpha_D = 1.33$; $[M]_D$ +32°.

Anal. Calc'd for $C_{33}H_{36}O_4$ (496.22): C, 79.81; H, 7.31.

Found: C, 79.71; H, 7.53.

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SUMMARY

1. The hydrogenation of $\Delta^{5,7}$-androstadiene-3β,17β-diol diacetate under a variety of conditions has been studied. Δ^7- and $\Delta^{8(14)}$-Androstene-3β, 17β-diol,

[9] A wide variance in the m.p. of this compound was noted.

the corresponding diacetates, and dibenzoates have been prepared and characterized.

2. The double bond in $\Delta^{8(14)}$-androstene-3β,17β-diol diesters did not migrate to the Δ^{14}-position under conditions which usually favor migration.

3. 8,14-Oxidoandrostane-3β,17β-diol diacetate has been prepared from the $\Delta^{8(14)}$-diacetate with monoperphthalic acid. The oxide on treatment with sulfuric acid gave the $\Delta^{8,14}$-diene.

4. $\Delta^{7,9(11)}$-Androstadiene-3β,17β-diol has been prepared by mercuric acetate dehydrogenation of Δ^{7}-androstene-3β,17β-diol. Its diacetate and dibenzoate have been prepared and characterized.

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