Abnormal Elimination Reactions of 3β,17β-Diacetoxy-5β,6β-epoxyandrostan-7β-ol

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Reaction of 3β,17β-diacetoxy-5β,6β-epoxyandrostan-7β-ol with phosphorus oxychloride affords 3β,17β-diacetoxyandrost-5-en-7-one whilst with methanesulphonyl chloride–sulphur dioxide it gives 17β-acetoxy-3β-methylsulphonyloxyandrost-5-en-7-one. Normal products are obtained with the epimeric 5α,6α-epoxy-7α-ols and in the absence of a 3β-substituent.

As an alternative approach to the preparation of androst-7-en-6-ones,[1] we examined the elimination reactions of some 5,6-epoxy-7-hydroxyandrostanes. Derivatives of 7β-hydroxy-steroids undergo elimination reactions to afford [2] the Δ^7-olefin whilst 5β,6β-epoxy-steroids are known [3] to rearrange with Lewis acids to generate the C-6 ketones. Steroidal 5-enes are readily oxidized [4] at C-7 to form αβ-unsaturated ketones from which 5,6-epoxy-7-hydroxy-steroids may be prepared.[5] Thus

[1] J. S. Cochrane and J. R. Hanson, *J. Chem. Soc.* (*C*), 1971, 3730.

[2] R. B. Turner, W. R. Meador, and R. E. Winkler, *J. Amer. Chem. Soc.*, 1957, **79**, 4122.

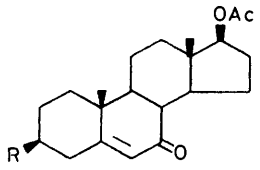
[3] J. W. Blunt, M. P. Hartshorn, and D. N. Kirk, *Tetrahedron*, 1966, **22**, 3195.

[4] K. Heusler and A. Wettstein, *Helv. Chim. Acta*, 1952, **35**, 284; L. F. Fieser, *J. Amer. Chem. Soc.*, 1953, **75**, 4394.

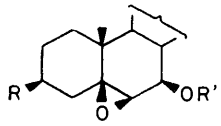
[5] D. Baldwin and J. R. Hanson, *J.C.S. Perkin I*, 1975, 1941

there was precedent for a route to androst-7-en-6-ones involving the elimination and rearrangement of 5,6-epoxyandrostan-7-ols. In the event the reactions took an unexpected course which forms the subject of this paper.

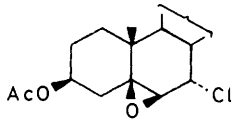
Reduction of 3β,17β-diacetoxyandrost-5-en-7-one (1) [4] with lithium tri-t-butoxyaluminium hydride followed by epoxidation with t-butyl hydroperoxide catalysed by vanadium acetylacetonate [6] afforded the 5β,6β-epoxy-



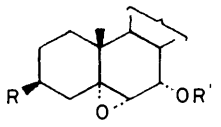
(1) R = OAc
(6) R = OMs



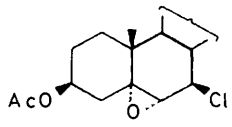
(2) R = OAc, R' = H
(4) R = OAc, R' = Ms
(5) R = OAc, R' = Ts
(11) R = R' = H; 17β—OH



(3)



(7) R = OAc, R' = H
(8) R = OAc, R' = Ms
(10) R = R' = H, 17β—OH



(9)

7β-alcohol (2). Reduction with sodium borohydride was less stereospecific affording a mixture of alcohols which were epoxidized and separated.[7] The magnitude of the H-7,H-8 coupling constants (see Table) were in accord [5,8] with the C-7 stereochemistry assigned to the alcohols.

Treatment of the 5β,6β-epoxy-7β-ol (2) with phosphorus oxychloride at room temperature gave mainly 3β,17β-diacetoxyandrost-5-en-7-one (1) which was identified by comparison with an authentic sample. This was accompanied by smaller amounts of 17β-acetoxyandrost-3,5-dien-7-one [9] and 3β,17β-diacetoxy-7α-chloroandrostane-5β,6β-epoxide (3). The magnitude of the H-7,H-8 coupling constant (see Table) led to the assignment of the stereochemistry at C-7 to the chloro-epoxide. When the reaction was carried out at −20 °C the chloro-epoxide was the only recoverable product. However a substantial amount of material was lost presumably as a water-soluble phosphate. Treatment of the alcohol with triphenylphosphine and carbon tetrachloride [10] in pyridine gave a good yield of the chloro-epoxide. Although this compound possessed a *trans*-relationship between the 8β-hydrogen atom and the 7α-chlorine atom, it was resistant to elimination. Reaction of the alcohol with thionyl chloride afforded the dimeric sulphite ester. The 7β-alcohol gave both a methanesulphonate (4) and a toluene-*p*-sulphonate (5) when treated with the corresponding acid chlorides. The toluene-*p*-sulphonate was accompanied by a small amount of the 7α-chloro-epoxide (3). However both derivatives were inert to reaction with refluxing pyridine or neutral alumina. The addition of sulphur dioxide to methanesulphonyl chloride has been shown to produce elimination from hindered alcohols.[11] However, reaction of 3β,17β-diacetoxy-5β,6β-epoxyandrostan-7β-ol (2) with methanesulphonyl chloride containing 5% sulphur dioxide in collidine–dimethylformamide surprisingly gave a high yield of 17β-acetoxy-3β-methylsulphonyloxyandrost-5-en-7-one (6). This compound was identified by comparison with an authentic sample prepared by the allylic oxidation of 17β-acetoxy-3β-methylsulphonyloxyandrost-5-ene with sodium chromate in acetic acid. The elimination of alcohols with hexamethylphosphoric triamide has been described.[12] However the product in this case was 17β-acetoxyandrost-3,5-dien-7-one rather than the Δ^7-olefin.

The formation of the Δ^5-7-ketones may be rationalized (Scheme 1) in the case of the acid-catalysed reaction by ring-opening of the epoxide prior to reaction of the alcohol.[5] However the reaction with methanesulphonyl chloride–sulphur dioxide was more unusual requiring not only the formation of the unsaturated ketone but also the displacement of a 3β-substituent with retention of configuration. Hence this reaction was examined further.

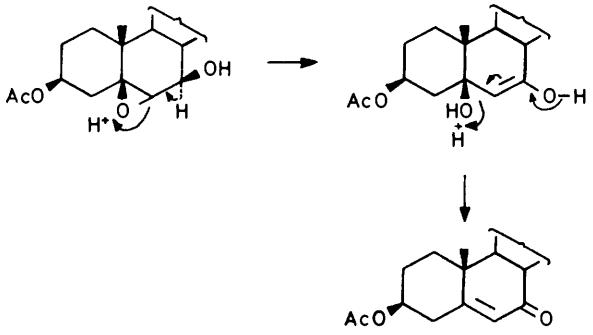
Both 3β,17β-diacetoxyandrost-5-en-7-one (1) and 3β-acetoxy-5β,6β-epoxyandrostan-17-one were inert to the

6-H and 7-H n.m.r. signals (p.p.m. from $SiMe_4$)

Compound	6-H	Coupling constant	7-H	Coupling constant	C-7 stereochemistry
5β,6β-Epoxides					
2	3.15	s	3.50	br, d 7 Hz	α-H
3	3.26	d, 3 Hz	4.31	t, *J* 3 Hz	β-H
4	3.45	s	4.74	d, *J* 9 Hz	α-H
5	3.15	br, s	4.73	q, *J* 1 and 9 Hz	α-H
11	3.04	br, s	3.52	m	α-H
5α,6α-Epoxides					
7	3.19	d, 5 Hz	3.83	m	β-H
8	3.28	d, 5 Hz	4.90	t, *J* 5 Hz	α-H
9	3.04	s	3.87	d, *J* 7 Hz	β-H
10	3.17	d, 5 Hz	3.76	m	β-H

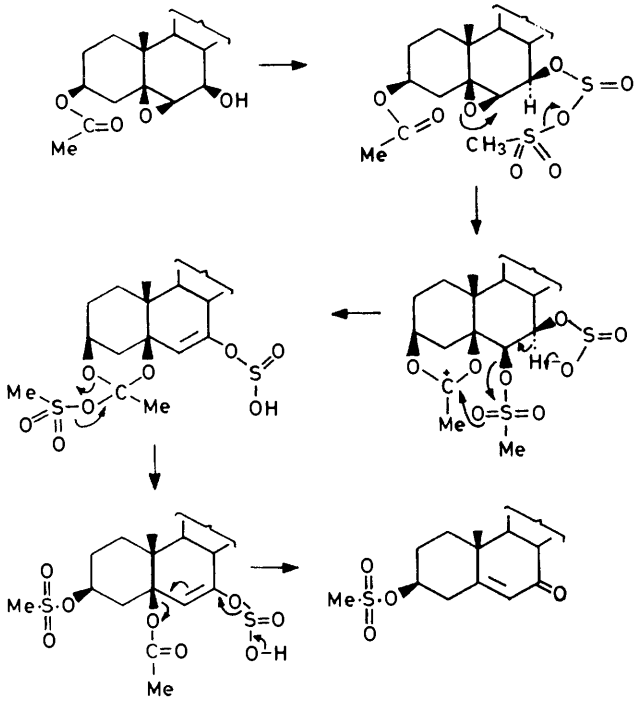
[6] K. B. Sharpless and R. C. Michaelson, *J. Amer. Chem. Soc.*, 1973, **95**, 6136.
[7] P. Morand and A. van Tongerloo, *Steroids*, 1973, **21**, 65.
[8] C. W. Shoppee and B. C. Newman, *J. Chem. Soc.*, (*C*), 1968, 981.
[9] A. Butenandt, E. Hausman, and J. Poland, *Ber.*, 1938, **71**, 1316.
[10] I. M. Downie, J. B. Holmes, and J. B. Lee, *Chem. and Ind.*, 1966, 900.
[11] G. G. Hazen and D. W. Rosenburg, *J. Org. Chem.*, 1964, **29**, 1930.
[12] R. S. Monson, *Tetrahedron Letters*, 1971, 567.

reaction conditions whilst 3β,17β-diacetoxy-5α,6α-epoxyandrostan-7α-ol (7) gave the 7α-methanesulphonate (8) together with a small amount of the 7β-chloro-epoxide (9). The 7β-chloro-epoxide (9) was the major product



SCHEME 1

on reaction of (7) with phosphorus oxychloride. When 5β,6β-epoxyandrostane-7β,17β-diol and 5α,6α-epoxyandrostane-7α,17β-diol were treated with methanesulphonyl chloride–sulphur dioxide the products were the 17β-mono-and 7,17β-di-methanesulphonates. The site of monoesterification in these compounds, was defined by the downfield shift of the 17α-proton resonance. There was no trace of an unsaturated ketone in the reaction product. Hence the reaction is specific for the 3β-acetoxy-5β,6β-epoxy-7β-alcohol. A plausible mechanism is given in Scheme 2 in which a stabilizing



SCHEME 2

and directing feature for the opening of the epoxide is the formation of a 3β,5β-acetoxylinium ion. This ion can also serve in the introduction of the 3β-methylsulphonyloxy-grouping.

EXPERIMENTAL

General experimental details have been described previously.[13]

3β,17β-*Diacetoxy*-7β-*hydroxyandrost*-5-*ene*.— Lithium aluminium hydride (578 mg) was added to t-butyl alcohol (4.66 g) under nitrogen. 3β,17β-Diacetoxyandrost-5-en-7-one (3 g) [4] in tetrahydrofuran (60 ml) was added to it and the solution was left at room temperature for 60 h. The excess of reagent was destroyed with water and the product was recovered in ether and purified by preparative layer chromatography on silica to afford 3β,17β-*diacetoxy*-7β-*hydroxyandrost*-5-*ene* (2.5 g) which crystallized from light petroleum–ether as needles, m.p. 122—125 °C (Found: C, 70.65; H, 8.5. $C_{23}H_{34}O_5$ requires C, 70.8; H, 8.7%), $\nu_{max.}$ 3 400, 1 740, 1 250, and 1 040 cm^{-1}; δ 0.82 (3 H, s, 18-H), 1.08 (3 H, s, 19-H), 2.02 (6 H, s, OAc), 3.86 (1 H, m, 7-H), 4.58 (2 H, m, 3- and 17-H), and 5.32 (1 H, d, *J* 3 Hz, 6-H).

3β,17β-*Diacetoxy*-5β,6β-*epoxyandrostan*-7β-*ol*.— t-Butyl hydroperoxide (800 mg) was added to a solution of 3β,17β-diacetoxy-7β-hydroxyandrost-5-ene (1 g) and vanadyl acetylacetonate (12 mg) in benzene (120 ml) at 60 °C. The solution was maintained at this temperature for 3 h. It was then cooled, diluted with ethyl acetate and washed thoroughly with acidified iron(II) sulphate, dilute hydrochloric acid, aqueous sodium hydrogen carbonate, water, and was then dried. Evaporation of the solvent gave 3β,17β-*diacetoxy*-5β,6β-*epoxyandrostan*-7β-*ol* (2) (800 mg) which crystallized from benzene–light petroleum as needles, m.p. 122—123 °C, $[\alpha]_D^{22}$ +10° (*c* 0.2) (Found: C, 68.0: H, 8.4. $C_{23}H_{34}O_6$ requires C, 68.0; H, 8.4%), $\nu_{max.}$ 3 450, 1 735, 1 250, 1 030, and 920 cm^{-1}; δ 0.76 (3 H, s, 18-H), 1.02 (3 H, s, 19-H), 2.00 (6 H, s, OAc), 3.15 (1 H, s, 6-H), 3.50 (1 H, br, d, *J* 7 Hz, 7-H), 4.58 (1 H, t, *J* 9 Hz, 17-H), and 4.78 (1 H, br, m, 3-H). Epoxidation of a crude mixture (2.7 g) obtained by the sodium borohydrate reduction of 3β,17β-diacetoxyandrost-5-en-7-one gave the above epoxide (1.5 g) and 3β,17β-*diacetoxy*-5α,6α-*epoxyandrostan*-7α-*ol* (7) (0.5 g) which crystallized from ether as prisms, m.p. 139—142 °C, $[\alpha]_D^{22}$ −108° (*c* 0.2) (Found: C, 69.0; H, 8.5. $C_{23}H_{34}O_6$ requires C, 68.0; H, 8.4%), $\nu_{max.}$ 3 445, 1 730, 1 250, 1 030, and 920 cm^{-1}; δ 0.73 (3 H, s, 18-H), 1.07 (3 H, s, 19-H), 1.98 (6 H, s, OAc), 3.19 (1 H, d, *J* 5 Hz, 6-H), 3.83 (1 H, m, 7-H), 4.59 (1 H, t, *J* 8 Hz, 17-H), and 4.90 (1 H, m, 3-H). The 7β-*methanesulphonate*, prepared with methanesulphonyl chloride in pyridine, crystallized from ethyl acetate as prisms, m.p. 133—134 °C, $[\alpha]_D^{20}$ −33 (*c* 0.25) (Found: C, 59.9; H, 7.1; S, 7.0. $C_{24}H_{36}O_8S$ requires C, 59.5; H, 7.4; S, 6.6%), $\nu_{max.}$ 1 730, 1 335, 1 250, 1 175, 1 040, 920, and 825 cm^{-1}; δ 0.76 (3 H, s, 18-H), 1.05 (3 H, s, 19-H), 1.99 (6 H, s, OAc), 3.03 (3 H, s, OMe), 3.45 (1 H, s, 6-H), 4.53 (1 H, t, *J* 8 Hz, 17-H), 4.60 (1 H, br,m, 3-H), and 4.74 (1 H, d, *J* 9 Hz, 7-H). The 7β-*toluene*-p-*sulphonate* (5), prepared with toluene-*p*-sulphonyl chloride in pyridine, crystallized from ethyl acetate–light petroleum as prisms, m.p. 147—149 °C, $[\alpha]_D^{22}$ −4° (*c* 0.7) (Found: C. 63.7; H, 7.0. $C_{30}H_{40}O_8S$ requires C, 64.3; H, 7.2%), $\nu_{max.}$ 1 730, 1 580, 1 360, and 1 250 cm^{-1}; δ 0.74 (3 H, s, 18-H) 1.02 (3 H, s, 19-H), 1.98 (6 H, s, OAc), 2.42 (3 H, s, $ArCH_3$), 3.15 (1 H, br, s, 6-H), 4.52 (1 H, t, *J* 8 Hz, 17-H), 4.60 (1 H,

[13] J. R. Hanson and T. D. Organ, *J. Chem. Soc.* (*C*), 1970, 513.

br,m, 3-H), 4.73 (1 H, q, *J* 1 and 9 Hz, 7-H), and 7.28 and 7.78 (each 2 H, d, *J* 8 Hz, Ar-H). Small amounts of 3β,-17β-diacetoxyandrost-5-en-7-one and the 7α-chloro-5β,6β-epoxide (3) (*vide infra*) were also isolated from this preparation.

Reaction of Thionyl Chloride with the Epoxy-alcohol (2).—Thionyl chloride (1.5 ml) in pyridine (5 ml) at 0 °C was added to a solution of 3β,17β-diacetoxy-5β,6β-epoxyandrostan-7β-ol (500 mg) in pyridine (15 ml) at −10 °C. The solution was stirred for 1 h at −10 °C and then poured into dilute hydrochloric acid. The product was recovered in ethyl acetate and the solvent evaporated to give *bis*-(3β,17β-*diacetoxy*-5β,6β-*epoxyandrostan*-7β-*yl*)*sulphite* (370 mg) which crystallized from ether as needles, m.p. 166—169 °C, $[\alpha]_D^{22}$ −73° (*c* 0.2) (Found: C, 64.5; H, 7.7; S, 3.7. $C_{46}H_{66}O_{13}S$ requires C, 64.3; H, 7.7; S, 3.7%), $\nu_{max.}$ 1 735, 1 250, and 1 195 cm^{-1}; δ 0.76 (6 H, s, 18 and 18′-H), 1.03 (6 H, s, 19 and 19′-H), 2.01 (12 H, s, OAc), 3.42 (2 H, s, 6 and 6′-H), 4.35 (1 H, d, *J* 8 Hz, 7-H), 4.55 (2 H, t, *J* 9 Hz, 17 and 17′-H), 4.80 (2 H, m, 3 and 3′-H), and 4.96 (1 H, d, *J* 8 Hz, 7′-H).

Elimination Reactions.—(i) 3β,17β-Diacetoxy-5β,6β-epoxyandrostan-7β-ol (1 g) in dry pyridine (30 ml) was treated with phosphorus oxychloride (1.5 ml) at room temperature for 65 h. The solution was poured into ice–water and the product (300 mg) was recovered in chloroform and purified by preparative layer chromatography to afford 17-acetoxyandrost-3,5-dien-7-one (40 mg), m.p. 224—227 °C and 3β,-17β-diacetoxyandrost-5-en-7-one (180 mg), m.p. 218—221 °C, both identified by comparison, i.r. and n.m.r., with authentic material. 3β,17β-*Diacetoxy*-7α-*chloro*-5β,6β-*epoxyandrostane* (3) (74 mg) crystallized from ether as needles, m.p. 149—150 °C, $[\alpha]_D^{21}$ −81° (*c* 0.1) (Found: C, 64.9; H, 7.8; Cl, 8.9. $C_{23}H_{33}ClO_5$ requires C, 65.0; H, 7.8; Cl, 8.4%), $\nu_{max.}$ 1 740, 1 240, and 720 cm^{-1}; δ 0.79 (3 H, s, 18-H), 1.02 (3 H, s, 19-H), 1.99 (6 H, s, OAc), 3.26 (1 H, d, *J* 3 Hz, 6-H), 4.31 (1 H, t, *J* 3 Hz, 7-H), 4.58 (1 H, t, *J* 8 Hz, 17-H), and 4.70 (1 H, br,m, 3-H). When the reaction was carried out at −20 °C the 7α-chloro-epoxide formed the sole product.

(ii) The epoxy-alcohol (2) (200 mg) was added to a solution of triphenylphosphine (400 mg) in carbon tetrachloride (15 ml) containing pyridine (1 ml) and heated under reflux for 8 h. The solvent was removed *in vacuo* and the product was purified by preparative layer chromatography to afford 3β,17β-diacetoxy-7α-chloro-5β,6β-epoxyandrostane (3) (120 mg) which crystallized from ether as needles, m.p. 152—153 °C, identical with the product obtained above.

(iii) The epoxy-alcohol (2) (1.5 g) in HMPT (5 ml) was heated for 2 h at 200 °C. The crude product was purified by preparative layer chromatography to afford 17β-acetoxyandrosta-3,5-dien-7-one (1.0 g) which crystallized from ether as needles, m.p. 224—226 °C, $[\alpha]_D^{21}$ −320° (*c* 0.18) (lit.,[9] m.p. 222 °C, $[\alpha]_D^{20}$ −400 °C), identical with an authentic sample prepared from 3β,17β-diacetoxyandrost-5-en-7-one.

(iv) A solution of the epoxy-alcohol (2) (16.24 g) in collidine (33 ml) and dimethylformamide (100 ml) was cooled to 10 °C and then methanesulphonyl chloride (10 ml) containing 5% anhydrous sulphur dioxide was added to it over 1—2 min. The temperature was maintained between 25—35 °C for 5 min and then the excess methanesulphonyl chloride was decomposed with water.

17β-*Acetoxy*-3β-*methylsulphonyloxyandrost*-5-*en*-7-*one* (10 g) (6) was precipitated by the further addition of water and crystallized from ethanol as needles, m.p. 129—130 °C, $[\alpha]_D$ −117° (*c* 0.15) (Found: C, 62.4; H, 7.6; S, 7.3. $C_{22}H_{32}O_6S$ requires C, 62.3; H, 7.5; S, 7.55%), $\nu_{max.}$ 1 730, 1 660, 1 630, 1 325, 1 250, 1 165, and 925 cm^{-1}; δ 0.83 (3 H, s, 18-H), 1.23 (3 H, s, 19-H), 2.00 (3 H, s, OAc), 2.99 (3 H, s, OMs), 4.58 (2 H, br, m, 3 and 17-H), and 5.70 (1 H, s, 6-H).

Oxidation of 17β-*Acetoxy*-3β-*methylsulphonyloxyandrost*-5-*ene*.—The steroid [1] (2.85 g) in acetic acid (10 ml) and acetic anhydride (5 ml) was treated with anhydrous sodium chromate (2.5 g) at 40 °C. The solution was left for 3 days and then poured into water. The product was recovered in ethyl acetate and crystallized from methanol to afford 17β-acetoxy-3β-methylsulphonyloxyandrost-5-en-7-one (6) (1.5 g) as needles, m.p. 132—133 °C, identical to the material described above.

Reaction of Methanesulphonyl Chloride–Sulphur Dioxide with 3β,17β-*Diacetoxy*-5α,6α-*epoxyandrostan*-7α-*ol*.—The steroid (0.5 g) in collidine (2.2 ml) and dimethylformamide (7.0 ml) was treated with methanesulphonyl chloride containing 5% anhydrous sulphur dioxide (0.7 ml) as described above. The product was purified by preparative layer chromatography on silica to afford (i) 3β,17β-diacetoxy-7β-chloro-5α,6α-epoxyandrostane (9), (0.15 g) which crystallized from ether as needles, m.p. 95—96 °C, identified by its i.r., n.m.r., and mass spectra (*vide infra*); (ii) 3β,17β-*diacetoxy*-7α-*methylsulphonyloxy*-5α,6α-*epoxyandrostane* (8) (0.75 g) which crystallized from ether–light petroleum as needles, m.p. 155—158 °C, $[\alpha]_D^{22}$ −128° (*c* 0.3) (Found: C, 59.7; H, 7.7. $C_{24}H_{36}O_8S$ requires C, 59.5; H, 7.4%), $\nu_{max.}$ 1 730, 1 240, 1 025, 800 cm^{-1}; δ 0.74 (3 H, s, 18-H), 1.08 (3 H, s, 19-H), 1.97 (6 H, s, OAc), 3.08 (3 H, s, OMs), 3.28 (1 H, d, *J* 4 Hz, 6-H), 4.58 (1 H, t, *J* 8 Hz, 17-H), and 4.90 (2 H, m, and t *J* 4 Hz, 3- and 7-H); (iii) 3β,17β-*diacetoxy*-6β-*chloroandrostane*-5α,5α-*diol* (0.16 g) which crystallized from chloroform as needles, m.p. 295—296 °C, $[\alpha]_D^{20}$ −112° (*c* 1.5) (Found: C, 62.7; H, 8.0. $C_{23}H_{35}ClO_6$ requires C, 62.4; H, 7.9%), $\nu_{max.}$ 3 450, 1 730, 1 240, 1 190, 1 040, and 760 cm^{-1}; δ 0.73 (3 H, s, 18-H), 1.07 (3 H, s, 19-H), 1.94 and 1.96 (each 3 H, s, OAc), 4.34 (1 H, dd, *J* 5 and 10 Hz, 7-H), 4.55 (1 H, t, *J* 8 Hz, 17-H), and 4.85 (2 H, m, 3- and 6-H).

3β,17β-*Diacetoxy*-7β-*chloro*-5α,6α-*epoxyandrostane*.—3β,-17β-Diacetoxy-5α,6α-epoxyandrostan-7α-ol (0.3 g) was dissolved in pyridine (10 ml), cooled to 0 °C, and treated with phosphorus oxychloride (0.45 ml). The mixture was left at −20 °C for 65 h. It was poured into water and the product was extracted with chlofororm. The extract was washed with water and dried. The solvent was evaporated to afford 3β,17β-*diacetoxy*-7β-*chloro*-5α,6α-*epoxyandrostane* (9) (90 mg) which crystallized from ether as needles, m.p. 100—102 °C, $[\alpha]_D^{19}$ −13° (*c* 0.24) (Found: C, 65.0; H, 7.7. $C_{23}H_{35}ClO_5$ requires C, 65.0; H, 7.8%), $\nu_{max.}$ 1 730, 1 240, 1 025, and 715 cm^{-1}; δ 0.78 (3 H, s, 18-H), 1.14 (3 H, s, 19-H), 1.99 (6 H, s, OAc), 3.04 (1 H, s, 6-H), 3.87 (1 H, d, *J* 7 Hz, 7-H), 4.53 (1 H, t, *J* 8 Hz, 17-H), and 4.87 (1 H, m, 3-H).

Reaction of Methanesulphonyl Chloride–Sulphur Dioxide with the 5,6-*Epoxyandrostan*-7,17-*diols*.—(i) 5β,6β-Epoxyandrostan-7β,17β-diol (0.5 g) was treated with methanesulphonyl chloride (0.7 ml) as described previously. The product was separated by preparative layer chromatography to afford 17β-*methylsulphonyloxy*-5β,6β-*epoxyandrostan*-7β-*ol* (180 mg) which crystallized from ether as needles, m.p. 78—80 °C, $[\alpha]_D^{20}$ −49° (*c* 3) (Found: C, 61.8; H, 8.9. $C_{20}H_{32}O_5S$ requires C, 62.5; H, 8.3%); $\nu_{max.}$ 3 500, 1 350,

1 170, and 900 cm^{-1}; δ 0.81 (3 H, s, 18-H), 1.00 (3 H, s, 19-H), 2.94 (3 H, s, OMe), 3.02 (1 H, br, s, 6-H), 3.48 (1 H, d, *J* 9 Hz, 7-H), at 4.42 (1 H, br, m, 17-H). 7β,17β-*Bismethylsulphonyloxy*-5β,6β-*epoxyandrostane* (100 mg) crystallized from light petroleum as needles, m.p. 78—81 °C, $[\alpha]_D^{20}$ 1° (*c* 1.2) (Found: C, 54.5; H, 7.2. $C_{21}H_{34}O_7S_2$ requires C, 54.5; H, 7.4%), $\nu_{max.}$ 1 350, 1 170, and 900 cm^{-1}; δ 0.83 (3 H, s, 18-H), 1.04 (3 H, s, 19-H), 2.95 and 3.04 (each 3 H, s, OMs), 3.37 (1 H, br,s, 6-H), 4.42 (1 H, m, 17-H), and 4.77 (1 H, d, *J* 9 Hz, 7-H).

(ii) Under similar conditions 5α,6α-epoxyandrostane-7α,17β-diol (0.5 g) gave 17β-*methylsulphonyloxy*-5α,6α-*epoxyandrostan*-7α-*ol* (90 mg) which crystallized from ethyl acetate as needles, m.p. 84—85 °C, $[\alpha]_D^{20}$ −4° (*c* 2) (Found: C, 62.4; H, 8.1. $C_{20}H_{32}O_5S$ requires C, 62.5; H, 8.3%), $\nu_{max.}$ 3 430, 1 340, 1 175, and 960 cm^{-1}; δ 0.82 (3 H, s, 18-H), 1.04 (3 H, s, 19-H), 2.94 (3 H, s, OMs), 3.07 (1 H, d, *J* 5 Hz, 6-H), 3.76 (1 H, m, 7-H), and 4.42 (1 H, m, 17-H).

7α,17β-*Bismethylsulphonyloxy*-5α,6α-*epoxyandrostane* (120 mg) crystallized from ethyl acetate as needles, m.p. 70—72 °C, $[\alpha]_D^{20}$ −17° (*c* 2) (Found: C, 55.5; H, 7.8. $C_{21}H_{34}O_7S_2$ requires C, 54.5; H, 7.4%), $\nu_{max.}$ 1 350, 1 170, and 960 cm^{-1}, δ 0.78 (3 H, s, 18-H), 1.05 (3 H, s, 19-H), 2.93 and 3.09 (each 3 H, s, OMs), 3.25 (1 H, d, *J* 4.5 Hz, 6-H), 4.45 (1 H, m, 17-H), and 4.90 (1 H, m, 7-H).

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