The Reaction of Some Substituted 2α,3α-Epoxy-5α-hydroxyandrostanes with Hydrogen Bromide in Acetic Acid

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Whereas the reaction of 2α,3α-epoxy-5α-hydroxyandrostanes with hydrogen bromide in acetic acid readily gives 4-methyloestratrienes, the presence of an additional 4β-acetoxy, 6α- or 6β-hydroxy group in the substrate leads to the formation of non-aromatic products. The 6α-alcohol gave 3α-acetoxy-2β-bromo-5β-androstane-6,17-dione, the structure of which was confirmed by X-ray crystallography, whilst the 6β-alcohol gave this ketone and 3α,6β-diacetoxy-2α,5α-epoxyandrostan-17-one.

Treatment of steroidal 5α-hydroxy-2α,3α-epoxides **1** with hydrogen bromide in glacial acetic acid leads to 4-methyl-oestratrienes **2** via a dienol–benzene rearrangement.[1] The reaction is modified by the presence of a C-6 carbonyl group as in **3** and the major product is then the 1-methyloestratrien-6-one **4**. Other examples of this aromatization reaction which we have uncovered,[2] show that it requires two double-bond equivalents and a carbocation source in the substrate and that these can be disposed at various positions on rings A and B of the steroids. The related dienone:phenol rearrangement[3] effectively utilizes three double bond equivalents and a carbo-cation source. In the light of the generality of the dienol–benzene rearrangement, we therefore considered the possibility that the steroidal dienone–phenol rearrangement might also be a more general reaction provided that there was a group present in the molecule which might generate a C-3 ketone. We have, therefore, examined the reaction of the 2α,3α-epoxy-5α-hydroxyandrostanes **10, 16** and **17** which contain additional substituents at C-4 or C-6 using conditions (hydrogen bromide in glacial acetic acid) which might, in the light of our previous work,[1] lead to aromatization. The results form the subject of this paper.

The substrates were prepared as follows. Dehydroisoandro-sterone **5** was converted into the 5α,17β-dihydroxyandrost-2-ene **6** following the modified literature procedure.[4] Oxidation with chromium trioxide[5] smoothly generated 5α-hydroxy-androst-2-ene-4,17-dione **7**. Since this compound could not be epoxidized with m-chloroperbenzoic acid (MCPBA), it was reduced with methanolic sodium borohydride to give the 4β,5α,17β-trihydroxyandrost-2-ene **8** which was, in turn, acetyl-ated with acetic anhydride in pyridine to give the 4β,17β-diacetate **9**. Reduction of the analogous 5α-hydroxycholest-2-en-4-one with sodium borohydride has been shown[6] to give the 4β-alcohol. Epoxidation of **9** with MCPBA gave the desired epoxide **10** (Scheme 1).

An alternative approach which was explored, involved the epoxidation of 3β,17β-diacetoxyandrost-4-ene **11**. This gave 3β,17β-diacetoxy-4α,5α-epoxyandrostane **12** and 4β,17β-diacet-oxy-3β,5α-dihydroxyandrostane **13**.[7] Treatment of the epoxide with acid gave further amounts of the latter by an acetoxy migration.[7] The 3β-alcohol was then converted into its methanesulphonate **14** with methanesulphonyl chloride. How-ever, in contrast to the reaction of 5α-hydroxy 3β-methane-sulphonates lacking a 4-acetoxy group,[1] treatment with colli-dine gave the 3α,5α-ether **15** rather than the Δ²-ene (Scheme 2). The electron-withdrawing effect of the 4β-acetate clearly modifies the elimination reaction of a 3-sulphonate in a similar manner to the way in which it affects the i-steroid rearrange-ment.[8] Similar 3α,5α-ether formation reactions have been
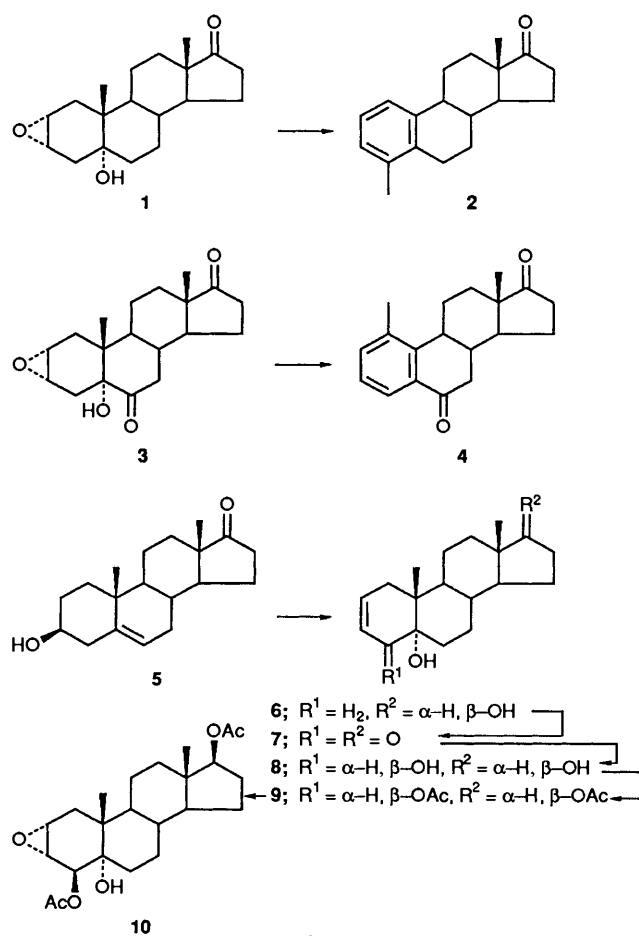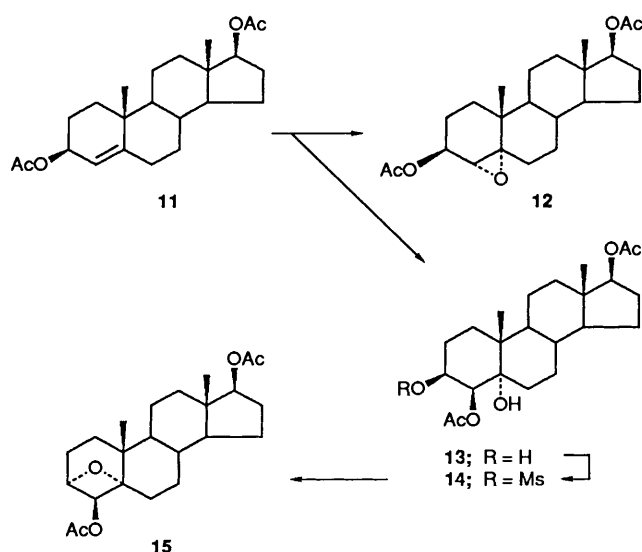

Scheme 1

observed[9] but in the presence of potassium tert-butoxide as the base.

5α,6α-Dihydroxy- and 5α,6β-dihydroxyandrost-2-en-17-one were each prepared from the corresponding methanesulphon-ates by elimination with collidine.[10] Epoxidation with MCPBA gave the required 2α,3α-epoxides **16** and **17**.

Treatment of the epoxide **10** with hydrogen bromide in glacial acetic acid gave the unstable bromo acetate **18** together with a trace of 4,17β-diacetoxyandrost-4-en-3-one **19**.[11] There were no detectable phenolic products. The structure of the unstable **18** was tentatively assigned on the basis of its ^{1}H NMR spectrum. This showed signals at δ 4.27 (1 H, br d, J 6.6 Hz, 2-CHBr), 4.66 [d, J 2.8 Hz, 4-CH(OAc)] and 4.87 [dd, J 1 and 2.8 Hz,

Scheme 2

3-C*H*(OAc)]. Irradiation of the signal at δ 4.87 collapsed the doublet at δ 4.66 and sharpened the signal at δ 4.27. These small ring A H–H coupling constants may be accommodated within the structure **18**.

Reaction of 5α,6α-dihydroxy-2α,3α-epoxyandrostan-17-one **16** with hydrogen bromide in glacial acetic acid gave 3α-acetoxy-2β-bromo-5βH-androstane-6,17-dione **20** the structure and stereochemistry of which was established by X-ray crystallography (see Fig. 1). The isomeric 5α,6β-dihydroxy 2α,3α-epoxide **17** gave the same diketone **20** together with a small amount of 4-methyloestra-1,3,5(10)-trien-17-one **2**, presumably formed by a reductive step. A further product was formulated as the diacetoxy ether **21**. The ¹H NMR spectrum revealed the presence of two acetoxy groups (δ 2.05 and 2.09), two C*H*(OAc) groups (δ 4.73 and 5.38) and a further CHO signal (δ 4.42). The absence of hydroxy absorption in the IR spectrum showed that this must

be an ether group. There were two possible structures which would accommodate this (**21** and **22**). These were distinguished by NOE and decoupling studies. Irradiation of the methyl signal (δ 1.08, H-19) produced NOE enhancements of the CH(OAc) signal at 4.73 (5%) and a double doublet (δ 2.55, *J* 7.1 and 13.9 Hz, 6%). The CH(OAc) signal was therefore assigned to the ring A group in either structure **21** or **22**. The CH(OAc) signal at δ 5.38 was a narrow triplet (*J* 2.8 Hz) characteristic of a H-6α signal. Decoupling experiments showed that the signal at δ 4.73 was coupled to the signal at δ 2.55 and also to a double doublet at δ 1.35. The signal at δ 2.55 was also coupled (*J* 13.9 Hz) to the signal at 1.35. These are therefore either the 4-H signals of structure **21** or the 1-H signals of **22**. An NOE experiment based on irradiating the signal at δ 5.38 (6-H) produced a 15% enhancement of the doublet at 1.35 which must therefore be at 4-H and thus the structure of the ether was 3α,6β-diacetoxy-2α,5α-epoxyandrostan-17-one **21**. The formation of the 6-ketone may be rationalized in terms of the dehydration of the 5α-hydroxy group and an initial diaxial opening of the 2α,3α-epoxide. However in the 5β-androstanes, the 2β- and 3α-groups then become equatorial substituents. With the 6β-alcohol dehydration takes place less easily. The diaxial opening of the epoxide produces a 2β-bromo substituent which is then displaced by a 5α-hydroxy group with the formation of the ether.

Experimental

IR spectra were determined as Nujol mulls and ¹H NMR spectra were obtained for solutions in deuteriochloroform on a Bruker WM 360 spectrometer (*J* values are given in Hz). Extracts were dried over sodium sulphate. Silica for chromatography was Merck 9385. Light petroleum refers to the fraction boiling in the range 60–80 °C.

Preparation of 4β,5α,17β-*Trihydroxyandrost-2-ene* **8**.—5α-Hydroxyandrost-2-ene-4,17-dione **7**[5] (350 mg) in methanol (10 cm³) was treated with sodium borohydride (160 mg) at 0 °C for 75 min. The excess reagent was destroyed with acetic acid (0.2 cm³) and then the solution was poured into water and extracted
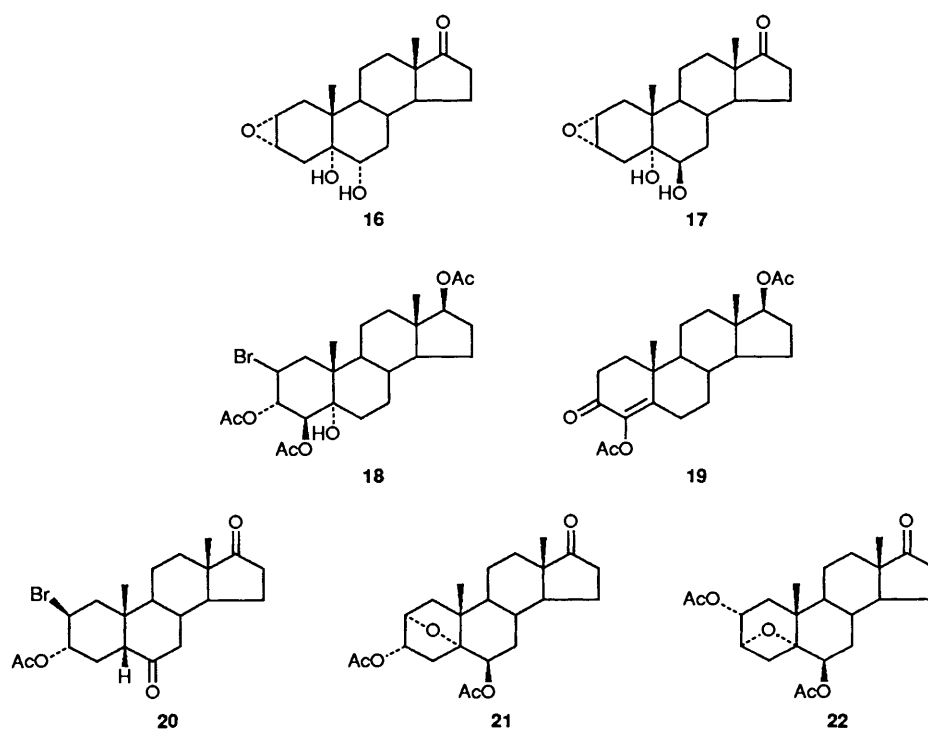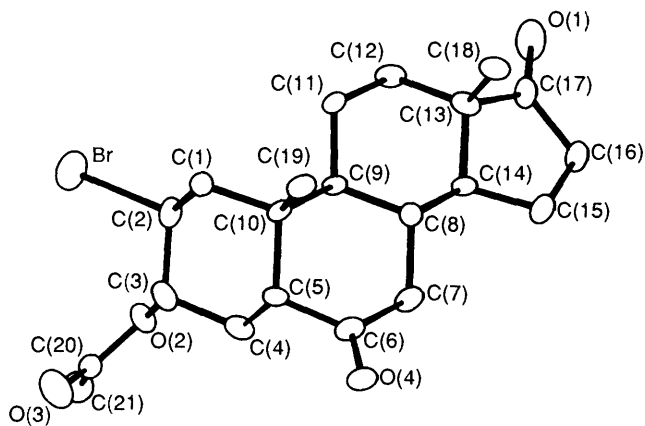
Fig. 1 X-ray molecular structure of 3α-acetoxy-2β-bromo-5β-androstane-6,17-dione (20)

with ethyl acetate. The extract was washed with water, dried and the solvent evaporated to afford the *title compound* 8 (301 mg) which crystallized from acetone as needles, m.p. 184–186 °C (Found: C, 70.5; H, 10.1. $C_{19}H_{30}O_3 \cdot H_2O$ requires C, 70.5; H, 9.9%), v_{max}/cm^{-1} 3394br; $\delta(C_5D_5N)$ 1.01 (3 H, s, 18-H), 1.45 (3 H, s, 19-H), 3.87 (1 H, t, *J* 8.4, 17-H), 4.32 (1 H, s, 4-H) and 5.95 and 6.06 (each 1 H, m, 2 and 3-H).

4β,17β-*Diacetoxy-5α-hydroxyandrost-2-ene* 9. This was prepared with acetic anhydride in pyridine at room temperature and crystallized from acetone–light petroleum as needles, m.p. 203–205 °C (Found: C, 69.0; H, 8.7. $C_{23}H_{34}O_5 \cdot 0.5H_2O$ requires C, 69.1; H, 8.8%), v_{max}/cm^{-1} 3514, 1729 and 1716; δ 0.79 (3 H, s, 18-H), 1.04 (3 H, s, 19-H), 2.04 and 2.05 (each 3 H, s, OAc), 4.59 (1 H, t, *J* 8.5, 17-H), 4.92 (1 H, d, *J* 4.4, 4-H), 5.69 (1 H, m, 2-H) and 5.94 (1 H, m, 3-H).

Preparation of 4β,17β-*Diacetoxy-5α-hydroxy-2α,3α-epoxy-androstane* 10.—4β,17β-Diacetoxy-5α-hydroxyandrost-2-ene 9 (220 mg) in chloroform (40 cm³) was treated with *m*-chloroperbenzoic acid (MCPBA) (250 mg) at 0 °C. The mixture was allowed to attain room temperature and stirred for 2 d. It was then washed with saturated aqueous sodium hydrogencarbonate and water and dried. The solvent was evaporated under reduced pressure to give a residue which was chromatographed on silica. Elution with 30% ethyl acetate–light petroleum gave the *title compound* 10 (170 mg) which crystallized from ethyl acetate–light petroleum as needles, m.p. 149–150 °C (Found: C, 67.8; H, 8.4. $C_{23}H_{34}O_6$ requires C, 67.9; H, 8.4%), v_{max}/cm^{-1} 3645 and 1741; δ 0.77 (3 H, s, 18-H), 1.03 (3 H, s, 19-H), 2.04 and 2.12 (each 3 H, s, OAc), 3.11 (1 H, d, *J* 2.4, 3-H), 3.27 (1 H, m, 2-H), 4.57 (1 H, t, *J* 8.5, 17-H) and 5.11 (1 H, s, 4-H).

Formation of 4β,17β-*Diacetoxy-3α,5α-epoxyandrostane.*—4β,17β-Diacetoxy-3β,5α-dihydroxyandrostane 13[7] (2 g) in dry, freshly redistilled pyridine (10 cm³) was treated with methanesulphonyl chloride (0.75 cm³) at 0 °C. The mixture was allowed to attain room temperature and stirred for 2 h. The solution was poured into dil. hydrochloric acid, and extracted with ethyl acetate. The extract was washed with dil. hydrochloric acid, saturated aqueous sodium hydrogencarbonate and water, and dried. The solvent was evaporated to give a residue of the methanesulphonate (2.2 g) which was heated at reflux under nitrogen with freshly redistilled collidine (trimethylpyridine) (25 cm³) for 2 h. The solution was poured into dil. hydrochloric acid (100 cm³) and stirred for 20 min. The products were recovered in ether. The extract was washed with dil. hydrochloric acid, saturated aqueous sodium hydrogencarbonate and water and dried. The solvent was evaporated to give a residue which was chromatographed on silica. Elution with 10% ethyl acetate–

light petroleum gave the *title compound* 15 (1.87 g) which crystallized from ethyl acetate–light petroleum as needles, m.p. 167–168 °C (Found: C, 70.8; H, 8.8. $C_{23}H_{34}O_5$ requires C, 70.7; H, 8.8%), v_{max}/cm^{-1} 1730; δ 0.80 (3 H, s, 18-H), 0.94 (3 H, s, 19-H), 2.04 and 2.08 (each 3 H, s, OAc), 4.61 (1 H, m, 3-H) and 5.06 (1 H, d, *J* 5.9, 4-H).

Preparation of 5α,6α-*Dihydroxy-2α,3α-epoxyandrostan-17-one* 16.—5α,6α-Dihydroxyandrost-2-en-17-one[10] (480 mg) in chloroform (30 cm³) was treated with MCPBA (500 mg) at 0 °C. The mixture was allowed to attain room temperature and stirred for 20 h. It was then washed with saturated aqueous sodium sulphite, saturated aqueous sodium hydrogen carbonate and water and dried. The solvent was evaporated under reduced pressure to afford the *title compound* 16 (398 mg) which crystallized from acetone as prisms, m.p. 158–159 °C (Found: C, 71.2; H, 8.8. $C_{19}H_{28}O_4$ requires C, 71.2; H, 8.8%), v_{max}/cm^{-1} 3617, 3420 and 1735; δ 0.85 (3 H, s, 18-H), 0.92 (3 H, s, 19-H), 3.34 and 3.44 (each 1 H, m, 2- and 3-H) and 3.48 (1 H, d, *J* 1.5, 6-H).

Preparation of 5α,6β-*Dihydroxy-2α,3α-epoxyandrostan-17-one* 17.—5α,6β-Dihydroxyandrost-2-en-17-one[10] (1 g) in chloroform (50 cm³) was treated with MCPBA (1 g) at 0 °C. The mixture was allowed to attain room temperature and stirred for 23 h. It was then washed with saturated aqueous sodium sulphite, saturated aqueous sodium hydrogen carbonate and water and dried. The solvent was evaporated to afford the *title compound* 17 (910 mg) which crystallized from acetone as prisms, m.p. 192–195 °C (Found: C, 71.2; H, 8.7. $C_{19}H_{28}O_4$ requires C, 71.2; H, 8.8%), v/cm^{-1} 3508, 3460 and 1727; δ 0.87 (3 H, s, 18-H), 1.13 (3 H, s, 19-H), 3.34 (1 H, m, 2-H), 3.47 (1 H, m, 3-H), 3.61 (1 H, s, 6-H) and 3.70 (1 H, s, OH, exchanged with ^2H_2O).

Reactions with Hydrogen Bromide in Glacial Acetic Acid.—(a) A solution of 4β,17β-diacetoxy-5α-hydroxy-2α,3α-epoxyandrostane 10 (160 mg) in glacial acetic acid (5 cm³) and hydrobromic acid (0.5 cm³; 48%) was heated at reflux for 20 min. The reaction was cooled and the solution neutralized with sodium hydrogen carbonate. The products were recovered in ethyl acetate. The extract was washed with water, dried and the solvent evaporated to give a gum which was chromatographed on silica. Elution with 10% ethyl acetate–light petroleum gave 4,17β-diacetoxy-androst-4-en-3-one[11] (11 mg) as an oil (λ_{max}/nm 244; calc. 245); v_{max}/cm^{-1} 1742, δ 0.92 (3 H, s, 18-H), 1.25 (3 H, s, 19-H), 2.06 and 2.07 (each 3 H, s, OAc) and 4.60 (1 H, t, *J* 8.5, 17-H). Elution with 15% ethyl acetate–light petroleum gave 3α,17β-diacetoxy-2β-bromo-5α-hydroxyandrostane (70 mg) as an unstable oil, v_{max}/cm^{-1} 3463 and 1741; δ 0.75 (3 H, s, 18-H), 1.13 (3 H, s, 19-H), 2.0 and 2.05 (each 3 H, s, OAc), 4.27 (1 H, d, *J* 6.6, 2-H), 4.54 (1 H, t, *J* 8.5, 17-H), 4.66 (1 H, d, *J* 2.8, 4-H) and 4.87 (1 H, dd, *J* 1 and 2.8, 3-H).

(b) A solution of 5α,6α-dihydroxy-2α,3α-epoxyandrostan-17-one 16 (200 mg) in glacial acetic acid (6 cm³) and hydrobromic acid (0.5 cm³; 48%) was heated at reflux for 25 min. The reaction was cooled and the solution was neutralized with sodium hydrogen carbonate. The products were recovered with ethyl acetate. The extract was washed with water and dried, and the solvent evaporated to give a gum which was chromatographed on silica. Elution with 30% ethyl acetate–light petroleum gave 3α-*acetoxy-2β-bromo-5β-androstan-6,17-dione* 20 (151 mg) which crystallized from acetone as plates or methanol as needles, m.p. 235–236 °C (Found: C, 59.4; H, 6.9. $C_{21}H_{29}BrO_4$ requires C, 59.3; H, 6.9%), v_{max}/cm^{-1} 1747, 1731 and 1700; δ 0.88 (3 H, s, 18-H), 0.95 (3 H, s, 19-H), 2.09 (3 H, s, OAc), 4.11 (1 H, m, 2-H) and 4.90 (1 H, m, 3-H).

(c) A solution of 5α,6β-dihydroxy-2α,3α-epoxyandrostan-17-one 17 (600 mg) in glacial acetic acid (15 cm³) and hydrobromic

Table 1 Fractional atomic coordinates (× 10⁴) with estimated standard deviations in parentheses

	x	y	z
Br	2691.0(9)	7822	5408.1(7)
O(1)	−210(5)	9138(12)	−1783(5)
O(2)	1851(5)	3805(10)	4655(4)
O(3)	2854(6)	2460(13)	6095(5)
O(4)	4736(4)	2020(9)	1299(5)
C(1)	3752(6)	7229(12)	3388(6)
C(2)	2746(7)	6489(14)	3984(6)
C(3)	2905(7)	4469(14)	4234(6)
C(4)	3044(7)	3436(12)	3147(6)
C(5)	4002(6)	4256(11)	2489(6)
C(6)	4025(5)	3203(11)	1406(6)
C(7)	3073(7)	3634(12)	488(6)
C(8)	2881(6)	5682(11)	286(5)
C(9)	2754(5)	6629(10)	1404(6)
C(10)	3850(6)	6333(12)	2257(6)
C(11)	2426(7)	8661(11)	1254(6)
C(12)	1368(6)	8974(12)	378(6)
C(13)	1584(5)	8083(13)	−719(5)
C(14)	1795(6)	6023(11)	−514(5)
C(15)	1665(7)	5183(14)	−1679(6)
C(16)	637(7)	6257(15)	−2282(6)
C(17)	547(6)	7994(15)	−1623(5)
C(18)	2556(7)	9012(13)	−1295(8)
C(19)	4980(6)	7052(12)	1812(7)
C(20)	1942(7)	2785(16)	5566(6)
C(21)	759(8)	2137(16)	5843(8)

Table 2 Intramolecular distances (Å) and angles (°) with estimated standard deviations in parentheses

Br–C(2)	1.976(8)	O(1)–C(17)	1.212(12)
O(2)–C(3)	1.441(10)	O(2)–C(20)	1.321(10)
O(3)–C(20)	1.192(10)	O(4)–C(6)	1.210(9)
C(1)–C(2)	1.517(12)	C(1)–C(10)	1.523(11)
C(2)–C(3)	1.527(14)	C(3)–C(4)	1.531(11)
C(4)–C(5)	1.538(11)	C(5)–C(6)	1.515(11)
C(5)–C(10)	1.564(12)	C(6)–C(7)	1.503(10)
C(7)–C(8)	1.542(12)	C(8)–C(9)	1.530(10)
C(8)–C(14)	1.515(9)	C(9)–C(10)	1.553(9)
C(9)–C(11)	1.551(11)	C(10)–C(19)	1.544(10)
C(11)–C(12)	1.539(10)	C(12)–C(13)	1.512(11)
C(13)–C(14)	1.554(12)	C(13)–C(17)	1.527(8)
C(13)–C(18)	1.531(12)	C(14)–C(15)	1.521(11)
C(15)–C(16)	1.538(12)	C(16)–C(17)	1.513(14)
C(20)–C(21)	1.506(13)		
C(3)–O(2)–C(20)	119.0(6)	C(2)–C(1)–C(10)	113.0(7)
Br–C(2)–C(1)	108.6(6)	Br–C(2)–C(3)	109.2(5)
C(1)–C(2)–C(3)	111.2(7)	O(2)–C(3)–C(2)	108.2(7)
O(2)–C(3)–C(4)	107.0(7)	C(2)–C(3)–C(4)	109.8(6)
C(3)–C(4)–C(5)	112.4(7)	C(4)–C(5)–C(6)	108.2(6)
C(4)–C(5)–C(10)	113.8(6)	C(6)–C(5)–C(10)	111.1(6)
O(4)–C(6)–C(5)	122.0(6)	O(4)–C(6)–C(7)	121.5(7)
C(5)–C(6)–C(7)	116.4(6)	C(6)–C(7)–C(8)	113.8(6)
C(7)–C(8)–C(9)	109.6(6)	C(7)–C(8)–C(14)	110.9(6)
C(9)–C(8)–C(14)	109.5(6)	C(8)–C(9)–C(10)	111.7(6)
C(8)–C(9)–C(11)	112.6(6)	C(10)–C(9)–C(11)	112.5(6)
C(1)–C(10)–C(5)	106.4(6)	C(1)–C(10)–C(9)	113.4(6)
C(1)–C(10)–C(19)	107.4(6)	C(5)–C(10)–C(9)	108.9(6)
C(5)–C(10)–C(19)	108.4(6)	C(9)–C(10)–C(19)	112.1(6)
C(9)–C(11)–C(12)	112.9(6)	C(11)–C(12)–C(13)	109.9(6)
C(12)–C(13)–C(14)	108.9(6)	C(12)–C(13)–C(17)	116.8(6)
C(12)–C(13)–C(18)	112.8(7)	C(14)–C(13)–C(17)	99.6(7)
C(14)–C(13)–C(18)	113.6(6)	C(17)–C(13)–C(18)	104.5(6)
C(8)–C(14)–C(13)	111.5(6)	C(8)–C(14)–C(15)	120.8(7)
C(13)–C(14)–C(15)	104.7(6)	C(14)–C(15)–C(16)	102.7(7)
C(15)–C(16)–C(17)	106.3(6)	O(1)–C(17)–C(13)	125.2(9)
O(1)–C(17)–C(16)	126.3(7)	C(13)–C(17)–C(16)	108.5(7)
O(2)–C(20)–O(3)	123.0(8)	O(2)–C(20)–C(21)	111.5(7)
O(3)–C(20)–C(21)	125.5(9)		

acid (1.5 cm³; 48%) was heated under reflux for 25 min. The reaction was cooled and the solution was neutralized with sodium hydrogen carbonate. The products were recovered in ethyl acetate. The extract was washed with water and dried and the solvent evaporated to give a gum which was chromatographed on silica. Elution with 7% ethyl acetate–light petroleum gave 4-methyloestra-1,3,5(10)-trien-17-one **2** (20 mg) which crystallized from ethyl acetate–light petroleum as plates, m.p. 190–191 °C (lit.,[10] 190–192 °C); v_{max}/cm⁻¹ 1731; δ 0.90 (3 H, s, 18-H), 2.23 (3 H, s, Ar-Me), 7.04 (1 H, d, J 7.3, 3-H), 7.10 (1 H, t, J 7.7, 2-H) and 7.19 (1 H, d, J 7.8, 1-H). Elution with 10% ethyl acetate–light petroleum gave 3α,6β-*diacetoxy*-2α,5α-*epoxyandrostan*-17-*one* **21** (47 mg) which crystallized from acetone as plates, m.p. 215–217 °C (Found: C, 68.1; H, 8.0. $C_{23}H_{32}O_6$ requires C, 68.3; H, 8.0%), v_{max}/cm⁻¹ 1741; δ 0.90 (3 H, s, 18-H), 1.08 (3 H, s, 19-H), 2.05 and 2.09 (each 3 H, s, OAc), 4.42 (1 H, d, J 6.7, 2-H), 4.73 (1 H, dd, J 2.7 and 7.2, 3-H) and 5.38 (1 H, t, J 2.8, 6-H). Elution with 30% ethyl acetate–light petroleum gave 3α-acetoxy-2β-bromo-5β-androstane-6,17-dione **20** (295 mg) identical (IR and NMR spectroscopy) to the sample described above.

Crystal Structure Determination of Compound **20**.—*Crystal data.* $C_{21}H_{29}BrO_4$, $M = 425.4$, monoclinic, space group $P2_1$, $a = 11.466(3)$, $b = 7.375(2)$, $c = 11.983(2)$ Å, $\beta = 95.79(1)°$, $u = 1008.2$ Å³, $Z = 2$, $D_c = 1.40$ g cm⁻³, $F(000) = 444$. Monochromated Mo-Kα radiation, $\lambda = 0.710\,69$ Å, $\mu = 20.4$ cm⁻¹.

Data were collected using a piece *ca.* 0.6 × 0.5 × 0.1 mm, cut from a much larger needle-plate crystal, on an Enraf-Nonius CAD4 diffractometer operating in the θ–2θ mode with $\Delta\theta = (0.8 + 0.35\tan\theta)°$ and a maximum scan time of 1 min. A total of 1928 unique reflections were measured for $2 < \theta < 25°$ and $+h, +k, \pm l$, and 1228 reflections with $|F^2| > 3\sigma(F^2)$ were used in the refinement where $\sigma(F^2) = \{\sigma^2(I) + (0.04I)^2\}^{\frac{1}{2}}/L_p$. There was no correction for absorption.

The structure was solved by routine heavy atom methods and refined by full matrix least squares with non-hydrogen atoms anisotropic. Hydrogen atoms were held fixed at cal-

culated positions with $u_{iso} = 1.3\ u_{eq}$ for the atom to which they are bonded. The weighting scheme was $w = 1/\sigma^2(F)$ and the final residuals were $R = 0.052$, $R' = 0.063$ ($R = 0.056$, $R' = 0.068$ for the opposite absolute structure. Programs from the Enraf-Nonius SDP-Plus package were run on a microVax II computer. Fractional atomic co-ordinates and intramolecular distances and angles are given in tables 1 and 2. Hydrogen atom co-ordinates, temperature factors and torsional angles have been deposited with the Cambridge Crystallographic Data Centre.*

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