Reactions of Derivatives of Steroidal 3,4,5- and 3,5,6-Triols with Hydrobromic Acid

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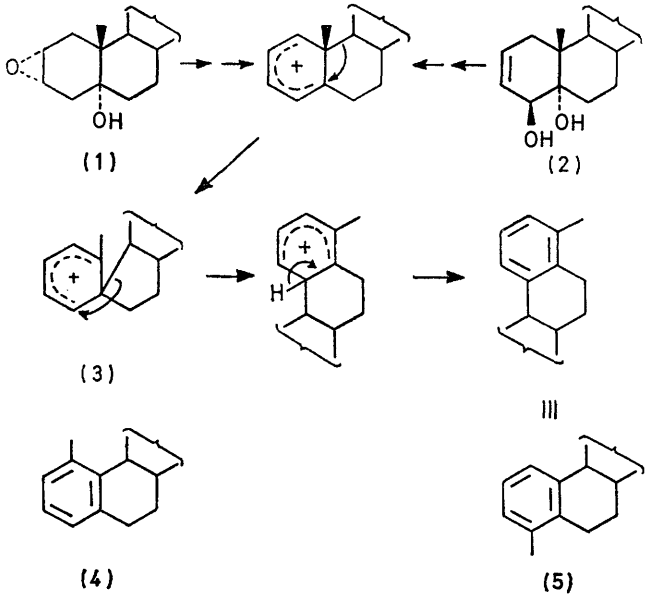
3β,17β-Diacetoxy-4α,5α-dihydroxy-, 3β,17β-diacetoxy-4β,5α-dihydroxy-, and 4β,17β-diacetoxy-3β,5α-dihydroxy-androstane gave 17β-acetoxy-4-methyloestra-1,3,5(10)-triene and testosterone acetate on treatment with hydrobromic acid in glacial acetic acid. 3β-Acetoxy-4α,5α-dihydroxyandrostane-6,17-dione gave a 1-methyl aromatic steroid and androst-4-ene-3,6,17-trione, whilst 3β,17β-diacetoxy-4α,5α-dihydroxyandrostan-11-one gave a low yield of the 1-methyl aromatic steroid together with 17β-acetoxyandrost-4-ene-3,11-dione. Whereas 3β,6β-diacetoxy-5α-hydroxy-steroids gave 4-methyloestratrienes, 3β,6α,17β-triacetoxy-5α-hydroxyandrostane gave 3β,17β-diacetoxyandrostan-6-one, and a 6α-methanesulphonate gave an A-homo-B-nor-steroid.

We have shown that a series of steroidal hydroxy-epoxides [*e.g.* (1)] [1] and enediols [*e.g.* (2)] [2] rearrange on treatment with hydrobromic acid in glacial acetic acid with the formation of aromatic, and in some instances, ketonic products. 4-Methyloestra-1,3,5(10)-trienes (5) are formed *via* a spiro-carbonium ion (3). When the formation of the ion is inhibited, then 1-methyloestratrienes (4) are formed by an alternative



pathway involving a C-10 ⟶ C-1 methyl migration. Ketonic products arise when dehydration leads to an enol. We now describe this balance between aromatic and ketonic products in the reaction of some steroidal triols and their derivatives under these conditions.

3β,17β-Diacetoxy-4β,5α-dihydroxyandrostane (6) and 4β,17β-diacetoxy-3β,5α-dihydroxyandrostane (7) were prepared [3] by hydrolysis of the corresponding 3β-acetoxy-4α,5α-epoxide; 3β,17β-diacetoxy-4α,5α-dihydroxyandrostane (8) was prepared by osmylation of 3β,17β-diacetoxyandrost-4-ene. Both 3β,17β-diacetoxy-4β,5α-dihydroxyandrostane and its 4α-epimer gave testosterone acetate (9) and 17β-acetoxy-4-methyloestra-1,3,5(10)-triene on treatment with hydrobromic acid in glacial acetic acid. Whilst the formation of testosterone acetate from the 4β-epimer is unexceptional requiring only a diaxial elimination followed by hydrolysis of the dienol acetate, its formation from the 4α-epimer requires comment. Diaxial elimination of the C-4 proton and the C-5α hydroxy-group could afford 3β,17β-diacetoxy-androstan-4-one. Transposition of the 3β-acetoxy-group to C-4 through the C-3(4) enol followed by elimination could then lead to testosterone acetate. 4β,17β-Diacetoxy-3β,5α-dihydroxyandrostane gave both 17β-acetoxy-4-methyloestra-1,3,5(10)-triene and testosterone acetate. On the other hand the corresponding 3β-methanesulphonate, which presumably reacts by O–alkyl fission, gave, as would be expected, only aromatic products.

In the dienone–phenol rearrangement [4] the presence of a C-6 carbonyl function serves to destabilize a C-5 carbonium ion and prevents the formation of a spiro-intermediate, whilst a carbonyl group at C-11 reduces the migratory aptitude of the 9,10-bond. Aromatization then occurs *via* the alternative C-10 ⟶ C-1 methyl

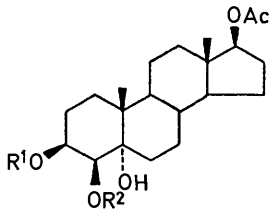
[1] J. R. Hanson and H. J. Shapter, *J.C.S. Perkin I*, 1972, 1445; D. Baldwin and J. R. Hanson, *ibid.*, p. 1889; A. G. Ogilvie and J. R. Hanson, *ibid.*, p. 1981.

[2] J. R. Hanson, *Tetrahedron Letters*, 1972, 4501; D. Baldwin, A. M. Holtom, and J. R. Hanson, *J.C.S. Perkin I*, 1973, 1704.

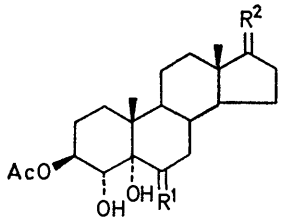
[3] S. Julia and B. Furer, *Bull. Soc. chim. France*, 1966, 1106.

[4] D. Burn, V. Petrow, and G. Weston, *J. Chem. Soc.*, 1962, 29.

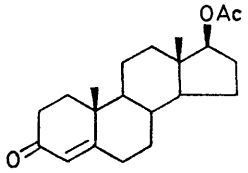
migration. 3β-Acetoxy-4α,5α-dihydroxyandrostane-6,17-dione (10), prepared by osmylation of the corresponding C-4 olefin,[5] gave 1-methyloestra-1,3,5(10)-triene-6,17-dione [1] and androst-4-ene-3,6,17-trione [6] on



(6) R^1 = Ac, R^2 = H
(7) R^1 = H, R^2 = Ac,



(8) R^1 = H_2, R^2 = β-OAc, α-H
(10) R^1 = R^2 = O



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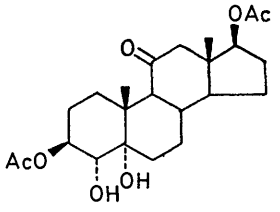

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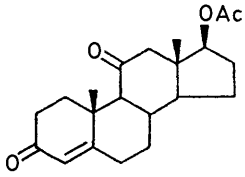

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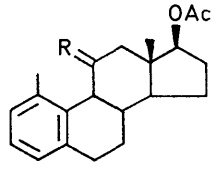
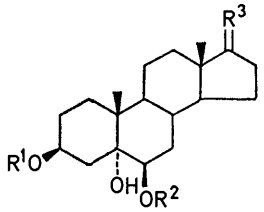
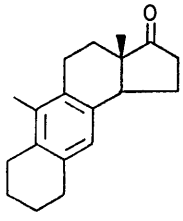


(13) R = O
(14) R = H_2

treatment with hydrobromic acid in glacial acetic acid. 3β,17β-Diacetoxy-4α,5α-dihydroxyandrostan-11-one (11) was prepared by osmylation of 3β,17β-diacetoxyandrost-4-en-11-one.[7] The magnitude of $J_{3,4}$ (9 Hz) was in accord with the presence of a C-4α hydroxy-group. 17β-Acetoxyandrost-4-ene-3,11-dione (12) [8] was the major product when the diol (11) was treated with hydrobromic acid in glacial acetic acid. In contrast to the reaction of 3β,17β-diacetoxy-4α,5α-epoxyandrostan-11-one,[1] the minor aromatic product was 17β-acetoxy-1-methyloestra-1,3,5(10)-trien-11-one (13). This compound was assigned the 1-methyl structure on the following basis. The aromatic C–H pattern in the n.m.r. spectrum resembled that of 17β-acetoxy-1-methyloestratriene. However the C-1 methyl group was significantly shielded. Furthermore the shift reagent $Eu(fod)_3$ [9] produced a marked downfield shift in the position of the aromatic *C*-methyl resonance compared with the 11-deoxy-compound (14) ($\Delta\tau$ 0·61 p.p.m. at a molar ratio of 0·69 : 1). Steroids possessing a 5α,6-glycol system show an interesting pattern of reactivity.[10] Thus 3β,6β-diacetoxy-5α-hydroxyandrostan-17-one undergoes the Westphalen rearrangement [11] to form a 5β-methyl-9-ene in an acetic acid–acetic anhydride mixture containing sulphuric acid. Recently Mazur [12] has shown that 5α,6β-dibromides form 4-methyloestratrienes on treatment with acetyl bromide containing hydrogen bromide. Similar aromatic products have been obtained by treatment of 3-substituted 5α,6α-epoxides with hydrobromic acid in glacial acetic acid.[1] 3β,6β-Diacetoxy-5α-hydroxyandrostan-17-one (15), 3β,6β,17β-triacetoxy-5α-hydroxyandrostane (16), and 6β-acetoxy-5α-hydroxy-3β-methoxyandrostan-17-one (17) each gave a 4-methyloestra-1,3,5(10)-triene on treatment with hydrobromic acid in glacial acetic acid. In the case of the 17-ketones this was accompanied by a trace of the anthrasteroid (18).[13] In none of these cases



(15) R^1 = R^2 = Ac, R^3 = O
(16) R^1 = R^2 = Ac, R^3 = β-OAc, α-H
(17) R^1 = Me, R^2 = Ac, R^3 = O



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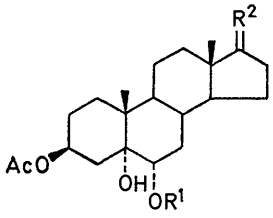
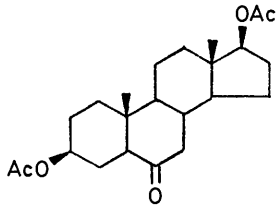


(19) R^1 = Ac, R^2 = β-OAc, α-H
(20) R^1 = Ms, R^2 = O



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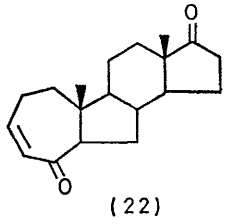

(22)

were we able to isolate products arising from a backbone rearrangement. In contrast 3β,6α,17β-triacetoxy-5α-hydroxyandrostane (19) gave 3β,17β-diacetoxy-

[5] L. Labler, F. Slama, and F. Sorm, *Coll. Czech. Chem. Comm.*, 1968, **33**, 2226.
[6] A. Butenandt and B. Riegel, *Ber.*, 1936, **69**, 1163.
[7] C. E. Morreal, *Steroids*, 1966, **8**, 671.
[8] O. Mancera, G. Rosenkranz, and F. Sondheimer, *J. Chem. Soc.*, 1953, 2189.
[9] R. E. Rondeau and R. E. Sievers, *J. Amer. Chem. Soc.*, 1971, **93**, 1522.
[10] M. Ehrenstein, *J. Org. Chem.*, 1941, **6**, 626.
[11] For a review see D. N. Kirk and M. P. Hartshorn, 'Steroid Reaction Mechanisms,' Elsevier, London, 1968, pp. 257—262.
[12] J. Libman and Y. Mazur, *Chem. Comm.*, 1971, 729.
[13] J. Schmitt, J. J. Panouse, M. Pluchet, A. Hallot, P. J. Cornu, and P. Comoy, *Bull. Soc. chim. France*, 1965, 1934.

androstan-6-one (21) [14] on treatment with this reagent. The product (21) was identified by comparison with an authentic sample prepared from 3β,17β-diacetoxyandrost-5-ene by hydroboration and oxidation. On the other hand 3β-acetoxy-5α-hydroxy-6α-methylsulphonoxyandrostan-17-one underwent O–alkyl fission with rearrangement to form the A-homo-B-nor-steroid (22) rather than an aromatic product. This unsaturated ketone showed carbonyl absorption in the i.r. at 1735 and 1670 cm^{-1}; its n.m.r. spectrum contained an AB system at τ 4·02 and 3·63 (*J* 12·5 Hz). The resonance at τ 3·63 appeared as a doublet of triplets (*J* 4 Hz) indicating that there were two protons allylic to the αβ-unsaturated ketone. Steroidal 5α-hydroxy-6α-toluene-*p*-sulphonates are known [15] to undergo a pinacolic rearrangement to form A-homo-B-nor-steroids. Structure (22) merely represents an extension of this in which the acetoxy-group has been eliminated in a subsequent step with the formation of the unsaturated ketone.

EXPERIMENTAL

General experimental details have been described previously.[16]

4β,17β-Diacetoxy-3β,5α-dihydroxyandrostane (7) [3] had m.p. 229°, $[\alpha]_D^{20}$ +5° (*c* 0·3) (lit.,[3] m.p. 228—230°, $[\alpha]_D$ +4·3°), τ 9·24 (3H, s), 8·88 (3H, s), 7·96 (3H, s), 7·88 (3H, s), 5·71 (1H, m), 5·42 (1H, t, *J* 8 Hz), and 5·06 (1H, d, *J* 4 Hz). Chromatography of the mother liquors from its preparation on alumina gave 3β,17β-diacetoxy-4β,5α-dihydroxyandrostane (6), m.p. 205—206°, $[\alpha]_D^{20}$ −3° (*c* 0·27) (lit.,[3] m.p. 205—207° $[\alpha]_D$ +3·6°) (Found: C, 67·4; H, 8·9. Calc. for $C_{23}H_{36}O_6$: C, 67·6; H, 8·9%), τ 9·22 (3H, s), 8·82 (3H, s), 7·98 (3H, s), 7·93 (3H, s), 6·32br (1H, s, $W_{\frac{1}{2}}$ 5 Hz), 5·40 (1H, t, *J* 8 Hz), and 4·66 (1H, m). The 3β-*methanesulphonate* of 4β,17β-diacetoxy-3β,5α-dihydroxyandrostane, prepared with methanesulphonyl chloride in pyridine, crystallized from acetone–light petroleum as plates, m.p. 176—177° (decomp.), $[\alpha]_D^{20}$ 0° (*c* 0·25) (Found: C, 57·6; H, 7·7. $C_{24}H_{38}O_8S,H_2O$ requires C, 57·15; H, 7·9%), $\nu_{max.}$ 3500, 1745, and 1710 cm^{-1}, τ 9·21 (3H, s), 8·85 (3H, s), 7·96 (3H, s), 7·87 (3H, s), 7·00 (3H, s), 5·40 (1H, t, *J* 7 Hz), and 4·70 (2H, m).

3β,17β-*Diacetoxy*-4α,5α-*dihydroxyandrostane* (8).—3β,17β-Diacetoxyandrost-4-ene [17] (0·5 g) in pyridine (3 ml) was treated with osmium tetroxide (0·5 g) overnight. The solution was treated with an excess of aqueous sodium hydrogen sulphite and the steroid was recovered in chloroform. The extract was thoroughly washed with dilute hydrochloric acid and chromatographed on alumina. Elution with 40% ethyl acetate–light petroleum gave 3β,17β-*diacetoxy*-4α,5α-*dihydroxyandrostane* (350 mg), which crystallized from ethyl acetate–light petroleum as needles, m.p. 205—208°, $[\alpha]_D^{20}$ +10° (*c* 0·3) (Found: C, 67·4; H, 9·0. $C_{23}H_{36}O_6$ requires C, 67·6; H, 8·9%), $\nu_{max.}$ 3550 and 1725 cm^{-1}, τ 9·20 (3H, s), 8·98 (3H, s), 7·95 (3H, s), 7·89 (3H, s), 6·38 (1H, d, *J* 9 Hz), 5·37 (1H, t, *J* 8 Hz), and 4·95 (1H, m).

3β-*Acetoxy*-4α,5α-*androstane*-6,17-*dione* (10).—A solution of 3β-acetoxyandrost-4-ene-6,17-dione [5] (670 mg) and osmium tetroxide (500 mg) in pyridine (20 ml) was stirred at room temperature overnight. A solution of sodium disulphite (0·9 g) in water (15 ml) and pyridine (10 ml) was then added. After a further 30 min, the orange solution was extracted with dichloromethane. The combined extracts were washed with water, dried, and evaporated to afford 3β-*acetoxy*-4α,5α-*dihydroxyandrostane*-6,17-*dione* (400 mg), which crystallized from methanol as needles, m.p. 239—241°, $[\alpha]_D^{20}$ +15° (*c* 0·2) (Found: C, 66·9; H, 7·95. $C_{21}H_{30}O_6$ requires C, 66·6; H, 8·0%), $\nu_{max.}$ 3480, 1740, 1730, and 1715 cm^{-1}, τ 9·15 (6H, s), 7·94 (3H, s), 7·19 (1H, d, *J* 3 Hz), 5·75 (1H, q, *J* 10 and 3 Hz) (this resonance collapsed to a doublet, *J* 10 Hz, when the solution was treated with deuterium oxide), and 4·9br (1H, m).

3β,17β-*Diacetoxy*-4α,5α-*dihydroxyandrostan*-11-*one* (11).—3β,17β-Diacetoxyandrost-4-en-11-one [7] (500 mg) in pyridine (10 ml) was treated with osmium tetroxide (500 mg) for 4 h. The solution was treated with an excess of aqueous sodium disulphite and the steroid was recovered in chloroform. The extract was washed thoroughly with dilute hydrochloric acid, dried, and evaporated to give 3β,17β-*diacetoxy*-4α,5α-*dihydroxyandrostan*-11-*one* (350 mg), which crystallized from acetone–light petroleum as needles, m.p. 235—236°, $[\alpha]_D^{20}$ +20° (*c* 0·3) (Found: C, 65·3; H, 7·5. $C_{23}H_{34}O_7$ requires C, 65·4; H, 8·1%), $\nu_{max.}$ 3550br, 1720, and 1700 cm^{-1}, τ 9·26 (3H, s), 8·83 (3H, s), 7·98 (3H, s), 7·93 (3H, s), 6·42 (1H, d, *J* 9 Hz), 5·20 (1H, t, *J* 8 Hz), and 5·10 (1H, m).

3β,6β,17β-*Triacetoxy*-5α-*hydroxyandrostane* (16).—3β,17β-Diacetoxy-5α,5α-epoxyandrostane (3·0 g) in acetone (100 ml) was treated with a solution of periodic acid (3·5 g) in water (30 ml) at room temperature for 5 h. The solution was carefully diluted with water and the product (2·1 g) filtered off and recrystallized from aqueous methanol. It was acetylated with acetic anhydride in pyridine to give 3β,6β,17β-*triacetoxy*-5α-*hydroxyandrostane* (1·7 g), which crystallized from ether–light petroleum as needles, m.p. 170—171° (change of form at 145—150°), $[\alpha]_D^{20}$ −2° (*c* 0·2) (Found: C, 66·5; H, 8·4. $C_{25}H_{38}O_7$ requires C, 66·6; H, 8·5%), $\nu_{max.}$ 3450 and 1730br cm^{-1}, τ 9·20 (3H, s), 8·85 (3H, s), 7·98 (3H, s), 7·95 (3H, s), 7·93 (3H, s), 5·38 (1H, t, *J* 8 Hz), 5·25br (1H, s), and 4·90 (1H, m).

3β,17β-*Diacetoxy*-5α,6α-*dihydroxyandrostane*.— 3β,17β-Diacetoxyandrost-5-ene (1·2 g) in pyridine (10 ml) was treated with osmium tetroxide (1 g) for 24 h. An excess of aqueous sodium hydrogen sulphite was added and the solution was stirred for 1 h, then poured into dilute hydrochloric acid. The product was recovered in chloroform. The *diol* crystallized from acetone–light petroleum as needles, m.p. 174—175°, $[\alpha]_D^{20}$ +62° (*c* 0·2) (Found: C, 67·3; H, 8·9. $C_{23}H_{36}O_6$ requires C, 67·6; H, 8·9%), $\nu_{max.}$ 3550, 1730, and 1710 cm^{-1}, τ 9·24 (3H, s), 9·03 (3H, s), 7·98 (6H, s), 6·30 (1H, m), 5·40 (1H, t, *J* 8 Hz), and 4·95 (1H, m). 3β,6α,17β-*Triacetoxy*-5α-*hydroxyandrostane* (19), prepared with acetic anhydride in pyridine, crystallized from acetone–light petroleum as needles, m.p. 175°, $[\alpha]_D^{20}$ +5° (*c* 0·2) (Found: C, 66·3; H, 8·3. $C_{25}H_{38}O_7$ requires C, 66·6; H, 8·5%), $\nu_{max.}$ 3450, 1740, and 1710 cm^{-1}, τ 9·24 (3H, s), 8·96 (3H, s), 7·97 (6H, s), 7·93 (3H, s), 5·40 (1H, t, *J* 8 Hz), and 5·00 (2H, m).

3β-*Acetoxy*-5α-*hydroxy*-6α-*methylsulphonoxyandrostan*-17-*one* (20), prepared from 3β-acetoxy-5α,6α-dihydroxyandrostan-17-one [18] with methanesulphonyl chloride in pyridine, crystallized from light petroleum as needles, m.p.

[14] D. L. Garmaise and C. W. Shoppee, *J. Chem. Soc.*, 1953, 245.

[15] M. Nussim and Y. Mazur, *Tetrahedron*, 1968, **24**, 5337.

[16] J. R. Hanson and T. D. Organ, *J. Chem. Soc.* (*C*), 1970, 573.

[17] S. Julia and C. Moutonnier, *Bull. Soc. chim. France*, 1964, 321.

[18] A. A. Akhrem and I. G. Zavel'skaya, *Zhur. obshchei. Khim.*, 1962, **32**, 50 (*Chem. Abs.*, 1962, **57**, 13,821).

188—189°, $[\alpha]_D^{20}$ +68° (*c* 0·2) (Found: C, 60·0; H, 7·7; $C_{22}H_{34}O_7S$ requires C, 59·7; H, 7·75%), $\nu_{max.}$ 3520, 1735, and 1720 cm^{-1}, τ 9·17 (3H, s), 8·98 (3H, s), 8·00 (3H, s), 6·98 (3H, s), 5·20 (1H, m), and 4·90 (1H, m).

6β-*Acetoxy*-5α-*hydroxy*-3β-*methoxyandrostan*-17-*one* (17).—3β-Methoxyandrost-5-en-17-one [19] (2·0 g) in chloroform (50 ml) was treated with *m*-chloroperbenzoic acid (2·5 g) at room temperature overnight. The solution was diluted with chloroform, shaken with aqueous iron(II) sulphate, dilute hydrochloric acid, aqueous sodium hydrogen carbonate, and water, dried, and evaporated to give 5α,6α-*epoxy*-3β-*methoxyandrostan*-17-*one* (1·5 g), which crystallized from acetone as plates, m.p. 165—167°, $[\alpha]_D^{20}$ −11° (*c* 0·2) (Found: C, 76·0; H, 8·8. $C_{20}H_{28}O_3$ requires C, 75·9; H, 8·9%), $\nu_{max.}$ 1735 cm^{-1}, τ 9·18 (3H, s), 8·92 (3H, s), 7·05 (1H, d, *J* 4 Hz), and 6·67 (3H, s, +1H, m). The epoxide (1·2 g) in acetone (100 ml) was treated with periodic acid (3 g) in water (10 ml) at room temperature for 6 h. The lachrymatory solution was concentrated and diluted with water, and the product was recovered in ethyl acetate and chromatographed on alumina. Elution with 10% methanol in ether gave 5α,6β-*dihydroxy*-3β-*methoxyandrostan*-17-*one* (520 mg), which crystallized from methanol as poorly soluble needles, m.p. 281—282° (Found: C, 71·55; H, 9·9. $C_{20}H_{32}O_4$ requires C, 71·4; H, 9·6%), $\nu_{max.}$ 3500 and 1730 cm^{-1}. The 6β-*acetate* (17), prepared with acetic anhydride in pyridine, crystallized from acetone–light petroleum as needles, m.p. 200—201°, $[\alpha]_D^{20}$ +23° (*c* 0·2) (Found: C, 70·1; H, 9·5. $C_{22}H_{34}O_5$ requires C, 69·8; H, 9·05%), $\nu_{max.}$ 3500, 1735, and 1715 cm^{-1}, τ 9·12 (3H, s), 8·85 (3H, s), 7·94 (3H, s), 6·67 (3H, s), 6·45 (1H, m), and 5·21 (1H, m).

Reactions with Hydrobromic Acid in Glacial Acetic Acid.—(*a*) 3β,17β-Diacetoxy-4β,5α-dihydroxyandrostane (6) (450 mg) in glacial acetic acid (4 ml) and 48% hydrobromic acid (1 ml) was heated under reflux for 15 min. The solution went rapidly blue, then red. It was cooled and poured into an excess of aqueous sodium hydrogen carbonate. The steroids were recovered in ether; the extract was washed with water, dried, and evaporated. The residue (250 mg) was chromatographed on alumina. Elution with 6% ether–light petroleum gave 17-bromo-4-methyloestratriene (20 mg) as an oil, identified by its mass spectrum. Elution with 15% ether–light petroleum gave 17β-acetoxy-4-methyloestra-1,3,5(10)-triene (5) (36 mg), m.p. 186° (lit.,[13] 188°), identified by its i.r. spectrum. Elution with ether gave testosterone acetate (9) (10 mg), m.p. 140—142°, identified by its i.r. spectrum.

(*b*) 17β-Acetoxy-4-methyloestra-1,3,5(10)-triene was obtained under similar conditions from the following steroids:

Steroid	Yield of oestratriene (mg)
3β,17β-Diacetoxy-4α,5α-dihydroxyandrostane (8) (175 mg)	35 [a]
4β,17β-Diacetoxy-3β,5α-dihydroxyandrostane (7) (200 mg)	30 [b]
4β,17β-Diacetoxy-5α-hydroxy-3β-methylsulphonoxyandrostane (200 mg)	40
3β,6β,17β-Triacetoxy-5α-hydroxyandrostane (16) (175 mg)	42
3β,17β-Diacetoxy-5α,6β-dihydroxyandrostane (450 mg)	60 [c]

[a] Together with testosterone acetate (15 mg). [b] Together with 17-bromo-4-methyloestratriene (8 mg) and testosterone acetate (15 mg). [c] Together with 17-bromo-4-methyloestratriene (60 mg).

(*c*) 3β,6β-Diacetoxy-5α-hydroxyandrostan-17-one (15) (1 g) gave the anthrasteroid (80 mg), m.p. 133—135° (lit.,[3] 140°), and 4-methyloestratriene-17-one (160 mg), m.p. 178° (lit.,[20] 184—186°) identified by their i.r. spectra.

6β-Acetoxy-5α-hydroxy-3β-methoxyandrostan-17-one (17) (210 mg) gave 4-methyloestratriene-17-one (45 mg), identified by its i.r. spectrum.

(*d*) 3β-Acetoxy-4α,5α-dihydroxyandrostane-6,17-dione (10) (100 mg), dissolved in glacial acetic acid (2 ml) and 48% hydrobromic acid (0·5 ml), was heated under reflux for 15 min. The solution was poured into aqueous sodium hydrogen carbonate and the steroid was recovered in ether. The extract was washed with water, dried, and evaporated. The residue (60 mg) was chromatographed (preparative t.l.c.) in 40% ethyl acetate–light petroleum to give 1-methyloestra-1,3,5(10)-triene-6,17-dione (10 mg), which crystallized from light petroleum as needles, m.p. 159—160° (lit.,[1] 156—158°), and androst-4-ene-3,6,17-trione (10 mg), which crystallized from light petroleum as needles, m.p. 220—221° (lit.,[6] 216—217°) ($\lambda_{max.}$ 248 nm; *m/e* 300). The products were identified by comparison of their i.r. spectra with those of authentic samples.

(*e*) 3β,17β-Diacetoxy-4α,5α-dihydroxyandrostan-11-one (11) (580 mg) in glacial acetic acid (4 ml) and 48% hydrobromic acid (1 ml) was heated under reflux for 15 min. The red solution was poured into aqueous sodium hydrogen carbonate and the steroid was recovered in chloroform and chromatographed on alumina. Elution with light petroleum gave 17β-*acetoxy*-1-*methyloestra*-1,3,5(10)-*trien*-11-*one* (13) (10 mg), m.p. 208—209° (Found: C, 76·6; H, 8·4. $C_{21}H_{26}O_3$ requires C, 77·3; H, 8·0%), $\nu_{max.}$ 1735, 1710, and 1590 cm^{-1}, τ 9·22 (3H, s), 8·11 (3H, s), 8·00 (3H, s), 6·52 (1H, d, *J* 10 Hz, 9-H), 5·12 (1H, t, *J* 8 Hz), and 3·10 (3H, m). Further elution, with 25% ether–light petroleum, gave 17β-acetoxyandrost-4-ene-3,11-dione (12) (160 mg), which crystallized from acetone–light petroleum as needles, m.p. 160—162° (lit.,[8] 162—163°), $\nu_{max.}$ 1720, 1700, 1665, and 1610 cm^{-1}, τ 9·20 (3H, s), 8·58 (3H, s), 7·96 (3H, s), 5·20 (1H, t, *J* 8 Hz), and 4·28 (1H, s).

(*f*) 3β,6α,17β-Triacetoxy-5α-hydroxyandrostane (19) (550 mg) in glacial acetic acid (4 ml) containing 48% hydrobromic acid (1 ml) was heated under reflux for 15 min. The red solution was poured into aqueous sodium hydrogen carbonate. The steroid was recovered in chloroform and chromatographed on alumina. Elution with 30—50% ether–light petroleum gave 3β,17β-diacetoxyandrostan-6-one (21) (210 mg), which crystallized from acetone–light petroleum as needles, m.p. 178—179° (lit.,[14] 176—178°), identified by its i.r. spectrum. In another experiment 17-bromo-4-methyloestratriene (10 mg), identified by its mass spectrum, and 17β-acetoxy-4-methyloestratriene (20 mg), identified by its i.r. spectrum, were also obtained.

(*g*) 3β-Acetoxy-5α-hydroxy-6α-methylsulphonoxyandrostan-17-one (20) (290 mg) in glacial acetic acid (4 ml) containing hydrobromic acid (1 ml) was heated under reflux for 15 min. The red solution was poured into aqueous sodium hydrogen carbonate. The steroid was recovered in chloroform and chromatographed on alumina. Elution with 10—20% ether–light petroleum gave 10(5 → 6)abeo-*androst*-3-*ene*-5,17-*dione* (22) (80 mg), which crystallized from light petroleum as blades, m.p. 130—131°, $[\alpha]_D^{20}$ +46° (*c* 0·2) (Found: C, 79·8; H, 9·1. $C_{19}H_{26}O_2$ requires C, 79·7; H,

[19] A. Butenandt and W. Grosse, *Ber.*, 1936, **69**, 2776.

[20] E. Caspi, P. K. Grover, N. Grover, E. J. Lynde, and T. Nussbaumer, *J. Chem. Soc.*, 1962, 1710.

9·15%), $\nu_{max.}$ 1735 and 1670 cm^{-1}, τ 9·11 (3H, s), 8·93 (3H, s), 4·02 (1H, d, J 12·5 Hz), and 3·63 (1H, dt, J 12·5 and 4 Hz), $\lambda_{max.}$ 228 nm (ε 8500).

3β,17β-*Diacetoxyandrostan*-6-*one*.— 3β,17β-Diacetoxyandrost-5-ene (1·2 g) in tetrahydrofuran (25 ml) was treated with M-borane in tetrahydrofuran (15 ml) under nitrogen for 30 min. Water (20 ml) was added, followed dropwise by 2N-sodium hydroxide (20 ml) and 30% hydrogen peroxide (20 ml) over 30 min. After a further 1 h the solution was acidified with dilute hydrochloric acid and extracted with ether. The extract was washed with aqueous iron(II) sulphate, dried, and evaporated. The residue was taken up in acetone (15 ml) and treated with 8N-chromium trioxide reagent (1 ml) for 30 min. Methanol (1 ml) was added; the solution was concentrated and diluted with water and the steroid was recovered in ether. Chromatography on alumina gave, in the fractions eluted with 40% ether–light petroleum, 3β,17β-diacetoxyandrostan-6-one (21) (350 mg), which crystallized from acetone–light petroleum as needles, m.p. 174—176°, $[\alpha]_D^{20}$ −32° (c 0·2) (Found: C, 70·45; H, 8·9. Calc. for $C_{23}H_{34}O_5$: C, 70·7; H, 8·8%), $\nu_{max.}$ 1740 and 1710 cm^{-1}, τ 9·13 (6H, s), 7·98 (3H, s), 7·96 (3H, s), and 5·36 (1H, t, J 8 Hz).

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