Unsaturated Steroids. Part 2.[1] A Novel Route to Anthrasteroids: *X*-Ray Crystal Structure of 1(10 → 6)*abeo*-Cholesta-5,7,9-trien-3-yl *p*-Bromobenzoate.

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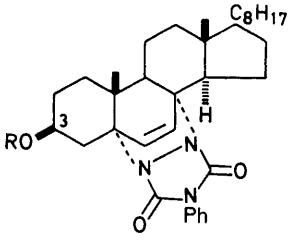
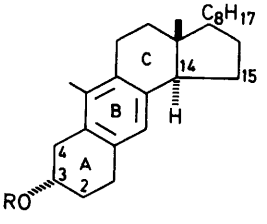
Treatment of the adduct from a steroidal 5,7-diene and 4-phenyl-1,2,4-triazoline-3,5-dione with boron trifluoride–diethyl ether gives the corresponding anthrasteroid. The structure of the product derived from cholesta-5,7-dien-3β-ol has been determined by *X*-ray crystallography. Oxidation of the anthrasteroid with the Moffat reagent furnishes the corresponding 3-ketone, which can be dehydrogenated with tri-*N*-methylanilinium perbromide to the corresponding naphthol. The various anthrasteroids are oxidised by dichlorodicyano-1,4-benzoquinone to the corresponding 14-enes.

ANTHRASTEROIDS, frequently of ill-defined stereochemistry, have previously been available, in unsatisfactory yield, by the vigorous treatment of unsaturated steroids and steroidal alcohols or ketones, with acidic reagents.[2] We now report [3] a much superior route, from steroidal 5,7-dienes.

When the adduct of type (1; R = H, Ac, or PhCO) of a steroidal 5,7-diene with 4-phenyl-1,2,4-triazoline-3,5-dione is treated at room temperature with boron trifluoride–ether complex in solution in benzene, oxidative rearrangement occurs smoothly to give the corresponding anthrasteroid of type (2; R = H, Ac, or PhCO), in high yield, in which the stereochemistry at C-14 is retained. The n.m.r. spectrum of the product (2; R = H) from 7-dehydrocholesterol clearly showed the presence of the aromatic ring, having signals at τ 7.9 (3 H, s, $ArCH_3$) and 3.55 (1 H, s, aromatic). The structure was established unequivocally by a single crystal *X*-ray analysis of the *p*-bromobenzoate (2; R = *p*-BrC_6H_4·CO).



(1)



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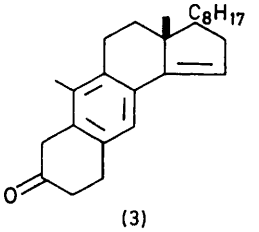
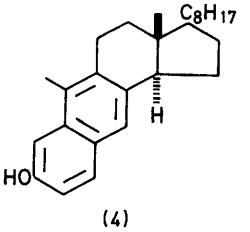


(3)



(4)

The details of the analysis are described in the Experimental section. A view of the molecule illustrating the crystallographic numbering scheme is given in Figure 1, and Figure 2 shows the *cis*-torsion angles for the condensed ring system. The aromatic nature of ring B is

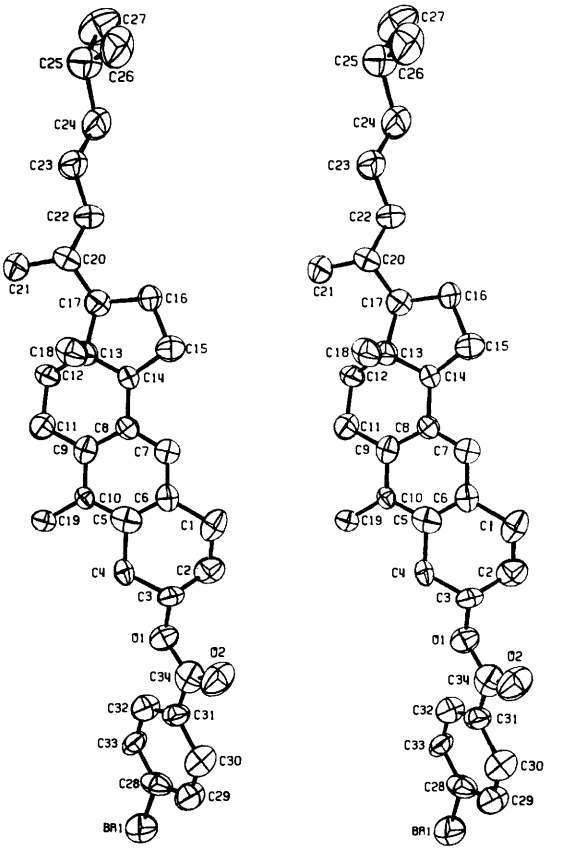


FIGURE 1 Stereoview of the molecule (2; R = *p*-BrC_6H_4·CO) illustrating the crystallographic numbering scheme; thermal ellipsoids are at the 50% probability level

indicated by the planarity of the ring (Figure 2), the similarity of its bond lengths (mean 1.390 Å), and the location of the hydrogen atom on C(7). The planarity of ring B largely determines the conformations of rings A and C. The pattern of torsion angles in ring A is characteristic of a half-chair conformation. The presence of the five-membered ring D as well as the planar ring B

[1] Part 1, J. Brynjolffssen, D. Hands, J. M. Midgley, and W. B. Whalley, *J.C.S. Perkin I*, 1976, 826.

[2] See for example, N. L. Wendler, 'Molecular Rearrangements,' vol. 2, ed. P. de Mayo, Interscience, New York, 1964, pp. 1019, 1063.

[3] Preliminary report, N. Bosworth, J. M. Midgley, C. J. Moore, W. B. Whalley, G. Ferguson, and W. C. Marsh, *J.C.S. Chem. Comm.*, 1974, 719.

causes ring C to adopt a sofa conformation with C(13) outside the sofa plane. Finally, the torsion angles in ring D suggest a conformation intermediate between a half-chair and an envelope conformation with C(13) at

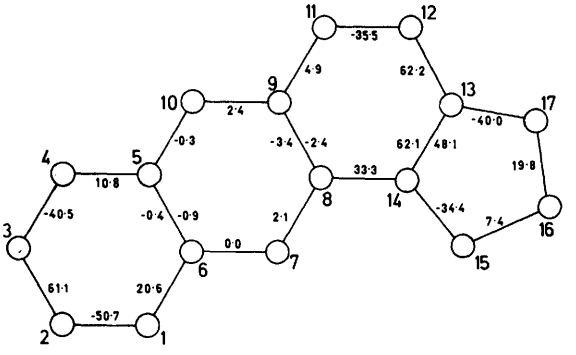
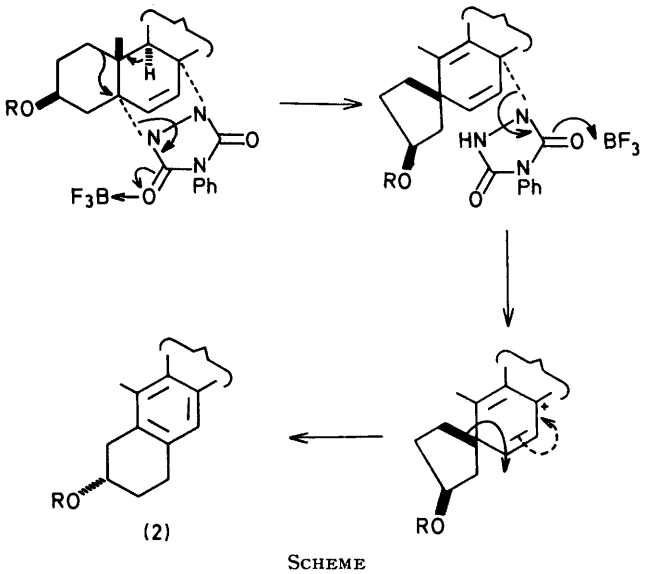


FIGURE 2 Schematic view of the ring system displaying the *cis*-torsion angles

the flap. The conformation may be described alternatively by the phase angle $\Delta = 15.7°$ and the angle of puckering $\phi_m = 45.8°$.[4]

The bond lengths and angles show no significant differences from accepted values.[5]

The change of configuration at C-3 indicates that the oxidative rearrangement proceeds by way of a mechanism of the type shown in the Scheme.



SCHEME

This route to anthrasteroids appears to be of general utility and has been applied successfully to a variety of steroidal 5,7-dienes; only the adduct of 7-dehydrodiosgenin acetate did not rearrange satisfactorily, owing to the breakdown of the spiran system under the influence of the boron trifluoride. The yield in the two-step process from the diene is generally greater than 90%.

Oxidation of the anthrasteroid of type (2; R = H) with the Moffat reagent (or, less satisfactorily, with Jones reagent) furnished the corresponding ketone. Attempts to aromatise ring A in the 3-ketone, the alcohol (2; R = H), or the ester (2; R = Bz), by using dichlorocyano-1,4-benzoquinone, gave the corresponding 14-ene, which with the Moffat reagent formed the ketone of type (3).

Aromatisation of the 3-oxo-anthrasteroid to the naphthol derivatives of type (4) occurred rapidly with tri-*N*-methylanilinium perbromide.

EXPERIMENTAL

Optical rotations were determined for solutions in chloroform.

General Experimental Conditions.—The steroidal 5,7-diene, dissolved in methylene chloride, was titrated at room temperature with a solution of 4-phenyl-1,2,4-triazoline-3,5-dione [6] in acetone, until a slightly pink colouration persisted. After removal of solvent the adduct (formed in quantitative yield) was purified from methanol. A solution of this adduct (1 g) in benzene (25 ml) was mixed with boron trifluoride–ether complex (5 ml) at room temperature; 12 h later the mixture was diluted with water (100 ml) and the product extracted with ether and crystallised from methanol.

Although homogeneous (n.m.r.; t.l.c.) several 3-hydroxyanthrasteroids could not be induced to crystallise; in all cases however the 3α-esters crystallised readily.

1(10 ⟶ 6)abeo-*Cholesta*-5,7,9-*trien*-3α-*ol*. The *adduct* of cholesta-5,7-dien-3β-ol formed needles (from methanol), m.p. 158—160°, $[\alpha]_D$ −81.0° (*c* 1.47) (Found: C, 75.0; H, 9.0; N, 7.6. $C_{35}H_{49}N_3O_3$ requires C, 75.1; H, 8.8; N, 7.5%). The 3β-*acetate* formed needles (from methanol), m.p. 133—136°, $[\alpha]_D^{21}$ −91.4° (*c* 2.26) (Found: C, 73.6; H, 8.6; N, 7.0. $C_{37}H_{51}N_3O_4$ requires C, 73.8; H, 8.5; N, 7.0%). The 3β-*benzoate* separated from dichloromethane–methanol in needles, m.p. 188—189°, $[\alpha]_D^{21}$ −70.8° (*c* 2.0) (Found: C, 76.2; H, 8.1; N, 6.5. $C_{42}H_{53}N_3O_4$ requires C, 76.0; H, 8.1; N, 6.3%).

1(10 ⟶ 6)abeo-*Cholesta*-5,7,9-*trien*-3α-*ol* did not crystallise (Found: C, 84.5; H, 11.1. $C_{27}H_{42}O$ requires C, 84.8; H, 11.1%); the p-*bromobenzoate* formed needles, m.p. 152°, $[\alpha]_D^{18}$ −8.4° (*c* 3.0) (Found: C, 72.3; H, 8.0; Br, 14.2. $C_{34}H_{45}BrO_2$ requires C, 72.2; H, 8.0; Br, 14.1%). The *benzoate* formed stout prisms, m.p. 95—98° (from methanol) (Found: C, 84.0; H, 9.7. $C_{34}H_{46}O_2$ requires C, 83.9; H, 9.5%), $[\alpha]_D^{22}$ +6.4° (*c* 1.5). The *acetate* formed plates, m.p. 81—83° (from ethanol), $[\alpha]_D^{22}$ −10° (*c* 1.14) (Found: C, 82.0; H, 10.4. $C_{29}H_{44}O_2$ requires C, 82.0; H, 10.4%).

Obtained by Moffat oxidation of the alcohol, 1(10 ⟶ 6)-*abeo*-cholesta-5,7,9-triene-3-one did not crystallise (Found: M^+, 380.3061. $C_{27}H_{40}O$ requires *M*, 380.3079). Oxidation of this ketone with tri-*N*-methylanilinium perbromide gave 1(10 ⟶ 6)abeo-*cholesta*-1,3,5,7,9-*pentaen*-3-*ol* (4) in needles, m.p. 132° (decomp.) [from light petroleum (b.p. 40—60°)], tenaciously retaining solvent, $[\alpha]_D^{21}$ +276.0° (*c* 1.40) (Found: M^+, 378.2931. $C_{27}H_{38}O$ requires *M*, 378.2923). The corresponding 3-*acetate* formed needles, m.p. 82° (from ether–ethanol), $[\alpha]_D^{22}$ +36.0° (*c* 0.68) (Found: C, 82.6; H, 9.5. $C_{29}H_{40}O_2$ requires C, 82.8; H, 9.6%), $\nu_{max.}$ 1 755 cm^{-1} (ester), τ 7.71 (3 H, s, OAc), 7.50 (3 H, s, ArCH_3), 2.92 (1 H, dd, $J_{1.2}$ 9.5, $J_{2.4}$ 2.5 Hz, H-2), 2.75 (1 H, s, H-7),

[4] C. Altona, H. J. Geise, and C. Romers, *Tetrahedron*, 1968, **24**, 13.

[5] L. E. Sutton, Chem. Soc. Special Publ. No. 18, 1965.

[6] D. H. R. Barton, T. Shioiri, and D. A. Widdowson, *J. Chem. Soc.* (*C*), 1971, 1968.

2.39 (1 H, d, $J_{2,4}$ 2.5 Hz, H-4), and 2.36 (1 H, d, $J_{1,2}$ 9.5 Hz, H-1).

1(10 → 6)abeo-*Ergosta*-5,7,9,22-*tetraen*-3α-*ol*.— This compound did not crystallise and was characterised as the p-*bromobenzoate*, which separated from methanol in glistening plates, m.p. 134—135°, $[\alpha]_D^{18}$ −11.7° (*c* 2.7) (Found: C, 72.5; H, 7.7; Br, 14.1. $C_{35}H_{45}BrO_2$ requires C, 72.8; H, 7.9; Br, 13.8%), $\nu_{max.}$ 1 712 cm^{-1} (ester), τ 7.91 (3 H, s, ArCH_3), 4.75 (2 H, m, H-22 and -23), and 3.3 (1 H, s, ArH).

Oxidation of this alcohol (1.58 g) in dimethyl sulphoxide (6 ml) and benzene (24 ml) containing dicyclohexylcarbodiimide (4.12 g) and pyridinium trifluoroacetate (0.38 g) occurred during 24 h at room temperature. Ether (50 ml) was then added, followed by oxalic acid (1.08 g) in methanol (10 ml). After evolution of gas had ceased, water (50 ml) was added and the precipitate of dicyclohexylurea was removed. The organic phase was washed, dried, and evaporated to yield 1(10 → 6)abeo-*ergosta*-5,7,9,22-*tetraen*-3-*one* (1 g) in plates, m.p. 97—99° (from ether–ethanol), $[\alpha]_D^{19}$ 0° (*c* 2.25) (Found: C, 85.9; H, 10.3. $C_{28}H_{40}O$ requires C, 85.7; H, 10.3%), $\nu_{max.}$ ($CHCl_3$) 1 713 cm^{-1} (C=O), τ 7.88 (3 H, s, ArCH_3), 4.72 (2 H, m, H-22 and -23), and 3.22 (1 H, s, ArH).

A solution of this ketone (0.3 g) in tetrahydrofuran (20 ml) and tri-*N*-methylanilinium perbromide (0.3 g, 1 equiv.) was maintained at 0 °C for 1 h. The product was purified from methanol to yield 1(10 → 6)abeo-*ergosta*-1,3,5,7,9,22-*hexaen*-3-*ol* (0.2 g) in needles, m.p. 145°, $[\alpha]_D^{21}$ +1.1° (*c* 1.1). This material tenaciously retained solvent and did not afford satisfactory elemental analyses (Found: M^+, 390.2923. $C_{28}H_{38}O$ requires *M*, 390.2943). The corresponding *acetate* separated from ether–ethanol in needles, m.p. 119°, $[\alpha]_D^{21}$ −98.0° (*c* 0.63) (Found: C, 83.1; H, 9.3. $C_{30}H_{40}O_2$ requires C, 83.3; H, 9.3%), $\nu_{max.}$ 1 754 cm^{-1} (ester), τ 7.73 (3 H, s, OAc), 7.52 (3 H, s, ArCH_3), 4.75 (2 H, m, H-22 and -23), 2.91 (1 H, dd, $J_{1,2}$ 9 Hz, $J_{2,4}$ 2 Hz, H-2), 2.77 (1 H, s, H-7), 2.36 (1 H, d, $J_{2,4}$ 2 Hz, H-4), and 2.32 (1 H, d, $J_{1,2}$ 9 Hz, H-1).

1(10 → 6)abeo-*Ergosta*-5,7,9,14,22-*pentaen*-3-*one*.— A solution of dichlorodicyano-1,4-benzoquinone (DDQ) (0.6 g) in benzene (25 ml) was added dropwise to a stirred solution of 1(10 → 6)*abeo*-ergosta-5,7,9,22-tetraen-3α-ol (1 g) in benzene (25 ml) at room temperature. After 15 min the insoluble quinol was collected and the product isolated from the organic phase to yield 1(10 → 6)abeo-*ergosta*-5,7,9,14,22-*pentaen*-3α-*ol* (0.8 g) in needles, m.p. 150° (from methanol), $[\alpha]_D^{20}$ −117.0° (*c* 1.3), $\nu_{max.}$ 3 600 cm^{-1} (OH), τ 7.92 (3 H, s, ArCH_3), 6.02 (1 H, m, H-3), 4.73 (2 H, m, H-22 and -23), 4.18 (1 H, m, H-15), and 2.97 (1 H, s, ArH) (Found: C, 85.8; H, 10.5. $C_{28}H_{40}O$ requires C, 85.7; H, 10.3%).

Oxidation of this alcohol by the Moffat procedure gave the *ketone* (35%), which formed plates, m.p. 103° (from ether–ethanol), $[\alpha]_D^{21}$ −139.6° (*c* 1.12) (Found: C, 85.8; H, 9.9. $C_{28}H_{38}O$ requires C, 86.1; H, 9.8%), $\nu_{max.}$ 1 716 cm^{-1} (C=O), τ 7.89 (3 H, s, ArCH_3), 6.60 (2 H, s, H_2-4), 4.74 (2 H, m, H-22 and -23), 4.10 (1 H, m, H-15), and 2.80 (1 H, s, ArH).

Oxidation of 1(10 → 6)*abeo*-ergosta-5,7,9,22-tetraen-3α-ol benzoate with DDQ similarly gave the 1(10 → 6)-abeo-*ergosta*-5,7,9,14,22-*pentaen*-3α-*yl benzoate* in needles, m.p. 144° (from acetone–ethanol), $[\alpha]_D^{21}$ −128.0° (*c* 1.63) (Found: C, 84.5; H, 9.0. $C_{35}H_{44}O_2$ requires C, 84.6; H, 8.9%), $\nu_{max.}$ 1 712 cm^{-1} (ester).

Oxidation of the corresponding *p*-bromobenzoate gave 1(10 → 6)abeo-*ergosta*-5,7,9,14,22-*pentaen*-3α-*yl* p-*bromobenzoate*, which formed needles, m.p. 151° (from methanol), $[\alpha]_D^{21}$ −119.0° (*c* 1.4) (Found: C, 73.1; H, 7.7; Br, 13.8. $C_{35}H_{43}BrO_2$ requires C, 73.0; H, 7.3; Br, 13.9%), $\nu_{max.}$ 1 715 cm^{-1} (ester).

1(10 → 6)abeo-3α-*Acetoxyandrosta*-5,7,9-*trien*-17-*one*.— The *adduct* of 3β-acetoxyandrost-5,7-dien-17-one formed needles, m.p. 218°, $[\alpha]_D^{18}$ −35.2° (*c* 1.8) (Found: C, 68.7; H, 6.6; N, 8.3. $C_{29}H_{33}N_3O_5$ requires C, 69.2; H, 6.6; N, 8.4%). 1(10 → 6)abeo-3α-*Acetoxyandrosta*-5,7,9-*trien*-17-*one* formed needles, m.p. 131° (from methanol), $[\alpha]_D^{18}$ +12.3° (*c* 8.6) (Found: C, 77.1; H, 8.2. $C_{21}H_{26}O_3$ requires C, 77.3; H, 8.0%), τ 7.94 (3 H, s, ArCH_3), 7.91 (3 H, s, OAc), and 3.33 (1 H, s, ArH).

1(10 → 6)abeo-3α-*Acetoxypregna*-5,7,9-*trien*-20-*one*.— The *adduct* of 3β-acetoxypregna-5,7-dien-20-one formed needles, m.p. 187° (from methanol), $[\alpha]_D^{18}$ −27.2° (*c* 1.89) (Found: C, 69.8; H, 6.6; N, 7.9. $C_{31}H_{37}N_3O_5$ requires C, 70.0; H, 7.0; N, 7.9%). 1(10 → 6)abeo-3α-*Acetoxypregna*-5,7,9-*trien*-20-*one* formed shimmering plates, m.p. 147° (from methanol), $[\alpha]_D^{18}$ +12.3° (*c* 8.6) (Found: C, 78.3; H, 8.2. $C_{23}H_{30}O_3$ requires C, 77.9; H, 8.5%).

1(10 → 6)abeo-3α,17α-*Diacetoxypregna*-5,7,9-*trien*-20-*one*.—The *adduct* of 3β,17α-diacetoxypregna-5,7-dien-20-one formed needles, m.p. 206° (from ethanol), $[\alpha]_D^{18}$ −54.5° (*c* 1.7) (Found: C, 67.1; H, 6.9; N, 7.3. $C_{33}H_{39}N_3O_7$ requires C, 67.2; H, 6.8; N, 7.1%). 1(10 → 6)abeo-3α,17α-*Diacetoxypregna*-5,7,9-*trien*-20-*one* formed pale yellow prisms, m.p. 220° (from ethanol), $[\alpha]_D$ −83.5° (*c* 1.60) (Found: C, 72.6; H, 7.8. $C_{25}H_{32}O_5$ requires C, 72.8; H, 7.8%), τ 7.9—8.0 (12 H, m, 2 OAc, ArCH_3, and H_3-21), and 3.32 (1 H, s, ArH).

1(10 → 6)abeo-*Stigmasta*-5,7,9-*trien*-3α-*yl Acetate*.— The *adduct* of stigmasterol acetate formed needles, m.p. 165° (from ethanol), $[\alpha]_D^{20}$ −103.0° (*c* 1.16) (Found: C, 74.5; H, 8.6; N, 6.8. $C_{39}H_{53}N_3O_4$ requires C, 74.6; H, 8.5; N, 6.7%). The corresponding *benzoate* formed needles, m.p. 204—207° (from acetone–methanol), $[\alpha]_D^{18}$ −85° (*c* 2.0) (Found: C, 76.7; H, 8.1; N, 6.1. $C_{44}H_{55}N_3O_4$ requires C, 76.6; H, 8.0; N, 6.1%). 1(10 → 6)abeo-*Stigmasta*-5,7,9-*trien*-3α-*yl acetate* formed needles, m.p. 92—94° (from acetone–ethanol), $[\alpha]_D^{21}$ −9.9° (*c* 1.65) (Found: C, 82.9; H, 10.3. $C_{31}H_{46}O_2$ requires C, 82.6; H, 10.3%), τ 7.94 (3 H, s, OAc), 7.92 (3 H, s, ArCH_3), and 3.34 (1 H, s, Ar*H*). The corresponding *benzoate* separated from acetone–propan-2-ol in needles, m.p. 110°, $[\alpha]_D^{18}$ −2.0° (*c* 1.37) (Found: C, 84.1; H, 9.4. $C_{36}H_{48}O_2$ requires C, 84.3; H, 9.4%). 1(10 → 6)abeo-*Stigmasta*-5,7,9-*trien*-3α-*ol* formed prisms, m.p. 130—134° (from acetone), $[\alpha]_D^{18}$ −13.4° (*c* 1.9) (Found: C, 85.3; H, 10.9. $C_{29}H_{44}O$ requires C, 85.2; H, 10.9%). Oxidation of this alcohol with Jones reagent (4N) gave (quantitatively) the 3-*ketone*, which formed needles, m.p. 116—119° (from ethyl acetate), $[\alpha]_D^{18}$ +31.5° (*c* 0.76) (Found: C, 85.4; H, 10.4. $C_{29}H_{42}O$ requires C, 85.7; H, 10.4%).

1(10 → 6)abeo-*Androsta*-5,7,9-*trien*-17-*one*.—The *adduct* from androsta-5,7-dien-17-one formed needles, m.p. 220° (from ethanol), $[\alpha]_D^{18}$ −105.5° (*c* 2.0) (Found: C, 72.5; H, 6.9; N, 9.5. $C_{27}H_{31}N_3O_3$ requires C, 72.8; H, 7.0; N, 9.4%). 1(10 → 6)abeo-*Androsta*-5,7,9-*trien*-17-*one* separated from acetone–ethanol in needles, m.p. 135—138° (Found: C, 85.0; H, 9.0. $C_{19}H_{24}O$ requires C, 85.0; H, 9.0%), $\nu_{max.}$ 1 740 cm^{-1}, τ 7.95 (3 H, s, ArCH_3) and 3.30 (1 H, s, ArH).

1(10 → 6)abeo-3α-*Chloroandrosta*-5,7,9-*trien*-17-*one*.—The *adduct* of 3β-chloroandrosta-5,7-dien-17-one formed plates, m.p. 210° (from ethanol) (Found: C, 67.8; H, 6.1; Cl, 7.3; N, 8.4. $C_{27}H_{30}ClN_3O_3$ requires C, 67.6; H, 6.3; Cl, 7.4; N, 8.8%). 1(10 → 6)abeo-3α-*Chloroandrosta*-5,7,9-*trien*-17-*one* formed needles, m.p. 189° (from acetone) (Found: C, 75.3; H, 7.6. $C_{19}H_{23}ClO$ requires C, 75.4; H, 7.6%), $\nu_{max.}$ 1 748 cm^{-1}, τ 7.90 (3 H, s, ArCH_3) and 3.24 (1 H, s, ArH).

1(10 → 6)abeo-*Ergosta*-5,7,9-*trien*-3α-*ol*.—Prepared from the adduct of 22,23-dihydroergosterol,[1] this 3α-*ol* formed needles, m.p. 125—128° (from acetone), $[\alpha]_D^{18}$ −23.0° (*c* 1.04) (Found: C, 85.3; H, 10.6. $C_{28}H_{44}O$ requires C, 84.8; H, 11.2%), τ 7.89 (3 H, s, ArCH_3) and 3.32 (1 H, s, ArH). Oxidation of this alcohol with Jones reagent (4N) gave (quantitatively) 1(10 → 6)abeo-*ergosta*-5,7,9-*trien*-3-*one* in needles, m.p. 97—100° (from methylene chloride–propan-2-ol), $[\alpha]_D^{18}$ 0° (*c* 2.25) (Found: C, 86.0; H, 10.3. $C_{28}H_{42}O$ requires C, 85.2; H, 10.7%).

TABLE 1

Final fractional co-ordinates (× 10^4) with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
Br(1)	0 957(1)	2 500 *	10 422(2)
O(1)	3 405(3)	1 900(7)	9 224(7)
O(2)	3 458(3)	0 432(7)	10 622(9)
C(1)	4 563(4)	0 818(10)	7 956(12)
C(2)	4 001(4)	0 882(12)	8 075(11)
C(3)	3 958(4)	1 732(10)	9 152(11)
C(4)	4 115(4)	2 892(9)	8 737(11)
C(5)	4 597(4)	2 910(10)	8 097(10)
C(6)	4 797(4)	1 928(9)	7 733(10)
C(7)	5 223(4)	1 983(9)	7 079(10)
C(8)	5 428(4)	2 979(8)	6 810(10)
C(9)	5 237(4)	3 962(10)	7 201(10)
C(10)	4 803(4)	3 944(9)	7 854(10)
C(11)	5 475(4)	5 073(10)	6 973(12)
C(12)	5 911(4)	5 039(10)	6 142(12)
C(13)	6 254(4)	3 973(10)	6 468(10)
C(14)	5 867(4)	3 034(8)	6 038(10)
C(15)	6 203(5)	2 010(10)	6 004(12)
C(16)	6 685(4)	2 494(13)	5 534(10)
C(17)	6 636(4)	3 789(11)	5 507(12)
C(18)	6 557(4)	3 897(11)	7 983(11)
C(19)	4 569(4)	4 985(10)	8 223(12)
C(20)	7 187(4)	4 343(10)	5 801(11)
C(21)	7 143(5)	5 586(12)	5 872(15)
C(22)	7 476(5)	4 005(12)	4 716(14)
C(23)	8 087(5)	4 121(12)	5 226(14)
C(24)	8 372(5)	3 776(11)	4 170(13)
C(25)	8 993(4)	3 803(12)	4 702(13)
C(26)	9 186(5)	2 899(11)	5 776(13)
C(27)	9 241(5)	3 660(15)	3 500(14)
C(28)	1 659(4)	2 050(11)	10 299(12)
C(29)	1 897(5)	1 120(11)	10 971(13)
C(30)	2 399(5)	0 862(12)	10 857(13)
C(31)	2 654(4)	1 521(10)	10 074(11)
C(32)	2 407(4)	2 425(16)	9 399(11)
C(33)	1 903(4)	2 734(10)	9 520(11)
C(34)	3 198(4)	1 177(10)	10 005(11)

* Held invariant to fix the origin in space group *C*2.

1(10 → 6)abeo-22,23-*Epoxyergosta*-5,7,9-*trien*-3α-*yl Benzoate*.—Prepared from the adduct [6] of the benzoate of 22,23-epoxyergosterol the 3α-*benzoate* formed needles, m.p. 207—209° (from ether–methanol), $[\alpha]_D^{21}$ −9.0° (*c* 0.6) (Found: C, 81.6; H, 9.0. $C_{35}H_{46}O_3$ requires C, 81.7; H, 9.0%), devoid of hydroxylic or ketonic carbonyl i.r. absorption.

The *adduct* of 7-dehydrodiosgenin acetate formed needles, m.p. 165° (from aqueous ethanol), $[\alpha]_D^{18}$ −136° (*c* 2.1) (Found: C, 70.2; H, 7.3; N, 6.6. $C_{37}H_{47}N_3O_6$ requires C, 70.6; H, 7.5; N, 6.7%).

TABLE 2

Final (i) bond lengths (Å) and (ii) valency angles (°), with estimated standard deviations in parentheses

(i)			
Br(1)–C(28)	1.93(1)	C(13)–C(17)	1.56(2)
O(1)–C(3)	1.46(1)	C(13)–C(18)	1.53(1)
O(1)–C(34)	1.37(1)	C(14)–C(15)	1.52(2)
O(2)–C(34)	1.20(1)	C(15)–C(16)	1.55(2)
C(1)–C(2)	1.49(2)	C(16)–C(17)	1.57(2)
C(1)–C(6)	1.51(2)	C(17)–C(20)	1.53(2)
C(2)–C(3)	1.52(2)	C(20)–C(21)	1.51(2)
C(3)–C(4)	1.55(2)	C(20)–C(22)	1.52(2)
C(4)–C(5)	1.54(2)	C(22)–C(23)	1.54(2)
C(5)–C(6)	1.38(2)	C(23)–C(24)	1.49(2)
C(5)–C(10)	1.40(2)	C(24)–C(25)	1.56(2)
C(6)–C(7)	1.42(2)	C(25)–C(26)	1.53(2)
C(7)–C(8)	1.37(2)	C(25)–C(27)	1.51(2)
C(8)–C(9)	1.38(2)	C(28)–C(29)	1.38(2)
C(8)–C(14)	1.53(2)	C(28)–C(33)	1.39(2)
C(9)–C(10)	1.43(2)	C(29)–C(30)	1.37(2)
C(9)–C(11)	1.52(2)	C(30)–C(31)	1.40(2)
C(10)–C(19)	1.48(2)	C(31)–C(32)	1.36(2)
C(11)–C(12)	1.56(2)	C(31)–C(34)	1.48(2)
C(12)–C(13)	1.55(2)	C(32)–C(33)	1.39(2)
C(13)–C(14)	1.50(1)		
(ii)			
C(3)–O(1)–C(34)	117.7(8)	C(8)–C(14)–C(13)	114.4(8)
C(2)–C(1)–C(6)	113.5(11)	C(8)–C(14)–C(15)	118.5(9)
C(1)–C(2)–C(3)	109.7(9)	C(13)–C(14)–C(15)	106.2(8)
O(1)–C(3)–C(2)	112.0(8)	C(14)–C(15)–C(16)	101.9(9)
O(1)–C(3)–C(4)	102.3(9)	C(15)–C(16)–C(17)	108.3(9)
C(2)–C(3)–C(4)	110.7(9)	C(13)–C(17)–C(16)	101.1(9)
C(3)–C(4)–C(5)	114.8(9)	C(13)–C(17)–C(20)	121.3(9)
C(4)–C(5)–C(6)	119.5(10)	C(16)–C(17)–C(20)	113.4(9)
C(4)–C(5)–C(10)	117.9(9)	C(17)–C(20)–C(21)	111.5(9)
C(6)–C(5)–C(10)	122.5(10)	C(17)–C(20)–C(22)	110.0(9)
C(1)–C(6)–C(5)	122.4(10)	C(21)–C(20)–C(22)	110.9(9)
C(1)–C(6)–C(7)	119.7(10)	C(20)–C(22)–C(23)	112.5(10)
C(5)–C(6)–C(7)	117.8(10)	C(22)–C(23)–C(24)	112.5(10)
C(6)–C(7)–C(8)	120.9(10)	C(23)–C(24)–C(25)	113.5(10)
C(7)–C(8)–C(9)	121.3(10)	C(24)–C(25)–C(26)	110.7(10)
C(7)–C(8)–C(14)	120.7(9)	C(24)–C(25)–C(27)	109.2(10)
C(9)–C(8)–C(14)	118.0(9)	C(26)–C(25)–C(27)	110.7(11)
C(8)–C(9)–C(10)	119.5(10)	C(29)–C(28)–Br(1)	118.3(7)
C(8)–C(9)–C(11)	122.3(10)	C(33)–C(28)–Br(1)	118.3(7)
C(10)–C(9)–C(11)	118.2(10)	C(29)–C(28)–C(33)	123.4(10)
C(5)–C(10)–C(9)	117.8(10)	C(28)–C(29)–C(30)	117.7(12)
C(5)–C(10)–C(19)	121.2(10)	C(29)–C(30)–C(31)	120.5(12)
C(9)–C(10)–C(19)	121.0(10)	C(30)–C(31)–C(32)	120.9(10)
C(9)–C(11)–C(12)	115.4(10)	C(30)–C(31)–C(34)	116.8(10)
C(11)–C(12)–C(13)	111.1(9)	C(32)–C(31)–C(34)	122.3(10)
C(12)–C(13)–C(14)	105.3(7)	C(31)–C(32)–C(33)	120.4(12)
C(12)–C(13)–C(17)	113.8(9)	C(28)–C(33)–C(32)	117.1(11)
C(12)–C(13)–C(18)	112.5(9)	O(1)–C(34)–O(2)	121.8(10)
C(14)–C(13)–C(17)	101.1(9)	O(1)–C(34)–C(31)	110.9(9)
C(14)–C(13)–C(18)	112.3(9)	O(2)–C(34)–C(31)	127.0(11)
C(17)–C(13)–C(18)	111.1(8)		

X-*Ray Crystal Structure Analysis of the* p-*Bromobenzoate* (2; R = *p*-BrC_6H_4·CO).—The crystals were needles, elongated along the *c* axis. Preliminary cell parameters and space group data were obtained from various rotation, precession, and Weissenberg photographs; accurate cell parameters were obtained by a least-squares procedure applied to 12 general reflections measured on a Hilger and Watts diffractometer.

Crystal data. $C_{34}H_{45}BrO_2$, *M*. 565.6. Monoclinic, *a* = 25.853(3), *b* = 12.102(1), *c* = 10.049(1) Å, β = 104.38(1)°, *U* = 3 045.6 Å^3, *Z* = 4, D_c = 1.23 g cm^{-3}, *F*(000) = 1 200. 20 °C, Mo-K_α radiation, λ = 0.710 69 Å, μ = 14.6 cm^{-1}. Space group $C2/m(C_{2h}^3)$ or $C2(C_2^3)$ from absent reflections: *hkl*, *h* + *k* = 2*n* + 1; C_2 from structure analysis.

The intensities of all reflections with $2\theta(\text{Mo-}K_\alpha) < 46°$ were measured with a PDP8-I controlled Hilger and Watts Y290 four-circle diffractometer fitted with a graphite monochromator. A θ/ω step scan was employed with 0.01° steps, a counting time of 1 s per step, and a scan width of 0.7° in θ. Background counts of 17.5 s were made at the beginning and end of each scan. The intensities of 3 standard reflections, well separated in reciprocal space, were measured after every 100 reflections throughout the data collection. Their final intensities were within 1.2% of the starting values, indicating excellent crystal and machine stability. Lorentz and polarisation factors were applied, and the structure amplitudes derived. Of the 2 238 unique data, 554 reflections had intensities less than 3σ above background, where $\sigma(I)$ is defined by $[S + 4(B_1 + B_2) + 0.07\ S]^{1/2}$ (S is the scan count and B_1 and B_2 the background counts), and were excluded from the subsequent refinement.

Structure analysis. The structure was solved in a straightforward manner. The positions of the bromine atom and the remaining atoms of the *p*-bromobenzoate group were determined from a sharpened Patterson synthesis. With the *y* co-ordinate of the bromine atom set at 1/4 to fix the origin in space group *C*2 (*C*2/*m* was eliminated because of the known optical activity), these 10 atoms were used as input into the recycling procedure of Karle.[7] Three iterations of tangent refinement followed by *E*-maps were sufficient to locate all non-hydrogen atoms. Subsequent refinement proceeded smoothly. Isotropic full-matrix least-squares followed by anisotropic block-diagonal least-squares refinement reduced *R* to 0.090. At this stage a difference synthesis revealed the presence of all 45 hydrogen atoms. These were subsequently included in the structure factor calculation but not in the refinement. The final *R* value was 0.076 for the 1 684 reflections greater than 3σ above background and 0.083 for all 2 238 reflections. Throughout the refinement the function minimised was $\Sigma w(F_o - F_c)^2$ with w taken as the reciprocal of the variance in F_o as determined from counting statistics. The usefulness of this weighting scheme was confirmed from an analysis of $w(F_o - F_c)^2$, average values of which over ranges of $|F_o|$ were approximately constant. The scattering factors for the non-hydrogen atoms were those of ref. 8; that for the hydrogen atoms is from ref. 9. Table 1 contains the final positional parameters for the Br, O, and C atoms; Table 2 lists the final bond lengths and angles. The measured and final calculated structure amplitudes in addition to the thermal parameters are listed in Supplementary Publication No. SUP 21972 (5 pp.).*

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* For details of Supplementary Publications see Notice to Authors No. 7, *J.C.S. Perkin I*, 1976, Index issue.

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