Conformational Studies. Part 7.[1] Crystal and Molecular Structure of 17β-Bromoacetoxy-19-nor-5α-androstan-3-one and 17β-Bromoacetoxy-5α-androstan-3-one

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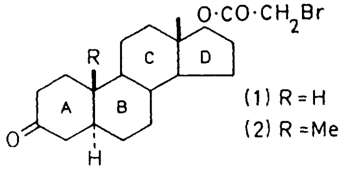
The crystal and molecular structures of the title compounds have been determined by *X*-ray crystallography. Whereas the 19-nor-derivative (1) $C_{20}H_{29}BrO_3$, crystallises in the orthorhombic system, space group $P2_12_12_1$ with $Z = 4$ in a unit cell of dimensions $a = 6.134(1)$, $b = 12.580(2)$, and $c = 25.297(3)$ Å, the other (2) $C_{21}H_{31}BrO_3$, crystallises in the monoclinic space group $P2_1$ with $Z = 2$ in a unit cell $a = 12.972(2)$, $b = 7.321(1)$, $c = 10.580(2)$ Å, $\beta = 99.71(1)$°. Both structures were solved by the heavy-atom method and refined by full-matrix least-squares calculations from three-dimensional diffractometer data, to R 0.961 for 1 057 reflections (1), and R 0.042 for 1 075 reflections (2). The conformation of ring A in both molecules is affected by intramolecular packing effects. Ring A in (1) is abnormally flattened whereas in (2) it is more puckered than expected. Bond lengths and angles are normal.

As part of an investigation into the correlation of the conformation of steroids with other physical parameters we have examined a series of steroids by *X*-ray crystallography. We report here our analyses of 17β-bromoacetoxy-19-nor-5α-androstan-3-one (1) and of 17β-bromoacetoxy-5α-androstan-3-one (2). Details of the analysis are described in the Experimental section.



The molecular conformations are shown in Figures 1 and 2 together with the atom numbering schemes used. Geise *et al.*[2] have reported a set of ' standard ' values for torsional angles in steroid molecules which are the weighted means of the torsion angles in the molecules studied. Table 1 compares the torsional angles of ring A in (1) and (2) with the ' standard ' values.

The results show clearly that ring A in (1) does not have the ideal, undistorted chair conformation which might be expected. Torsion angles ϕ(2–3–4–5) and ϕ(3–4–5–10) differ from the standard values by 9.6° and 8.3° respectively. The reduced torsional angle ϕ(3–4–5–10) indicates that ring A in (1) is somewhat flattened. Further evidence for the flattening of ring A is the distance of C(3) from the best plane through atoms C(1)—(5), and C(10) (0.086 *vs.* 0.26 Å in cyclohexanone).

TABLE 1

Comparisons of torsional angles (°) in ring A of (1), (2), a ' standard ' set, and 17β-hydroxy5α-androstan-3-one (3)

Angle ϕ	(1)	(2)	Standard [a]	(3) [b]
10–1–2–3	−55.4(1.2)	−50.1(0.9)	−55.8	−55:2
1–2–3–4	45.1(1.4)	46.2(0.9)	52.3	51.1
2–3–4–5	−43.0(1.4)	−48.1(0.9)	−52.6	−49.0
3–4–5–10	48.2(1.2)	54.1(0.8)	56.5	51.2
4–5–10–1	−58.2(1.1)	−58.1(0.7)	−55.1	−55.9
5–10–1–2	61.3(1.1)	56.8(0.7)	54.9	57.5

[a] From ref. 2. [b] From ref. 5.

By way of contrast a slightly flattened ring A might be expected in (2) because of the presence of the methyl group at C(10). The interaction between this methyl and the axial hydrogen atoms at C(2) and C(4) would

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[1] Part 6, R. Ahmad, R. Carrington, J. M. Midgley, W. B. Whalley, U. Weiss, G. Ferguson, and P. J. Roberts, preceding paper.

[2] H. J. Geise, C. Altona, and C. Romers, *Tetrahedron*, 1967, **23**, 439.

be expected to cause rotation about bonds C(1)–C(2) and C(4)–C(5) in such a way as to relieve the interaction.

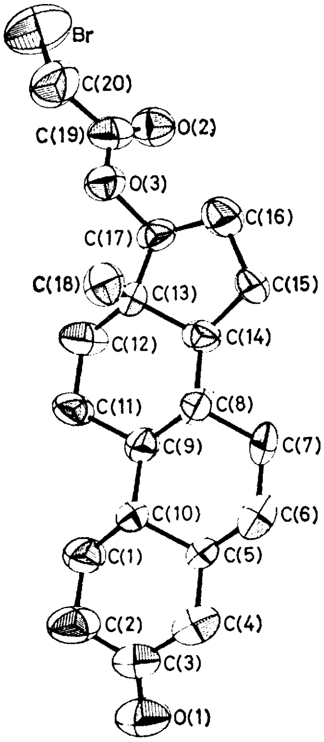

FIGURE 1 A diagram of the molecule of (1) showing the atom numbering

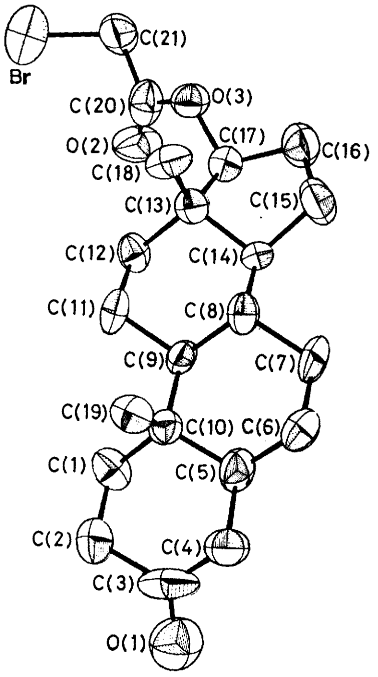

FIGURE 2 A diagram of the molecule of (2) showing the atom numbering scheme used in the analysis

It appears from Table 1 that the conformation of ring A in (2) in the crystalline state is not the flattened chair anticipated. Unexpectedly, the conformation is closer to that of the ideal chair than that of (1) as evidenced by the torsional angle ϕ(3–4–5–10) of 54.1 in (2) and 48.2° in (1) (' standard ' 56.5°). Atom C(3) is displaced some 0.537 Å below the best plane through atoms C(1), C(2), C(4), C(5), a distance significantly larger than that (0.495 Å) observed in (1). This implies that a force large enough to overcome interactions between the C(19) methyl group and the axial hydrogen atoms at C(2) and C(4) must be present to account for the deformation of ring A.

TABLE 2

Intermolecular contacts <3.5 Å in (1) and (2)

(*a*) In (1)

C(4) · · · O(1^{I})	3.46	C(20 · · · O(1^{III})	3.47
C(5) · · · O(1^{II})	3.47		

(*b*) In (2)

C(21) · · · O(1^{IV})	3.37	C(2) · · · O(1^{VI})	3.50
C(4) · · · O(1^{V})	3.49		

Roman numeral superscripts refer to the following equivalent positions relative to the reference molecule at x,y,z:

I	$-\frac{1}{2}+x, \frac{1}{2}-y, 1-z$	IV	$1+x, y, z$
II	$\frac{1}{2}+x, \frac{1}{2}-y, 1-z$	V	$-x, -\frac{1}{2}+y, 1-z$
III	$-\frac{3}{2}-x, -y, \frac{1}{2}+z$	VI	$-x, \frac{1}{2}+y, 1-z$

TABLE 3

Molecular dimensions in (1)

(*a*) Bond lengths (Å), with estimated standard deviations in parentheses

Br–C(20)	1.871(15)	C(11)–C(9)	1.551(13)
C(20)–C(19)	1.518(15)	C(9)–C(8)	1.528(12)
C(19)–O(2)	1.189(13)	C(9)–C(10)	1.556(12)
C(19)–O(3)	1.331(12)	C(8)–C(7)	1.519(13)
C(17)–O(3)	1.461(10)	C(7)–C(6)	1.543(17)
C(17)–C(16)	1.513(14)	C(6)–C(5)	1.493(15)
C(17)–C(13)	1.504(12)	C(5)–C(10)	1.551(12)
C(16)–C(15)	1.544(14)	C(10)–C(1)	1.491(14)
C(15)–C(14)	1.513(12)	C(5)–C(4)	1.529(16)
C(14)–C(8)	1.523(13)	C(4)–C(3)	1.514(15)
C(14)–C(13)	1.540(12)	C(3)–C(2)	1.441(16)
C(13)–C(12)	1.528(14)	C(3)–O(1)	1.220(11)
C(13)–C(18)	1.539(14)	C(2)–C(1)	1.549(17)
C(12)–C(11)	1.548(16)		

(*b*) Bond angles (°); mean estimated standard deviation 0.8°

Br–C(20)–C(19)	112.7	C(11)–C(9)–C(8)	113.2
C(20)–C(19)–O(2)	127.6	C(1) – C(9)–C(10)	110.9
O(20)–C(19)–O(3)	105.8	C(8)–C(9)–C(10)	110.9
O(2)–C(19)–O(3)	126.5	C(9)–C(8)–C(14)	111.5
C(13)–O(3)–C(17)	117.0	C(9)–C(8)–C(7)	111.7
O(3)–C(17)–C(16)	114.0	C(14)–C(8)–C(7)	112.7
O(3)–C(17)–C(13)	110.0	C(6)–C(7)–C(8)	111.3
C(13)–C(17)–C(16)	105 6	C(5)–C(6)–C(7)	112.6
C(17)–C(16)–C(15)	105.2	C(4)–C(5)–C(6)	109.4
C(16)–C(15)–C(14)	103.4	C(4)–C(5)–C(10)	110.6
C(15)–C(14)–C(13)	105.0	C(6)–C(5)–C(10)	111.5
C(15)–C(14)–C(8)	120.1	C(5)–C(10)–C(1)	108.5
C(8)–C(14)–C(13)	111.6	C(5)–C(10)–C(9)	109.7
C(14)–C(13)–C(17)	97.8	C(1)–C(10)–C(9)	113.2
C(14)–C(13)–C(12)	109.0	C(3)–C(4)–C(5)	113.6
C(14)–C(13)–C(18)	111.8	C(2)–C(3)–C(4)	116.6
C(12)–C(13)–C(17)	117.2	C(2)–C(3)–O(1)	123.1
C(12)–C(13)–C(18)	111.2	C(4)–C(3)–O(1)	120.3
C(17)–C(13)–C(18)	109.2	C(1)–C(2)–C(3)	112.4
C(11)–C(12)–C(13)	115.1	C(10)–C(1)–C(2)	111.1
C(9)–C(11)–C(12)	111.1		

For both molecules an explanation of the unexpected ring A conformations lies in intermolecular packing effects, and stereodiagrams of the crystal structures are shown in Figures 3 and 4. In both crystal structures the shortest contacts between adjacent molecules (Table 2) are all associated with the ring A carbonyl oxygen atom which is surrounded in each case by three other molecules with H · · · O contacts in the range 2.42—2.77 Å. structures an acidic hydrogen atom on the carbon adjacent to the bromine atom is one of those involved in the C–H · · · O contacts. It is possible that these distances [C(20)–H · · · O(1) 3.47 in (I) and C(21)–H · · · O(1) 3.37 Å in (2)] exemplify weaker C–H · · · O hydrogen bonds than those in *o*-chloro-[3] and *o*-bromo-benzoylacetylene.[4] Since only 2—3 kcal mol^{-1} are required to twist or deform a torsion angle slightly, it appears reasonable to assume that molecular packing forces, with perhaps the aid of C–H · · · O hydrogen bond formation, are strong enough to deform ring A in both molecules slightly away from the conformation to be expected in an isolated molecule. Torsion-angle data

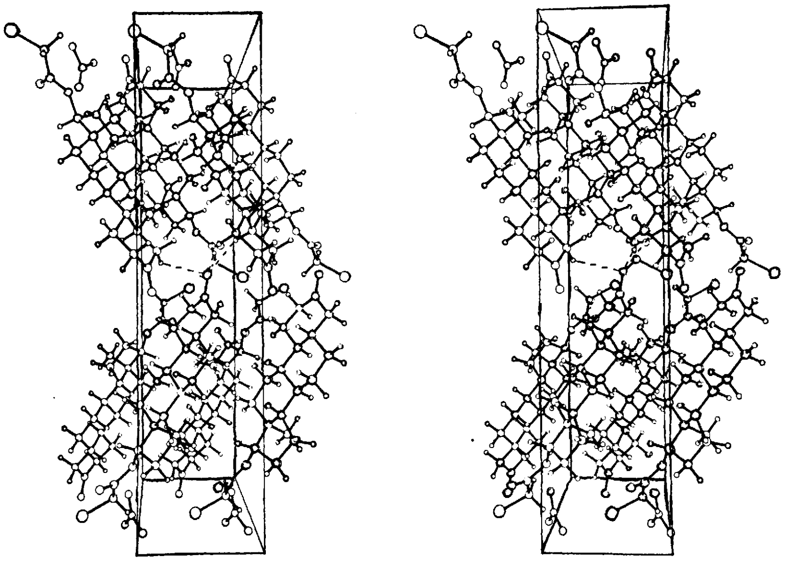

FIGURE 3 Stereodiagram of the molecular packing in (1). Dashed lines indicate the interactions with carbonyl oxygen O(1)

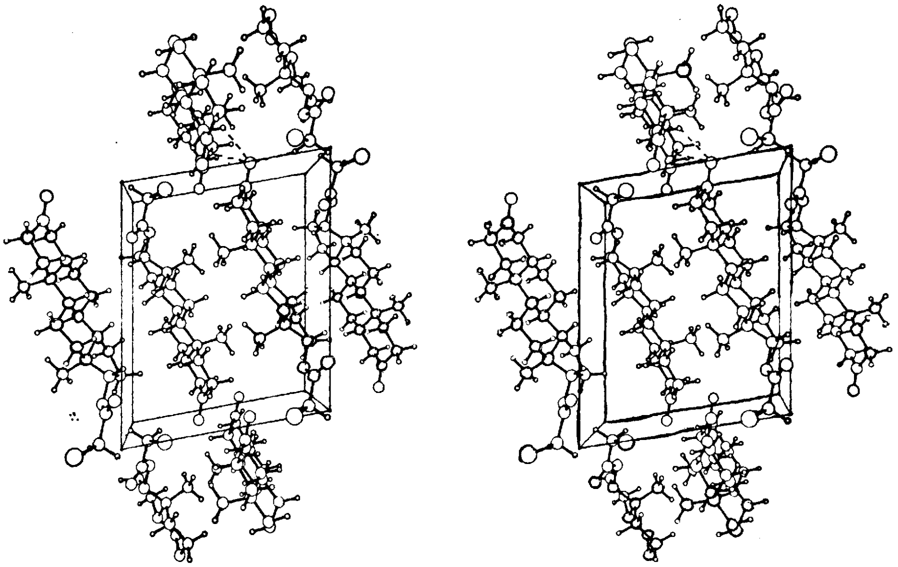

FIGURE 4 Stereodiagram of the molecular packing in (2)

In (1) if ring A were not slightly flattened, the C(4)–H · · · O(1) distance (3.46 Å) would have been much shorter and the C(5)–H · · · O(1) and C(20)–H · · · O(1) distances much longer. The opposite situation holds in (2) where the unexpected conformation of ring A leads to normal C–H · · · O distances. A flattening of ring A in this case would have resulted in the two distances C(2)–H · · · O(1) (3.50 Å) and C(4)–H · · · O(1) (3.49 Å) being much shorter and the C(21)–H · · · O(1) distance much longer. It is interesting that in both

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[3] G. Ferguson and J. Tyrrell, *Chem. Comm.*, 1965, 195.

[4] G. Ferguson and K. M. S. Islam, *J. Chem. Soc.* (*B*), 1968, 980.

for ring A of 17β-hydroxyandrostan-3-one monohydrate[5] are also given in Table 1. In this crystal structure too, the carbonyl oxygen O(1) is involved in intermolecular contacts (with the water of hydration), making meaningful comparison with ring A of (2) difficult.

TABLE 4

Molecular dimensions in (2)

(*a*) Bond lengths (Å), with estimated standard deviations in parentheses

Br–C(21)	1.883(10)	C(11)–C(9)	1.553(10)
C(21)–C(20)	1.515(11)	C(9)–C(8)	1.554(10)
C(20)–O(2)	1.195(11)	C(9)–C(10)	1.565(8)
C(20)–O(3)	1.355(10)	C(7)–C(6)	1.531(10)
O(3)–C(17)	1.475(8)	C(6)–C(5)	1.506(11)
C(17)–C(16)	1.564(14)	C(5)–C(4)	1.567(9)
C(17–C(13)	1.530(8)	C(5)–C(10)	1.522(11)
C(16)–C(15)	1.549(10)	C(10)–C(1)	1.531(11)
C(15)–C(14)	1.550(11)	C(10)–C(19)	1.532(9)
C(14)–C(8)	1.530(8)	C(1)–C(2)	1.532(10)
C(14)–C(13)	1.542(11)	C(2)–C(3)	1.503(14)
C(13)–C(12)	1.532(11)	C(3)–O(1)	1.224(10)
C(13)–C(18)	1.530(10)	C(3)–C(4)	1.491(14)
C(11)–C(12)	1.539(9)		

(*b*) Bond angles (°); mean standard deviation 0.6°

Br–C(21)–C(20)	110.0	C(8)–C(9)–C(10)	113.3
C(21)–C(20)–O(2)	126.6	C(10)–C(9)–C(11)	114.6
C(21)–C(20)–O(3)	106.7	C(9)–C(10)–C(1)	110.0
O(2)–C(20)–O(3)	126.4	C(9)–C(10)–C(5)	106.7
C(20)–O(3)–C(17)	115.9	C(1)–C(10)–C(5)	108.0
O(3)–C(17)–C(16)	107.5	C(1)–C(10)–C(19)	110.2
O(3)–C(17)–C(13)	112.1	C(5)–C(10)–C(19)	111.7
C(13)–C(17)–C(16)	105.7	C(9)–C(10)–C(19)	110.1
C(15)–C(16)–C(17)	104.3	C(9)–C(8)–C(14)	107.6
C(14)–C(15)–C(16)	104.0	C(9)–C(8)–C(7)	109.6
C(13)–C(14)–C(15)	104.0	C(14)–C(8)–C(7)	110.1
C(13)–C(14)–C(8)	113.8	C(6)–C(7)–C(8)	111.9
C(8)–C(14)–C(15)	118.8	C(5)–C(6)–C(7)	109.2
C(12)–C(13)–C(14)	108.0	C(4)–C(5)–C(6)	109.6
C(17)–C(13)–C(14)	98.0	C(4)–C(5)–C(10)	112.2
C(12)–C(13)–C(17)	115.6	C(6)–C(5)–C(10)	114.7
C(12)–C(13)–C(18)	110.6	C(3)–C(4)–C(5)	110.3
C(17)–C(13)–C(18)	110.8	C(2)–C(3)–C(4)	117.3
C(14)–C(13)–C(18)	113.4	C(2)–C(3)–O(1)	121.0
C(11)–C(12)–C(13)	110.9	C(4)–C(3)–O(1)	121.7
C(9)–C(11)–C(12)	112.7	C(1)–C(2)–C(3)	111.2
C(8)–C(9)–C(11)	110.9	C(10)–C(1)–C(2)	114.2

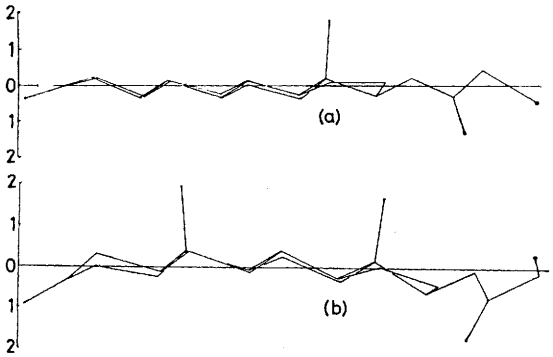

FIGURE 5 Atom displacements (Å) from the best plane through atoms C(1)—(13) in (a) (1) and (b) (2)

The conformations of rings B and C in (1) and (2) are normal chairs; ring D is in a C(13) envelope with C(13) being 0.71 in (1) and 0.73 Å in (2) from the plane of atoms C(14)—(17).

Bond distances and valency angles (Tables 3 and 4) are within the normal range. Mean dimensions include $C(sp^3)$–$C(sp^3)$ 1.535(3), $C(sp^3)$–$C(sp^2)$ 1.497(12), $C(sp^2)$=O 1.207(8), $C(sp^3)$–Br 1.887(6), $C(sp^3)$–O 1.468(7), and $C(sp^2)$–O 1.343(12) Å.

The overall shapes of the two derivatives are compared in Figure 5 where the relative displacement of the atoms from the best plane of the carbon atoms of the A, B, and C rings are shown. In (2) the skeleton is convex towards the β-side as is the case in 4,4-dimethyl-3-oxo derivatives;[6] such bending is explicable in terms of repulsions between the axial methyl groups and hydrogen atoms. By contrast, in (1) the molecular skeleton is very slightly convex to the α-side, in accord with the absence of the methyl group at C(10) and the intermolecular contacts previously described.

EXPERIMENTAL

17β-*Bromoacetoxy*-19-*nor*-5α-*androstan*-3-*one* (1).—A mixture of 17β-hydroxy-19-nor-5α-androstan-3-one (0.5 g), chloroacetic anhydride (1.5 g), and pyridine (0.5 ml) was heated at 100 °C during 3 h. The product was purified by chromatography on silica from benzene–light petroleum (b.p. 60—80 °C) (1 : 1) and then by crystallisation from light petroleum (b.p. 60—80 °C) containing a trace (0.1%) of acetone. 17β-*Chloroacetoxy*-19-*nor*-5α-*androstan*-3-*one* formed needles, m.p. 76—78 °C (Found: C, 67.9; H, 8.0; Cl, 10.2. $C_{20}H_{29}ClO_3$ requires C, 68.1; H, 8.3; Cl, 10.1%).

A solution of this chloroacetate (0.3 g) in acetone (25 ml), containing potassium bromide (0.75 g) was heated under reflux for 18 h. The product was purified from acetone–light petroleum (b.p. 40—60 °C) to yield needles of (1), m.p. 92—93 °C (Found: C, 60.6; H, 7.1; Br, 17.3. $C_{20}H_{29}BrO_3$ requires C, 60.4; H, 7.3; Br, 20.1%).

Crystal Data for (1).—$C_{20}H_{29}BrO_3$, $M = 397.4$. Orthorhombic, $a = 6.134(1)$, $b = 12.580(2)$, $c = 25.297(3)$ Å, $U = 1\,952$ Å^3, $D_m = 1.35$ (by flotation in aqueous potassium iodide), $Z = 4$, $D_c = 1.352$, $F(000) = 832$. Space group $P2_12_12_1$ (D_2^4, No. 19) uniquely from systematic absences $h00$ when h is odd, $0k0$ when k is odd, $00l$ when l is odd. Linear absorption coefficient for Cu-K_α radiation ($\lambda = 1.541\,8$ Å), $\mu = 32.8$ cm^{-1}.

The crystals were thin, transparent plates elongated along *a*. Preliminary oscillation, Weissenberg, and precession photographs indicated orthorhombic symmetry. The crystal chosen for data collection was an irregularly shaped rectangular plate with dimensions *ca.* 0.1 × 0.3 × 0.4 mm^3.

Accurate unit-cell parameters were obtained by a least-squares procedure applied to the 2θ values of 12 general reflections measured on a Hilger and Watts Y 290 four-circle diffractometer and intensity data were collected to $\theta_{max.}$ 57°. The θ—2θ scan technique was used with a symmetric scan of 0.8° and a scan rate of 0.6° min^{-1}; background counts of 20 s duration were measured at each end of the scan. The small variation in intensity (<5%) of the 3 standard reflections indicated good crystal stability.

Each intensity was corrected for background and its estimated standard deviation, σ(I) was given by $\sigma(I) =$

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[5] B. Busetta, C. Courseille, J. M. Fornies-Marquina, and M. Hospital, *Cryst. Structure Comm.*, 1972, **1**, 43.

[6] G. Ferguson, E. W. Macaulay, J. M. Midgley, J. M. Robertson, and W. B. Whalley, *Chem. Comm.*, 1970, 954.

$[S + 4(B_1 + B_2) + (P \times S)^2]^{1/2}$. S, B_1, and B_2 are the scan, and first and second background counts, and P is a factor introduced to avoid overweighting of the intense reflections. A value of 0.05 for P gave an adequate weighting scheme for the data. Of 1 457 independent reflections measured, 1 057 were considered observed having $I > 3\sigma(I)$. Data were corrected for Lorentz and polarisation factors, and absorption effects.

TABLE 5

Final positional parameters for (1); Br × 10^5, others × 10^4, with estimated standard deviations in parentheses

Atom	X/a	Y/b	Z/c
Br	−300(31)	61 672(15)	48 737(6)
O(1)	11 217(16)	6 426(7)	−172(3)
O(2)	1 790(12)	7.865(5)	4 097(2)
O(3)	4 426(12)	6 784(5)	3 791(2)
C(1)	8 127(21)	5 866(8)	974(4)
C(2)	9 839(24)	5 504(10)	560(4)
C(3)	10 894(18)	6 386(9)	303(4)
C(4)	11 650(22)	7 286(8)	657(4)
C(5)	994(19)	7 594(7)	1 082(3)
C(6)	11 013(24)	8 363(8)	1 457(5)
C(7)	9 470(21)	8 678(7)	1 913(4)
C(8)	8 616(17)	7 704(6)	2 201(3)
C(9)	7 530(15)	6 929(7)	1 818(3)
C(10)	9 138(15)	6 592(6)	1 372(3)
C(11)	6 543(20)	5 941(7)	2 095(4)
C(12)	5 091(26)	6 271(9)	2 568(4)
C(13)	6 324(16)	6 986(6)	2 954(3)
C(14)	7 108(17)	7 986(7)	2 658(3)
C(15)	7 874(18)	8 737(6)	3 087(3)
C(16)	6 403(21)	8 454(7)	3 562(4)
C(17)	5 007(18)	7 535(7)	3 374(3)
C(18)	8 227(18)	6 388(7)	3 216(4)
C(19)	2 806(19)	7 061(9)	4 112(3)
C(20)	2 653(25)	6 181(10)	4 522(5)
H(11)	6 834	6 318	768
H(12)	7 414	5 200	1 164
H(21)	8 968	5 035	264
H(22)	10 997	5 025	758
H(41)	11 990	7 988	424
H(42)	13 127	7 047	861
H(51)	8 596	7 992	894
H(61)	11 627	9 069	1 254
H(62)	12 518	7 979	1 636
H(71)	8 188	9 134	1 743
H(72)	10 383	9 183	2 193
H(81)	10 020	7 298	2 380
H(91)	6 172	7 377	1 644
H(101)	10 457	6 145	1 568
H(111)	5 543	5 507	1 821
H(112)	7 839	5 429	2 239
H(121)	3 745	6 712	2 421
H(122)	4 590	5 576	2 774
H(141)	5 866	8 428	2 438
H(151)	7 699	9 545	2 976
H(152)	9 589	8 571	3 175
H(161)	5 464	9 124	3 667
H(162)	7 417	8 196	3 889
H(171)	3 404	7 836	3 230
H(181)	9 158	6 913	3 468
H(182)	7 610	5 732	3 459
H(183)	9 311	6 051	2 919
H(201)	2 861	5 432	4 319
H(202)	3 934	6 287	4 806

Structure Solution and Refinement of (1).—The position of the bromine atom in the unit cell was obtained from a three-dimensional Patterson function. A Fourier synthesis phased on this atom alone using weighted structure amplitudes[7] revealed the molecular structure. A structure-factor calculation based on all the non-hydrogen atoms gave R 0.39. Ten cycles of refinement by block-diagonal least-squares methods with weights derived from the counting statistics and with all non-hydrogen atoms allowed anisotropic motion, reduced R to 0.075.

TABLE 6

Final positional parameters for (2); Br × 10^5, others × 10^4, with estimated standard deviations in parentheses

Atom	X/a	Y/b	Z/c
Br	96 859(9)	−25 000 *	80 132(10)
O(1)	−119(4)	1 981(10)	6 240(7)
O(2)	8 071(5)	−971(9)	9 744(7)
O(3)	8 355(3)	1 838(7)	8 945(4)
C(1)	2 494(6)	585(10)	6 280(7)
C(2)	1 368(6)	656(12)	5 558(8)
C(3)	771(5)	2 204(17)	6 026(7)
C(4)	1 299(5)	4 019(12)	6 188(7)
C(5)	2 439(5)	3 812(11)	6 948(6)
C(6)	2 940(6)	5 667(11)	7 157(8)
C(7)	4 007(6)	5 475(11)	8 042(8)
C(8)	4 727(5)	5 117(10)	7 502(6)
C(9)	4 175(5)	2 254(11)	7 235(5)
C(10)	3 072(4)	2 414(12)	6 338(5)
C(11)	4 900(6)	794(10)	6 816(6)
C(12)	5 922(5)	582(10)	7 782(7)
C(13)	6 485(5)	2 420(13)	8 031(6)
C(14)	5 717(5)	3 783(10)	8 485(6)
C(15)	6 414(6)	5 438(11)	8 983(8)
C(16)	7 471(6)	4 563(13)	9 582(7)
C(17)	7 341(5)	2 496(14)	9 218(6)
C(18)	6 904(5)	3 060(11)	6 838(6)
C(19)	3 221(5)	2 998(10)	4 990(6)
C(20)	8 586(5)	68(12)	9 241(8)
C(21)	9 661(6)	−288(13)	8 915(9)
H(11)	2 943	−434	5 809
H(12)	2 469	89	7 234
H(21)	1 438	754	4 536
H(22)	1 029	−693	5 689
H(41)	1 364	4 521	5 206
H(42)	862	4 975	6 623
H(51)	2 351	3 292	7 888
H(61)	3 076	6 168	6 258
H(62)	2 453	6 538	7 595
H(71)	4 401	6 791	8 174
H(72)	3 909	4 989	9 006
H(81)	4 902	4 586	6 580
H(91)	3 991	1 783	8 152
H(111)	5 101	1 125	5 884
H(112)	4 494	−562	6 696
H(121)	6 406	−455	7 435
H(122)	5 700	64	8 676
H(141)	5 314	3 302	9 285
H(151)	6 554	6 215	8 130
H(152)	6 093	6 269	9 606
H(161)	8 135	4 101	9 284
H(162)	7 562	4 670	10 653
H(171)	7 089	1 575	9 963
H(181)	6 260	3 262	6 054
H(182)	7 324	4 330	7 036
H(183)	7 437	2 052	6 533
H(191)	2 440	3 104	4 373
H(192)	3 601	4 281	5 000
H(193)	3 655	1 967	4 550
H(211)	10 192	−377	9 830
H(212)	9 834	831	8 380

* Held invariant to fix the origin in the refinement cycles.

A difference-Fourier synthesis was then calculated and all the hydrogen atoms were located in positions which compared favourably with calculated positions assuming C–H 1.08 Å. Five cycles of block-diagonal least-squares refinement, with the positional and isotropic thermal parameters (U 0.063 Å^2) of the twenty-nine hydrogen atoms held constant, reduced R to a final value of 0.061. The weighted residual R' $\{= [\Sigma w(F_o - F_c)^2/\varepsilon w F_o{}^2]^{1/2}\}$ for the observed

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[7] G. A. Sim in 'Computing Methods and the Phase Problem in *X*-Ray Crystal Structure Analysis,' eds. R. Pepinsky, J. M. Robertson, and J. C. Speakman, Pergamon, Oxford, 1961.

reflections was 0.079 and the maximum shift-to-error ratio was <0.3. A final difference synthesis was essentially featureless. Scattering factors for bromine, oxygen, carbon, and hydrogen were taken from ref. 8 and allowance was made for the real and imaginary parts of anomalous dispersion due to the bromine atoms.[8] Final atomic coordinates are in Table 5 and molecular dimensions in Table 3. Final values for observed and calculated structure factors, thermal parameters, and details of mean plane calculations for both (1) and (2) are deposited as Supplementary Publication No. SUP 22164 (16 pp.).*

17β-*Bromoacetoxy*-5α-*androstan*-3-*one* (2).—Prepared from 17β-hydroxy-5α-androstan-3-one as for the 19-nor-analogue, 17β-*chloroacetoxy*-5α-*androstan*-3-*one* was formed as needles, m.p. 138 °C (Found: C, 68.6; H, 8.6; Cl, 8.9. $C_{21}H_{31}ClO_3$ requires C, 68.7; H, 8.6; Cl, 9.7%). Compound (2) was prepared from this chloroacetate as for (1) as *needles*, m.p. 134—136 °C (Found: C, 61.3; H, 7.4; Br, 18.0. $C_{21}H_{31}BrO_3$ requires C, 61.3; H, 7.6; Br, 19.4%).

Crystal Data for (2).—$C_{21}H_{31}BrO_3$, $M = 411.4$. Monoclinic, $a = 12.972(2)$, $b = 7.321(1)$, $c = 10.580(2)$ Å, $\beta = 99.71(1)°$, $U = 990.4$ Å^3, $D_m = 1.37$ (by flotation), $Z = 2$, $D_c = 1.38$, $F(000) = 432$. Space group $P2_1$ (C_2^2 No. 4) from systematic absences: $0k0$ if $k = 2n + 1$, optical activity, and successful refinement. Cu-K_α radiation, $\lambda = 1.541\,8$ Å; μ(Cu-K_α) = 32.3 cm^{-1}. The crystals were thin plates elongated along b.

The experimental details for the collection of intensity data for (2) were essentially identical with those detailed for (1). The variation in intensity for 3 standard reflections was <3%. 1 386 independent reflections were surveyed and the intensities corrected for Lorentz, polarisation and absorption effects. The 1 075 reflections with $I > 3\sigma(I)$ were considered observed.

Structure Solution and Refinement of (2).—The structure was solved by the heavy-atom method. An initial Fourier synthesis phased with the bromine atom contribution was complicated by the inevitable pseudosymmetry. However, a careful selection of peaks led to the correct structure. Refinement by block-diagonal least-squares calculations with anisotropic thermal parameters lowered R to 0.070. The scattering factors used in the calculations were from ref. 8 as before and weights in the least-squares calculations were those derived from counting statistics. A difference-Fourier synthesis, calculated at R 0.070, revealed all the hydrogen atoms in reasonable positions assuming tetrahedral geometry. Hydrogen atom parameters were included with U 0.063 Å^2 in structure-factor calculations but were not refined. Five further cycles of block-diagonal least-squares refinement with the positional and thermal parameters of the thirty-one hydrogen atoms held constant, led R to 0.042 at convergence, where the maximum shift-to-error ratio was <0.2. The weighted residual R' was 0.053. A final difference synthesis was essentially featureless.

Table 6 contains the final positional parameters; details of interatomic distances and angles are in Table 4.

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* See Notice to Authors No. 7 in *J.C.S. Perkin II*, 1977, Index issue.

[8] ' International Tables for *X*-Ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1962.