917. *Urinary Steroids and Related Compounds. Part II.*[1] 11 : 17-*Disubstituted Androstanes carrying no Substituent at Position* 3.

By W. Klyne and Sheila Palmer (*née* Ridley).

A series of 5α-androstane derivatives carrying no substituent at position 3 have been prepared; these compounds include 11-monosubstituted and 11 : 17-disubstituted derivatives. Their physical properties (infrared spectra and molecular rotations) provide reference data for the assessment of vicinal action between positions 11 and 17.

Preparations recorded in Part I of this series[1] yielded considerable quantities of the androst-2-enes (I; R = :O, R′ = H, β-OH, and :O), which have now been used to afford, by standard methods, a series of 11 : 17-disubstituted androstanes and some other derivatives *not* substituted at position 3. These products provide reference values for optical rotations, infrared spectra, etc., which permit the assessment of vicinal action between positions 11 and 17, uncomplicated by the presence of substituents at position 3.*

Four 11-monoketones have recently been described by the Syntex group;[2] 5α-androstan-11-one had been prepared some years earlier by Steiger and Reichstein.[3]

Infrared Spectra.—These were measured for carbon disulphide solutions.

Carbonyl bands (Table 1). In the carbonyl stretching region (1750—1700 cm.$^{-1}$) the frequencies for the reference compounds agree with those found elsewhere for compounds containing other functional groups (see, *e.g.*, the review by Jones and Herling[4]). The 11β-acetoxyl and 17-oxo-groups mask each other; the only true reference value for 11β-acetoxyl is therefore that for 5α-androstan-11β-yl acetate itself.

Results in the " finger-print " region below 1350 cm.$^{-1}$ in general agree with, and supplement, the data already available in the literature;[4-6] for the 11 : 17-disubstituted compounds it is usually possible to recognise the main bands associated with the individual functions, although the absolute positions of the bands may be somewhat altered.[11]

17-Ketones have two strong bands[2] at about 1055 and 1010 cm.$^{-1}$. 11-Ketones have two or three bands at about 1080, 1050, and 1020 cm.$^{-1}$. The 17-ketone band (~1010 cm.$^{-1}$) occurs at a significantly higher wave-number in the 9(11)-unsaturated compounds (II and IV; R = :O) than in the saturated compounds. In the keto-acetates the bands of the two functions in the 1020—1030 cm.$^{-1}$ region inevitably mask one another as do the carbonyl and the hydroxyl bands at about 1050 cm.$^{-1}$ (see Tables 1 and 3). The strong 17β-acetate

* While this paper was in press it was brought to our notice that similar work had been carried out at the Upjohn Co., Kalamazoo, Mich. (cf. Babcock, *Abs. Meeting Amer. Chem. Soc.*, April, 1956).

[1] Part I, Klyne and Ridley, *J.*, 1956, 4825.
[2] Sondheimer, Batres, and Rosenkranz, *J. Org. Chem.*, 1957, **22**, 1090.
[3] Steiger and Reichstein, *Helv. Chim. Acta*, 1937, **20**, 817.
[4] R. N. Jones and Herling, *J. Org. Chem.*, 1954, **19**, 1252.
[5] R. N. Jones, Herling, and Katzenellenbogen, *J. Amer. Chem. Soc.*, 1955, **77**, 651.
[6] R. N. Jones and Herling, *ibid.*, 1956, **78**, 1152.

TABLE 1. *Infrared spectra: carbonyl bands.*

Substituents at 17 R	Substituents at 11 R′	Carbonyl stretching: 17-CO	11-CO	17β-OAc	11β-OAc	Below 1350 cm.⁻¹: 17-CO	11-CO	17β-OAc	11β-OAc
5α-Androstane derivatives (III)									
H_2	:O	—	1700,[a] 1704	—	—	—	1070, 1060, 1029	—	—
:O	H_2	1745[b]	—	—	—	1055, 1010	—	—	—
H_2	H, β-OAc	—	—	—	1725	—	—	—	1240, 1214i, 1026
H, β-OAc	H_2	—	—	1730	—	—	—	1245, 1220i, 1032	—
:O	H, β-OH	1742	—	—	—	1062,* 1015	—	—	—
:O	H, β-OAc	1740	—	—	1728	1052, 1010	—	—	1235, 1213i
H, β-OH	:O	—	1712	—	—	—	1082, 1053,* 1027	—	—
H, β-OAc	:O	—	1707	1737	—	—	1077, 1040, 1025	1235, 1215i	—
:O	:O	1748	1715	—	—	1010	1082, 1022 1050	—	—
H, β-OAc	H, β-OAc	—	—	1744—1735	—	—	—	1240, 1224i, 1030	
H, β-OAc	H, β-OH	—	—	1744	—	—	—	1247, 1220i, 1035 *	
5α-Androsta-9(11)-ene derivatives (IV)									
:O	—	1742	—	—	1059, 1022	—	—	—	—
H, β-OAc	—	—	—	1732	—	—	—	1239, 1034	
5α-Androsta-2 : 9(11)-diene derivatives (II)									
:O	—	1745	—	—	—	1061, 1025	—	—	—
H, β-OAc	—	—	—	1728	—	—	—	1235, 1032	
5α-Androst-2-ene derivatives (I)									
:O	H, β-OH	1743	—	—	—	1054,* 1010	—	—	—
O	:O	1740	1709	—	—	1006	1080, 1045	—	—

* Bands masking 1050 cm.⁻¹ region. i = inflexion.
[a] Ref. 2. [b] Rosenkranz and Zablow, *J. Amer. Chem. Soc.*, 1953, **75**, 903.

TABLE 2. *Infrared spectra: olefinic bands.*

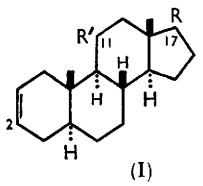
	Olefinic CH stretching	C=C stretching: Δ²	Δ⁹(¹¹)	Olefinic CH out-of-plane bending: Δ²	Δ⁹(¹¹)	Ref.
2-Enes						
5α-Cholest-2-ene	3034	1653	—	664, 774	—	8
11β-Hydroxy-5α-androst-2-en-17-one	3040	1653	—	662, 770	—	1
5α-Androst-2-ene-11 : 17-dione	3040	1653	—	662, 769	—	1
5α-Androst-2-en-17-one	—	1651	—	—	—	9
9(11)-Enes						
3β-Acetoxy-5α-ergost-9(11)-ene	3045	—	1640	—	820, 840	10
24-Hydroxy-5β-chol-9(11)-ene	3042	—	1644	—	827, 852	7
Me 5β-chol-9(11)-enate	3037	—	1643	—	—	7
5α-Androst-9(11)-en-17-one	3060	—	—	—	813	—
5α-Androst-9(11)-en-17β-ol	3060	—	1630	—	810	—
5α-Androst-9(11-)en-17β-yl acetate	3060	—	—	—	814	—
2 : 9(11)-Dienes						
5α-Androsta-2 : 9(11)-dien-17-one	3040	1663	—	665—653 (d)	818	—
5α-Androsta-2 : 9(11)-dien-17β-ol	3040	1661	1638 (sh)	657 (i), 665	820	—
5α-Androsta-2:9(11)-dien-17β-yl acetate	3040	1650	—	660 (i), 648	813	—

[7] Bladon, Fabian, Henbest, Koch, and Wood, *J.*, 1951, 2402.
[8] Henbest, Meakins, and Wood, *J.*, 1954, 800.
[9] R. N. Jones, Humphries, Packard, and Dobriner, *J. Amer. Chem. Soc.*, 1950, **72**, 86.
[10] Crawshaw, Henbest, and E. R. H. Jones, *J.*, 1954, 731.

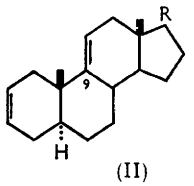
band which is normally [6] at 1247—1245 cm.$^{-1}$ is moved to 1239—1235 cm.$^{-1}$ in the 11-oxo-17β-acetate (III; R = H, β-OAc, R′ = :O) and the 9(11)-ene and 2 : 9(11)-diene 17β-acetates (IV and II; R = H, β-OAc).

Olefinic bands (Table 2). Olefinic C:CH bands at ~3040—3060 cm.$^{-1}$ are found in the spectra of all the unsaturated compounds.

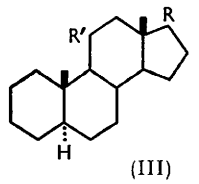
The C:C stretching bands for monounsaturated compounds show a characteristic difference between those for 2-enes (1657—1653 cm.$^{-1}$) and those for 9(11)-enes (1644—1640 cm.$^{-1}$), as found in previous work.[7,8] In the 2 : 9(11)-dienes the peak is in the 1660—1650 cm.$^{-1}$ region, with a shoulder on the smaller wave-number side in one case.



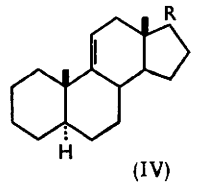
(I)



(II)



(III)



(IV)

These bands are often obscured in compounds containing ketone or acetoxyl groups;[7,9] our results confirm this.

The CH out-of-plane bending frequencies for 2-enes (disubstituted) and 9(11)-enes (trisubstituted) showed the characteristic differences indicated in previous work.[7,8] In the 2 : 9(11)-dienes both bands appeared. For 9(11)-enes the androstene derivatives show appreciable differences in the position of the ~800 cm.$^{-1}$ band from that for ergostene and cholene derivatives.[7,10]

Hydroxyl bands (Table 3). The free hydroxyl stretching band at 3645—3665 cm.$^{-1}$ is shown by all the hydroxyl compounds; in addition, the 11β-hydroxy-17-ketones, 17β-hydroxy-11-ketone, and 17β-acetoxy-11β-alcohol show evidence of hydrogen bonding (3500—3400 cm.$^{-1}$).[4]

TABLE 3. *Infrared spectra: hydroxyl bands.*

	Free OH stretching	Hydrogen-bonded OH stretching	C–OH stretching 11β-OH	17β-OH
5α-Androstan-11β-ol	3665	—	1055	—
5α-Androst-9(11)-en-17β-ol	3665	—	—	1055
5α-Androsta-2 : 9(11)-dien-17β-ol	3645	—	—	1062
5α-Androstane-11β : 17β-diol	3645	—	1052 (broad)	
17β-Acetoxy-5α-androstan-11β-ol	3660	Extensive H-bonding	*	—
11β-Hydroxy-5α-androstan-17-one	3645	Extensive H-bonding	*	—
11β-Hydroxy-5α-androst-2-en-17-one	3650	H-bonding	*	—
17β-Hydroxy-5α-androstan-11-one	3640	3500—3400	—	*

* Masked, see Table 1.

C–OH stretching bands at ~1050—1060 cm.$^{-1}$ are shown by all the hydroxy-compounds having no other substituent; masking occurs in the acetoxy-hydroxy- and hydroxy-keto-compounds, as indicated in Tables 1 and 3.

Molecular Rotations.—The molecular rotations (M_D) and differences (Δ values) for the principal compounds studied here, and for reference compounds in other series, are collected in Table 4. These values permit an assessment of vicinal action between positions 11 and 17. The principal findings in our work are as follows: (i) An 11β-hydroxyl group has little effect on functions at position 17. Acetoxyl and carbonyl groups at positions 11 and 17, or *vice versa*, show considerable vicinal action. (ii) 17-Substituents have a considerable effect on the 9(11)-double bond.

Comparison of the contributions of the 11-carbonyl group in the four monoketones prepared by Sondheimer, Batres, and Rosenkranz [2] shows some interesting effects. The Δ(C:O)-11 values are as follows: 5α-Androstane +176° (our value, +182°); 5β-androstane +140°; 5α-pregnane +129°; 5β-pregnane +105° (Ruff and Reichstein [11] found +111°); 5α-cholestane +118° (Table 4); and 5α-ergostane +120° (Table 4).

[11] Ruff and Reichstein, *Helv. Chim. Acta*, 1951, **34**, 70.

Differences between the 5α- and the 5β-series are not unexpected, but the differences of 25—45° between the C_{19} compounds of the androstane series on the one hand, and C_{21}, C_{27}, and C_{28} compounds (with a 17-side chain) on the other hand, are noteworthy.

TABLE 4. *Molecular rotations.*

Values in bold type are $[M]_D$ in $CHCl_3$; values in ordinary light type are Δ values at C-17 (*e.g.*, $[M]_D$ 17CH·OH − $[M]_D$ 17CH_2); values in italic type are Δ values at C-11 (*e.g.*, $[M]_D$ 11CO − $[M]_D$ 11CH_2).

	5α-Androstane series, No substituents at C-3							5α-Cholestane series		5α-Ergostane series	
11-Substituent	17-CH_2	17β-OH	Δ	17β-OAc	Δ	17CO	Δ	3β-OH	3β-OAc	3β-OH	3β-OAc
None	+2° [a]	**+29°** [a]	+27°	**+6°** [a]	+14°	**+260°** [b]	+258°	**+89°** [c]	**+60°** [c]	**+64°** [d]	**+27°** [d]
11β-OH	**+47**	**+84**	+37	**+23**	−24	**+288**	+241	—	—	**+118** [d]	**+115** [e]
Δ	*+45*	*+55*		*+17*		*+28*				*+54*	*+88*
11β-OAc	**+112**	—		**+89**	+23	**+238**	+126	—	—	**+208** [d]	**+155** [d]
Δ	*+110*			*+83*		*−22*				*+144*	*+128*
11-Oxo	**+184** *	**+162**	−22	**+58**	−126	**+389**	+205	—	**+178** [f]	—	**+147** [g]
Δ	*+182*	*+133*		*+52*		*+129*			*+118*		*+120*
9(11)-Ene	—	**+11**		**−16**		**+364**		**+104** [h]	**+96** [h]	**+116** [e]	**+75** [e]
Δ	—	*−18*		*−22*		*+104*		*+15*	*+36*	*+42*	*+58*
9(11)-Ene, with 2-ene	—	**+89**		**+42**		**+473**		—	—	—	—

* Ref. 2, +178°. [a] Unpublished values from Mr. P. M. Jones of this laboratory. [b] Rosenkranz, Kaufmann, and Romo, *J. Amer. Chem. Soc.*, 1949, **71**, 3689. [c] Barton and Cox, *J.*, 1948, 783. [d] Crawshaw, Henbest, E. R. H. Jones, and Wagland, *J.*, 1955, 3420. [e] Ref. 10. [f] Heusser, Heusler, Eichenberger, Honegger, and Jeger, *Helv. Chim. Acta*, 1952, **35**, 295. [g] Heusser, Eichenberger, Kurath, Dillenbach, and Jeger, *ibid.*, 1951, **34**, 2106. [h] Fieser and Huang, *J. Amer. Chem. Soc.*, 1953, **75**, 5356.

EXPERIMENTAL

M. p.s were determined on a hot stage and are corrected. Optical rotations were determined for chloroform solutions (*c* 0·7—1·3%) and the sodium D line, in a 1 dm. micro-tube, at room temperature (18—25°). Analytical samples were dried at 80°, or at least 20° below the m. p.

Infrared spectra were determined for carbon disulphide solutions with a Perkin-Elmer model 21 double-beam spectrophotometer, fitted with a sodium chloride prism, by Dr. A. A. Wagland, Roche Products Ltd., Welwyn Garden City.

Ultraviolet spectra were determined with a Unicam SP 500 spectrophotometer by Dr. G. W. Wood, Hatfield Technical College.

"Working up in the usual manner" implies washing the organic layer with water, 2N-sulphuric acid, water, saturated sodium hydrogen carbonate solution, and then water until washings are neutral.

Light petroleum refers to the fraction of b. p. 60—80°.

5α-Androsta-2 : 9(11)-dien-17-one (II; R = :O).—Redistilled phosphorus oxychloride (1 c.c.) was added dropwise to a solution of 11β-hydroxy-5α-androst-2-en-17-one (I; R = :O, R′ = H, β-OH) (200 mg.) in dry pyridine (4 c.c.) with external cooling. The solution was kept at room temperature overnight, and the steroid isolated by means of ether in the usual manner. The solid product (168 mg.) was chromatographed on alumina (6 g.). Elution with light petroleum and light petroleum–benzene (9 : 1) yielded material of m. p. 124—129° (91 mg.), crystallizing from *n*-pentane to yield the *dienone*, m. p. 131—133° (depressed m. p. when admixed with starting material), $[\alpha]_D$ + 173° (Found: C, 84·35; H, 9·7; $C_{19}H_{26}O$ requires C, 84·4; H, 9·7%), ε 6012, 4202, 1748, 480, and 166 at 2000, 2050, 2100, 2150, and 2200 Å, respectively.

Further elution of the column with light petroleum–benzene (1 : 3) and benzene gave unchanged starting material, crystallizing from acetone as needles, m. p. and mixed m. p. 129—133°.

5α-Androsta-2 : 9(11)-dien-17β-ol (II; R = H, β-OH).— A solution of lithium aluminium hydride (100 mg.) and 5α-androsta-2 : 9(11)-dien-17-one (II; R = O) (128 mg.) in dry ether (10 c.c.) was kept at room temperature overnight. Ethyl acetate and then water were added to decompose the excess of reagent, aqueous tartaric acid solution added, and the steroid isolated

with ether in the usual manner to give a solid (123 mg.). Chromatography on alumina (4 g.), elution with light petroleum–benzene (1 : 1 and 1 : 3) and benzene, and crystallization from light petroleum yielded 5α-*androsta*-2 : 9(11)-*dien*-17β-*ol*, m. p. 163—164° (with previous sublimation to give needles), $[\alpha]_D$ +33° (Found: C, 83·85; H, 10·4. $C_{19}H_{28}O$ requires C, 83·75; H, 10·35%).

The *acetate*, prepared with acetic anhydride and pyridine in the usual way and recrystallized from methanol, had m. p. 79—81°, with an abrupt change after several crystallizations to 97—99°, $[\alpha]_D$ + 13° (Found: C, 80·5; H, 9·55. $C_{21}H_{30}O_2$ requires C, 80·2; H, 9·6%).

11β-*Hydroxy*-5α-*androstan*-17-*one* (III; R = :O, R′ = H, β-OH).—A solution of 11β-hydroxy-5α-androst-2-en-17-one (I) (500 mg.) in ethyl acetate (60 c.c.) containing prereduced Adams catalyst (70 mg.) was shaken under slight positive pressure in hydrogen. Uptake ceased (4 min.) after the addition of 1 mol. of hydrogen. Removal of the catalyst and evaporation of the solvent yielded a solid which crystallized from acetone–pentane, to give the *hydroxy-ketone*, m. p. 178—179°, $[\alpha]_D$ +78° (Found: C, 78·3; H, 10·35. $C_{19}H_{30}O_2$ requires C, 78·55; H, 10·4%).

This hydroxy-ketone (150 mg.) was heated in dimethylaniline (3·6 c.c.), redistilled acetyl chloride (1·8 c.c.), and chloroform (5·4 c.c.) for 7·5 hr., then kept at room temperature overnight. After the addition of iced water, the steroid was worked up in ether in the usual manner, yielding a yellow gummy solid. Chromatography on alumina (6 g.) and elution with light petroleum–benzene (4 : 1 to 1 : 1) gave the 11β-*acetate*, prisms (from methyl alcohol), m. p. 116·5—118°, $[\alpha]_D$ +71° (Found: C, 75·7; H, 9·65. $C_{21}H_{32}O_3$ requires C, 75·8; H, 9·7%).

5α-*Androst*-9(11)-*en*-17-*one* (IV; R = :O).—Phosphorus oxychloride (1 c.c.) and 11β-hydroxy-5α-androstan-17-one (200 mg.) in pyridine (4 c.c.) gave, as above, a product which was chromatographed on alumina (6 g.); elution with light petroleum–benzene (9 : 1 and 4 : 1) gave 5α-*androst*-9(11)-*en*-17-*one* (74 mg.), plates (from methyl alcohol), m. p. 133—134° (with some previous softening and sublimation), $[\alpha]_D$ +134° (Found: C, 83·5; H, 10·3. $C_{19}H_{28}O$ requires C, 83·75; H, 10·35%), ε 5340, 3410, 1233, and 86 at 2000, 2050, 2100, and 2150 Å, respectively.

5α-*Androst*-9(11)-*en*-17β-*ol* (IV; R = H, β-OH).—The monounsaturated ketone (IV; R = :O) (179 mg.) was reduced with lithium aluminium hydride in ether as above. Chromatography on alumina (6 g.) and elution with light petroleum–benzene (1 : 1 to 1 : 3) gave crude 5α-*androst*-9(11)-*en*-17β-*ol*, needles (from light petroleum), m. p. 160·5—162° (subliming as needles and laths), $[\alpha]_D$ +4° (Found: C, 83·45; H, 11·0. $C_{19}H_{30}O$ requires C, 83·15; H, 11·05%). This alcohol (54 mg.) with pyridine and acetic anhydride in the usual manner gave the acetate, m. p. 66·5—69·5° (from methanol), $[\alpha]_D$ −5°.

5α-*Androstane*-11 : 17-*dione* (III; R = R′ = :O).—(a) *By hydrogenation of* 5α-*androst*-2-*ene*-11 : 17-*dione*. A solution of the androstenedione (413 mg.) in ethyl acetate (45 c.c.), hydrogenated over Adams catalyst as above (15 min.), gave a solid, which was filtered through alumina (12 g.) in light petroleum–benzene (1 : 1), further material being obtained by elution with the same solvents (3 : 1) and benzene. Crystallization from light petroleum and a trace of acetone gave 5α-*androstane*-11 : 17-*dione* as plates, m. p. 126—127·5° (200 mg.), and a second crop (86 mg.), m. p. 125—127°, $[\alpha]_D$ +135° (Found: C, 78·8; H, 9·75. $C_{19}H_{28}O_2$ requires C, 79·1; H, 9·8%). This compound gave no colour with tetranitromethane.

(b) *Chromic acid oxidation of* 5α-*androstane*-11β : 17β-*diol*. 8N-Chromic acid (aqueous) [7] was added dropwise to a solution of the diol (18 mg.) in acetone (5 c.c.), until excess of reagent was present. After a further minute's shaking water was added and the steroid worked up in ether in the usual manner. The solid product (16 mg.) was chromatographed on alumina (1 g.). Elution with light petroleum–benzene (3 : 1 and 1 : 1) and crystallization from methanol gave plates, m. p. 125—128°, undepressed on admixture with material prepared by method (a).

(c) *Chromic acid oxidation of* 11β-*hydroxy*-5α-*androstan*-17-*one*. The hydroxy-ketone was oxidized as in method (b); the product crystallized from *n*-pentane to give plates, m. p. and mixed m. p. 126—129°.

5α-*Androstane*-11β : 17β-*diol* (III; R = R′ = H, β-OH).—(a) *By hydrogenation*. A solution of 5α-androst-2-ene-11 : 17-dione (500 mg.) in acetic acid (55 c.c.) was hydrogenated using prereduced Adams catalyst (70 mg.). One mol. of hydrogen was absorbed in 6 min., 2 mols. in 30 min., and uptake ceased after 100 min. Removal of the catalyst and evaporation to dryness yielded a solid (512 mg.), m. p. 151—153° with a partial change to fine needles. Slow crystallization from light petroleum gave 5α-*androstane*-11β : 17β-*diol* as hair-like needles (485 mg.), m. p. 156—158° (with sublimation to larger needles). The infrared spectrum of this

product showed a small peak at 1717 cm.$^{-1}$ (11-CO); chromatography and crystallization of the product eluted with benzene–ether (19 : 1 to 1 : 1) gave needles, m. p. 160—162°, $[\alpha]_D$ +29° (no infrared ketone peak) (Found: C, 78·25; H, 10·85. $C_{19}H_{32}O_2$ requires C, 78·0; H, 11·05%).

(b) *By reduction with lithium aluminium hydride.* Lithium aluminium hydride (50 mg.) was added to a solution of 5α-androstane-11 : 17-dione (40 mg.) in dry ether (1 c.c.), and the whole kept at room temperature overnight. Working up in ether gave a gelatinous solid (42 mg.). Chromatography on alumina (1 g.), elution with benzene–ether (19 : 1 to 1 : 1), and crystallization from light petroleum gave the diol as fibrous needles, m. p. and mixed m. p. 161—163° (with sublimation), $[\alpha]_D$ +29°.

Acetylation with pyridine and acetic anhydride at room temperature overnight gave 5α-*androstane*-11β : 17β-*diol* 17-*monoacetate*, crystallizing from methanol as needles, m. p. 138—139°, $[\alpha]_D$ +7° (Found: C, 75·0; H, 10·25. $C_{21}H_{34}O_3$ requires C, 75·4; H, 10·25%).

11β : 17β-*Diacetoxy*-5α-*androstane*.—The preceding diol (150 mg.) was acetylated with acetyl chloride in dimethylaniline and chloroform as for the 11β-hydroxy-17-ketone. Chromatography of the product on alumina (6 g.) and elution with light petroleum–benzene (19 : 1 to 1 : 3) yielded a gummy solid (165 mg.), which gave the *diacetate*, m. p. 122—124° (113 mg.), on trituration with methanol. Further crystallization gave material of m. p. 123—125°, $[\alpha]_D$ +24° (Found: C, 73·0; H, 9·7. $C_{23}H_{36}O_4$ requires C, 73·4; H, 9·65%).

17β-*Hydroxy*-5α-*androstan*-11-*one* (III; R = H, β-OH, R′ = :O).—Sodium borohydride (18 mg.) was added to a solution of 5α-androstane-11 : 17-dione (286 mg.) in methanol (60 c.c.) at 0°, and the solution kept at this temperature for 1 hr. A few drops of acetic acid were added to decompose the excess of reagent. Working up in the usual way in ether gave a colourless solid (287 mg.). Chromatography on alumina (10 g.) and elution with benzene–ether (19 : 1 and 9 : 1) gave material, m. p. 148—151° (154 mg.) (with previous sublimation to needles). Crystallization from acetone–light petroleum then gave 17β-*hydroxy*-5α-*androstan*-11-*one*, needles, m. p. 149—151·5° (with previous sublimation), $[\alpha]_D$ +56° (Found: C, 78·4; H, 10·25. $C_{19}H_{30}O_2$ requires C, 78·55; H, 10·4%). This material (50 mg.) with acetic anhydride and pyridine gave the 17β-*acetate*, laths (from methanol), m. p. 106—108°, $[\alpha]_D$ +17° (Found: C, 75·95; H, 9·45. $C_{21}H_{32}O_3$ requires C, 75·8; H, 9·7%).

5α-*Androstan*-11β-*ol* (III; R = H_2, R′ = H, β-OH).—Potassium hydroxide (900 mg.), 100% hydrazine hydrate (1 c.c.), and 5α-androstane-11 : 17-dione (317 mg.) in triethylene glycol (45 c.c.) were heated under reflux for 30 min. The solution was then heated at 200° for 2 hr. Water and 2N-sulphuric acid were added to the cooled solution; extraction with ether and working up in the usual manner gave a brown gum (287 mg.) which was filtered in pentane through alumina (9 g.), to yield a gum (223 mg.). Reduction of this with lithium aluminium hydride in the usual manner gave a gummy solid (219 mg.), which on chromatography on alumina (20 g.) and elution with light petroleum gave 5α-*androstan*-11β-*ol* (144 mg.), plates (from light petroleum), m. p. 89—91°, $[\alpha]_D$ +17° (Found: C, 82·25; H, 11·7. $C_{19}H_{32}O$ requires C, 82·5; H, 11·7%).

Acetylation of this alcohol (123 mg.) with acetyl chloride, dimethylaniline, and chloroform gave the *acetate* as a gum which was purified by chromatography and distillation *in vacuo*. It then had $[\alpha]_D$ +35° (Found: C, 80·75; H, 11·0. $C_{21}H_{34}O_2$ requires C, 81·0; H, 10·75%). After a time part of this material solidified, enabling the product to be crystallized from methanol to yield prisms, m. p. 70—72°.

5α-*Androstan*-11-*one* (III; R = H_2, R′ = :O).—8N-Chromic acid was added dropwise to a solution of 5α-androstan-11β-ol (160 mg.) in acetone (5 c.c.) until an excess was present; after the addition of water the steroid was worked up in ether in the usual manner, to yield the ketone as needles (from methanol), m. p. 49—51·5°, $[\alpha]_D$ +68°.

Sondheimer, Batres, and Rosenkranz [2] give m. p. 49—50°, $[\alpha]_D$ +65°, for a sample obtained by high-vacuum distillation; Steiger and Reichstein [3] give m. p. 50—52°.

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