Conformational Studies. Part 12.[1] The Crystal and Molecular Structure of 17β-Iodoacetoxy-4,4-dimethyl-19-nor-5α-androstan-3-one and of 17β-Iodoacetoxy-4,4-dimethyl-5α-androstan-3-one

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The crystal and molecular structures of the title compounds have been determined by X-ray crystallography. The 19-nor-derivative (1), $C_{22}H_{33}IO_3$, crystallises in the orthorhombic system, space group $P2_12_12_1$ with four molecules in a unit cell of dimensions $a = 11.358(5)$, $b = 25.429(3)$, and $c = 7.516(7)$ Å; the 19-methyl derivative (2), $C_{23}H_{35}IO_3$, crystallizes in the orthorhombic space group $P2_12_12_1$ with four molecules in a unit cell $a = 14.917(3)$, $b = 19.466(3)$, $c = 7.490(3)$ Å. Both structures were solved by the heavy-atom method and refined by full-matrix least-squares calculations with three-dimensional diffractometer data, for (1) $R = 0.046$ for 1 110 reflections, for (2) $R = 0.040$ for 1 561 reflections. The conformation of ring A in both molecules exhibits a degree of flattening; ring D in (1) approximates to a C-13 envelope whilst the same ring in (2) has a conformation exactly intermediate between a C-13 and a C-14 envelope. Rings B and C in both molecules have normal chair conformations.

As part of an extensive investigation into the correlation of conformation with other physical parameters, together with attempts to evaluate the significance of methyl–hydrogen interactions in cyclohexane systems, we are examining [2] a series of steroids by X-ray crystallography. In this paper we report our analyses of 17β-iodoacetoxy-4,4-dimethyl-19-nor-5α-androstan-3-one (1) and of 17β-iodoacetoxy-4,4-dimethyl-5α-androstan-3-one (2). Details of the analyses are described in the Experimental section.
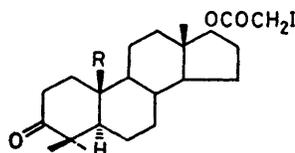
(1) R = H

(2) R = Me

The molecular conformations of (1) and (2) are shown in Figures 1 and 2 respectively, together with the atomic numbering schemes. Geise, Altona, and Romers [3] have reported a set of 'standard' values for torsional angles in steroid molecules; Table 1 compares the torsional angles in (1) and (2) with these 'standard' values. Since our preliminary communication,[4] new and more accurate data, reported in this paper, have been obtained for (2).

The results show clearly that ring A in (2) has a distorted (flattened) conformation in accord with general principles. Ring A in (1) exhibits a similar but lesser form of distortion. The angles $\phi(4,5,10,1)$ and $\phi(5,10,-1,2)$ are very similar in both steroids, suggesting that the environment at C-10 is the same in each and that the $1 \cdots 3$ interaction of the axial methyl groups at C(4) and C(10) is not relieved by displacement of C(19). The

differences in the remaining torsion angles arise from rotation about the C(4)–C(5) bond which results in a closing of the torsional angles in the more flexible portions of the ring.

Further evidence of the rotation about C(4)–C(5) is found (i) in the reduction of the distance of C(3) from the

TABLE 1

Comparison of torsion * angles (°) of a standard set,[3] with (1) and (2)

	Standard [3]	(1)	(2)
C(10)C(1)–C(2)C(3)	−55.8	−54.9	−53.1
C(1)C(2)–C(3)C(4)	+52.3	+56.8	+51.1
C(2)C(3)–C(4)C(5)	−52.6	−54.7	−46.8
C(3)C(4)–C(5)C(10)	+56.5	+50.4	+47.5
C(4)C(5)–C(10)C(1)	−55.1	−51.9	−50.9
C(5)C(10)–C(1)C(2)	+54.9	+52.6	+52.7
C(9)C(10)–C(5)C(6)	+58.0	+55.7	+59.1
C(10)C(5)–C(6)C(7)	−57.2	−57.2	−58.1
C(5)C(6)–C(7)C(8)	+53.4	+56.2	+53.4
C(6)C(7)–C(8)C(9)	−51.9	−55.3	−50.5
C(7)C(8)–C(9)C(10)	+54.6	+57.7	+54.2
C(8)C(9)–C(10)C(5)	−56.9	−57.1	−57.4
C(14)C(8)–C(9)C(11)	−52.8	−54.6	−51.4
C(8)C(9)–C(11)C(12)	+53.7	+55.3	+50.5
C(9)C(11)–C(12)C(13)	−55.0	−55.6	−53.5
C(11)C(12)–C(13)C(14)	+55.6	+53.5	+56.1
C(12)C(13)–C(14)C(8)	−59.2	−57.8	−61.0
C(13)C(14)–C(8)C(9)	+56.7	+59.0	+59.3
C(17)C(13)–C(14)C(15)		+46.5	+45.4
C(13)C(14)–C(15)C(16)		−36.6	−37.8
C(14)C(15)–C(16)C(17)		+11.5	+14.4
C(15)C(16)–C(17)C(13)		+18.0	+14.1
C(14)C(13)–C(17)C(16)		−38.9	−36.1

* The sign convention for the direction of the torsional angle is that of W. Klyne and V. Prelog (*Experientia*, 1960, **16**, 521).

plane defined by C(1)–C(2)–C(4)–C(5) to 0.55 Å in (2) as compared with 0.63 Å in (1), (ii) the increase in the Me · · · Me separation from the 'normal' 1-3 trans-annular distance of 2.52 to 3.30 Å in (2), (iii) the increase in the intramolecular distances C(20) · · · C(2) and C(20) · · · C(10) 3.20 and 3.36 Å respectively in (2) in contrast to 3.08 and 3.21 Å respectively in (1), and (iv)

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the difference in the values for the torsion angle $\phi O(1)-$C(3)–C(4)–C(21) which is 15.3° in (2) and 2.9° in (1).

An additional feature of the geometry of ring A in (2) merits comment. Inspection of the intramolecular non-bonded distances [Table 2(b)] illustrates dramatically that whilst the C(19) · · · C(2), C(19) · · · C(6), C(19) · · · C(8), and C(19) · · · C(11) distances are very similar and of an anticipated ' normal ' value, the C(19) · · · C(4) distance is significantly greater (at 3.31 Å). These observations provide the first definitive evidence in support of the previously discussed hypothesis [5] that the C(1),C(2),C(3),C(10) plane differs vectorially from the C(3),C(4),C(5),C(10) plane in ring A of steroidal 3-ketones. A similar, but understandably less dramatic effect, is apparent in the geometry of ring A in (1). The intermolecular contact distances [Table 2(d)] are clearly too great to be involved in this phenomenon which must be regarded as uniquely associated with the internal geometry of each molecule.

Rings B and C in (1) and (2) adopt normal chair conformations, but the conformation of ring D in (1)

TABLE 2

Interatomic distances (Å) and angles (°) in 17β-iodoacetoxy-4,4-dimethyl-5α-androstan-3-one (2) and 17β-iodo-acetoxy-4,4-dimethyl-19-nor-5α-androstan-3-one (1) with estimated standard deviations in parentheses

(a) Bonded distances

Distance	(1)	(2)
I–C(23)	2.155(10)	2.123(11)
O(1)–C(3)	1.203(16)	1.206(13)
O(2)–C(22)	1.174(15)	1.220(14)
O(3)–C(17)	1.457(13)	1.480(12)
O(3)–C(22)	1.354(15)	1.315(16)
C(1)–C(2)	1.522(18)	1.533(16)
C(2)–C(3)	1.469(19)	1.512(18)
C(3)–C(4)	1.546(19)	1.501(16)
C(4)–C(5)	1.554(16)	1.576(16)
C(4)–C(20)	1.548(19)	1.518(15)
C(4)–C(21)	1.503(18)	1.534(16)
C(5)–C(6)	1.534(17)	1.519(14)
C(5)–C(10)	1.565(15)	1.556(13)
C(6)–C(7)	1.488(18)	1.532(14)
C(7)–C(8)	1.537(16)	1.517(14)
C(8)–C(9)	1.541(15)	1.547(13)
C(8)–C(14)	1.533(14)	1.525(13)
C(9)–C(10)	1.535(15)	1.549(12)
C(9)–C(11)	1.543(16)	1.552(13)
C(10)–C(1)	1.488(15)	1.543(13)
C(10)–C(19)		1.534(13)
C(11)–C(12)	1.532(15)	1.530(13)
C(12)–C(13)	1.540(16)	1.534(14)
C(13)–C(14)	1.554(14)	1.530(13)
C(13)–C(17)	1.525(16)	1.518(14)
C(13)–C(18)	1.551(15)	1.531(13)
C(14)–C(15)	1.551(17)	1.511(13)
C(15)–C(16)	1.525(18)	1.534(16)
C(16)–C(17)	1.520(19)	1.530(15)
C(22)–C(23)	1.505(18)	1.473(16)

(b) Intramolecular non-bonded distances

Distance	(1)	(2)	Distance	(2)
C(18)–C(8)	3.15	3.11	C(19)–C(2)	3.16
C(18)–C(11)	3.11	3.09	C(19)–C(4)	3.31
C(18)–C(15)	3.01	3.01	C(19)–C(6)	3.09
C(18)–C(16)	3.07	3.14	C(19)–C(8)	3.10
C(20)–C(2)	3.08	3.20	C(19)–C(11)	3.09
C(20)–C(6)	3.11	3.15	C(19)–C(20)	3.30
C(20)–C(10)	3.21	3.36		
C(21)–C(6)	3.07	3.07		

TABLE 2 (Continued)

(c) Valency angles

Angle	(1)	(2)
C(2)–C(1)–C(10)	113.8	113.6
C(1)–C(2)–C(3)	109.9	111.8
C(2)–C(3)–C(4)	116.1	117.5
C(2)–C(3)–O(1)	121.8	119.6
C(4)–C(3)–O(1)	122.1	122.9
C(3)–C(4)–C(5)	107.0	109.4
C(3)–C(4)–C(20)	107.4	108.0
C(3)–C(4)–C(21)	109.2	108.4
C(5)–C(4)–C(20)	113.2	114.9
C(5)–C(4)–C(21)	110.9	109.0
C(20)–C(4)–C(21)	109.1	107.0
C(4)–C(5)–C(6)	113.3	114.4
C(4)–C(5)–C(10)	113.7	116.6
C(6)–C(5)–C(10)	110.6	111.4
C(5)–C(6)–C(7)	113.1	111.4
C(6)–C(7)–C(8)	110.3	113.1
C(7)–C(8)–C(9)	110.7	110.9
C(7)–C(8)–C(14)	110.6	112.3
C(5)–C(10)–C(9)	108.1	107.0
C(5)–C(10)–C(19)		113.6
C(9)–C(10)–C(19)		109.9
C(9)–C(11)–C(12)	114.3	113.7
C(11)–C(12)–C(13)	111.2	111.8
C(12)–C(13)–C(14)	107.8	107.4
C(12)–C(13)–C(17)	119.1	116.3
C(12)–C(13)–C(18)	111.0	110.6
C(14)–C(13)–C(17)	97.5	99.2
C(14)–C(13)–C(18)	111.9	113.5
C(17)–C(13)–C(18)	108.8	109.5
C(8)–C(14)–C(13)	114.4	114.0
C(8)–C(14)–C(15)	118.9	119.7
C(13)–C(14)–C(15)	104.7	104.2
C(14)–C(15)–C(16)	101.7	103.9
C(15)–C(16)–C(17)	107.4	105.0
C(13)–C(17)–C(16)	106.8	107.1
C(13)–C(17)–O(3)	116.2	117.4
C(9)–C(8)–C(14)	109.1	109.2
C(8)–C(9)–C(10)	112.0	113.2
C(8)–C(9)–C(11)	109.5	111.3
C(10)–C(9)–C(11)	112.7	114.2
C(1)–C(10)–C(5)	110.9	108.6
C(1)–C(10)–C(9)	112.3	107.8
C(1)–C(10)–C(19)		109.8
C(16)–C(17)–O(3)	107.4	104.3
C(23)–C(22)–O(2)	125.3	122.1
C(23)–C(22)–O(3)	109.0	113.3
O(2)–C(22)–O(3)	125.7	124.5
C(22)–C(23)–I	109.4	112.0
C(17)–O(3)–C(22)	118.5	119.5

Mean estimated standard deviations (°)

Angle	(1)	(2)	Angle	(1)	(2)
C–$\widehat{C}$–C	0.9	0.8	C–$\widehat{O}$–C	0.9	0.9
C–$\widehat{C}$–O	1.0	1.1	C–$\widehat{C}$–I	0.8	0.8
O–$\widehat{C}$–O	1.1	1.2			

(d) Shorter intermolecular distances

(1)

C(23) · · · O(3)[I]	3.35		C(7) · · · O(2)[IV]	3.42
O(1) · · · I(1)[II]	3.38		C(1) · · · O(1)[III]	3.45
C(10) · · · O(1)[III]	3.41			

Superscripts refer to the following transformations of the co-ordinates of the second atom

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

(2)

O(1) · · · C(23)[I]	3.23		O(2) · · · C(5)[II]	3.45
O(2) · · · C(1)[II]	3.29		O(1) · · · C(22)[I]	3.47
O(2) · · · C(3)[II]	3.29			

Superscripts refer to the following transformations of the co-ordinates of the second atom

I $\frac{3}{4} - x, -y, \frac{1}{2} + z$ II $\frac{3}{2} - x, -y, -\frac{1}{2} + z$

differs from that in (2). In (2) this ring adopts a conformation intermediate between that of a C(13) and a C(14) envelope ($\phi_m = 45.4°$, $\Delta = -1.6°$), whereas (1), in contrast, exhibits a half-chair conformation distorted * towards a C(13) envelope ($\phi_m = 46.6°$, $\Delta = 7.0°$). These distortions are apparent from the displacements of C(13) and C(14) from the plane of C(15), C(16), C(17) [+0.35 and −0.37 Å respectively in (2), and 0.45 and −0.30 Å respectively in (1)], which result in the D ring of (2) possessing an approximate twofold axis of symmetry running from the mid-point of C(13)–C(14) through C(16). No such symmetry elements exist in the corresponding ring of (1).

These observations are compatible with the concepts of ' conformational transmission '.[7]

The preparation of various additional ring A polymethylated steroidal-3-ones is recorded in the Experimental section.

EXPERIMENTAL

17β-*Iodoacetoxy-4,4-dimethyl-19-nor-5α-androstan-3-one*.— Prepared from 17β-hydroxy-4,4-dimethyl-19-nor-5α-androstan-3-one (0.45 g), chloroacetic anhydride (1.4 g), and pyridine (0.1 ml), 17β-*chloroacetoxy-4,4-dimethyl-19-nor-5α-androstan-3-one* separated from light petroleum as needles (0.5 g), m.p. 130 °C, $[\alpha]_D^{20} -18.8°$ (c, 1.0) (Found: C, 69.6; H, 8.8; Cl, 9.1. $C_{22}H_{33}ClO_3$ requires C, 69.4; H, 8.7; Cl, 9.3%); $\nu_{max.}$ (CCl₄) 1 761 (chloro-acetate) and 1 705 (>C=O) cm⁻¹.

A solution of this 17β-chloroacetate (0.25 g) and potassium iodide (1 g) in acetone (17 ml) was refluxed for 3 h. Purified from light petroleum, 17β-*iodoacetoxy-4,4-dimethyl-19-nor-5α-androstan-3-one* formed needles (0.2 g), m.p. 129 °C, $[\alpha]_D^{20} -2.6°$ (c, 0.8) (Found: C, 56.3; H, 7.0; I, 25.9. $C_{22}H_{33}IO_3$ requires C, 55.9; H, 7.0; I, 26.9%); $\nu_{max.}$ (CCl₄) 1 730 (iodoacetate) and 1 705 (>C=O) cm⁻¹.

17β-*Iodoacetoxy-4,4-dimethyl-5α-androstan-3-one*.— Prepared by the interaction of 17β-hydroxy-4,4-dimethyl-5α-androstan-3-one (0.5 g) with chloroacetic anhydride (1.5 g) and pyridine (0.5 ml) during 3 h, at 100 °C, 17β-*chloroacet-oxy-4,4-dimethyl-5α-androstan-3-one* formed needles (0.5 g), m.p. 144 °C from methanol–acetone, $[\alpha]_D^{20} -11.4°$ (c, 2.0) (Found: C, 70.1; H, 9.0; Cl, 8.9. $C_{23}H_{35}ClO_3$ requires C, 69.9; H, 8.9; Cl, 8.9%); $\nu_{max.}$ 1 737 (trichloro-acetate) and 1 710 cm⁻¹ (>C=O).

A solution of this chloroacetate (0.2 g) in acetone (18 ml) containing sodium bromide (0.6 g) was refluxed for 12 h. The product was purified from methanol–acetone to give 17β-*bromoacetoxy-4,4-dimethyl-5α-androstan-3-one* as plates (0.2 g), m.p. 146 °C, $[\alpha]_D^{20} -6.8°$ (c, 1.9) (Found: C, 62.2; H, 8.3; Br, 18.4. $C_{23}H_{35}BrO_3$ requires C, 62.8; H, 8.0; Br, 18.2%); $\nu_{max.}$ 1 735 (acetate) and 1 703 cm⁻¹ (>C=O). The same product was prepared by the action of bromo-acetyl bromide upon 4,4-dimethyl-5α-androstan-17β-ol-3-one. The mixed m.p. with the corresponding chloro-derivative was ca. 137 °C.

Interaction of 17β-chloroacetoxy-4,4-dimethyl-5α-andros-tan-3-one (0.05 g) in boiling acetone (35 ml) with potassium iodide, during 3 h, gave 17β-*iodoacetoxy-4,4-dimethyl-5α-androstan-3-one* (0.5 g) which formed needles, m.p. 141 °C from methanol, $[\alpha]_D^{20} +3.7°$ (c, 2.02) (Found: C, 56.4;

H, 7.2; I, 25.8. $C_{23}H_{35}IO_3$ requires C, 56.8; H, 7.3; I, 26.1%), $\nu_{max.}$ 1 730 (acetate) and 1 705 cm⁻¹ (>C=O).

2,2-*Dimethyl-6-methylene-5α-cholestan-3-one*.— 6-Methylene-5α-cholestan-3-one (1 g) was methylated by the methyl iodide–potassium t-butoxide process to yield 2,2-*dimethyl-6-methylene-5α-cholestan-3-one* (0.7 g) as prisms, m.p. 124 °C from acetone–methanol; τ 9.33 (s, CH_3, 3 H), 9.17 (s, CH_3, 3 H), 9.07 (s, 2 × CH_3, 6 H), 8.92 (s, CH_3, 3H), 8.73 (s, 2 × CH_3, 6 H); $\nu_{max.}$ 1 700 cm⁻¹ (six-membered ring >C=O) (Found: C, 84.5; H, 11.5. $C_{30}H_{50}O$ requires C, 84.6; H, 11.7%).

A solution of this ketone (0.5 g) in methylene chloride (100 ml) was stirred with a solution of sodium metaperiodate (0.52 g), potassium carbonate (0.06 g), and potassium permanganate (0.03 g) during 2 h. The product was isolated and purified from acetone–methanol to yield 2,2-*dimethyl-5α-cholestan*e-3,6-*dione* as prisms (0.45 g), m.p. 129 °C (Found: C, 81.4; H, 11.6. $C_{29}H_{48}O_2$ requires C, 81.3; H, 11.2%).

Reduction of this dione (0.2 g) by the Wolff–Kishner process gave 2,2-dimethyl-5α-cholestane (0.16 g), m.p. and mixed m.p. with an authentic specimen 80 °C, mixed m.p. with authentic 4,4-dimethyl-5α-cholestane 45—56 °C.

A solution of 2,2-dimethyl-6-methylene-5α-cholestan-3-one (3.3 g) in acetic acid (100 ml) containing 60% perchloric acid (0.25 ml) was kept at 100 °C during 1½ h. Purification of the product by chromatography on alumina from benzene–light petroleum (1 : 9) gave 2,2,6-*trimethylcholest-4-en-3-one* (2.1 g) as stout prisms, m.p. 88 °C from methanol, $[\alpha]_D +36°$ (c, 1.4), $\nu_{max.}$ 1 670 cm⁻¹ (αβ-unsaturated ketone); τ 4.27 (d, J 1.5 Hz, 4-H) (Found: C, 84.9; H, 12.0. $C_{30}H_{50}O$ requires C, 84.6; H, 11.7%).

2,2,4,4,6-*Pentamethylcholest-5-en-3-one*.—A solution of 2,2,6-trimethylcholest-4-en-3-one (0.4 g) in t-butyl alcohol (25 ml) containing dissolved potassium (0.2 g) and methyl iodide (0.5 ml) was kept at room temperature for 1 h. Purified from acetone–methanol, 2,2,4,4,6-*pentamethyl-cholest-5-en-3-one* formed needles (0.17 g), m.p. 139 °C; o.r.d. (cyclohexane) $[\phi]_{500}$ 0°, $[\phi]_{400}$ 0°, $[\phi]_{311}$ +1 100°, $[\phi]_{260}$ −3 150°, $[\phi]_{220}$ +4 530°, [A] + 43°; $\nu_{max.}$ 1 690 cm_D⁻¹ (>C=O) (Found: C, 84.6; H, 12.3. $C_{32}H_{54}O$ requires C, 84.3; H, 11.9%).

4α-*Methyl-5α-androstan-3-one*.—Methylation of androst-4-en-3-one (3.5 g) by the methyl iodide–t-butyl alcohol–t-butoxide technique formed 4-*methylandrost-4-en-3-one* (1.6 g) as needles, m.p. 93 °C from methanol, $[\alpha]_D^{20} +65°$ (c, 0.4); $\lambda_{max.}$ 251 nm (ε 12 000); $\nu_{max.}$ 1 660 cm⁻¹ (αβ-unsaturated ketone); τ 9.25 (s, 13-methyl, 3 H), 8.83 (s, 10-methyl, 3 H), and 8.22 (s, 4-methyl, 3 H) (Found: C, 83.7; H, 10.6. $C_{20}H_{30}O$ requires C, 83.8; H, 10.6%).

Hydrogenation of this ketone (0.1 g) in methanol (7 ml) with palladium–strontium carbonate (2%, 25 mg) gave 4β-*methyl-5α-androstan-3-one* (0.1 g) as prisms, m.p. 160 °C from methanol, $[\alpha]_D^{22} +12°$ (c, 0.7); $\nu_{max.}$ 1 710 cm⁻¹ (saturated ketone); τ 9.28 (s, 13-methyl, 3 H), 9.03 (d, J 10 Hz, 4β-methyl, 3 H), and 8.77 (s, 10-methyl, 3 H) (Found: C, 83.3; H, 10.9. $C_{20}H_{32}O$ requires C, 83.2; H, 11.2%).

Heating of this ketone (0.1 g) in boiling ethanol (10 ml) containing 20% sulphuric acid (0.1 ml) during 2 h gave quantitative conversion into 4α-*methyl-5α-androstan-3-one* which formed prisms from methanol, m.p. 123 °C; τ 9.28 (s, 13-methyl, 3 H), 9.03 (d, 4-methyl, J 7 Hz, 3 H), and 8.93 (s, 10-methyl, 3 H) (Found: C, 83.1; H, 11.2. $C_{20}H_{32}O$ requires C, 83.2; H, 11.2%).

2α-*Methyl- and 2,2-Dimethyl-androstan-3-one*.—Prepared

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* For definition of Δ and ϕ values see ref. 6.

from 5α-androstan-3-one in the usual manner, 2α-*methyl-5α-androstan-3-one* formed needles, m.p. 120 °C from methanol, $[\alpha]_D^{20}$ +36°; $\nu_{max.}$ 1 710 cm^{-1} (>C=O); τ 9.28 (s, 13-methyl, 3 H), 9.03 (d, J 6 Hz, 2-methyl, 3 H), and 8.95 (s, 10-methyl, 3 H) (Found: C, 83.2; H, 11.1. C_{20}-$H_{32}O$ requires C, 85.2; H, 11.2%).

2,2-*Dimethyl-5α-androstan-3-one* formed prisms, m.p. 155 °C from methanol, $[\alpha]_D^{20}$ +41° (c, 0.9); $\nu_{max.}$ 1 705 cm^{-1} (>C=O); τ 9.28 (s, 13-methyl, 3 H), 9.13 (s, CH_3, 3 H), and 8.77 (s, 2 × CH_3, 6 H) (Found: C, 83.5; H, 11.1. $C_{21}H_{34}O$ requires C, 83.4; H, 11.3%).

X-Ray Analysis.—Preliminary photographic studies and
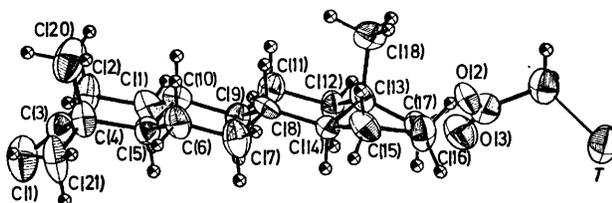
FIGURE 1   Molecular conformation of (1) with the numbering scheme

structure determinations of (I) and (II) were carried out at Glasgow.[8] Because of the unsatisfactory quality of the linear diffractometer data used in these analyses, the structures were redetermined using more accurate data measured by a four-circle diffractometer for (1) at Ottawa and for (2) at Guelph.

17β-*Iodoacetoxy-4,4-dimethyl-19-nor-5α-androstan-3-one* (1).—*Crystal data.* $C_{22}H_{23}O_3I$, M = 472.4. Orthorhombic, a = 11.358(5), b = 25.429(3), c = 7.516(7) Å, U = 2 170.8 Å^3, D_m = 1.44 g cm^{-3}, Z = 4, D_c = 1.45, $F(000)$ = 968. Space group $P2_12_12_1$ (D_2^4, No. 19) uniquely from systematic absences $h00$ if h = $2n$ + 1, $0k0$ if k = $2n$ + 1, $00l$ if l = $2n$ + 1. Mo-K_α radiation, λ = 0.710 69 Å; μ(Mo-K_α) = 15.6 cm^{-1}.

Intensities were measured by the 0/20 scan technique on a Picker four-circle diffractometer using Mo-K_α radiation. A rapid fall off of intensity with θ limited data
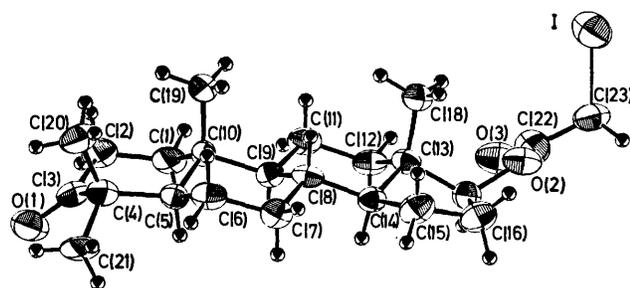
FIGURE 2   Molecular conformation of (2) with the numbering scheme

collection to θ ≤ 22°. Data were corrected for Lorentz and polarization effects but not for absorption. A total of 1 556 unique reflections were measured of which 1 110 had I > 3σ(I) and were used in the refinement of the structure.

The structure was refined by block-diagonal least-squares calculations with anisotropic thermal parameters starting from the non-hydrogen co-ordinates previously determined.[8] A difference synthesis before the conclusion of the refinement showed maxima in expected positions for all hydrogen atoms; these were allowed for (in geometrically expected
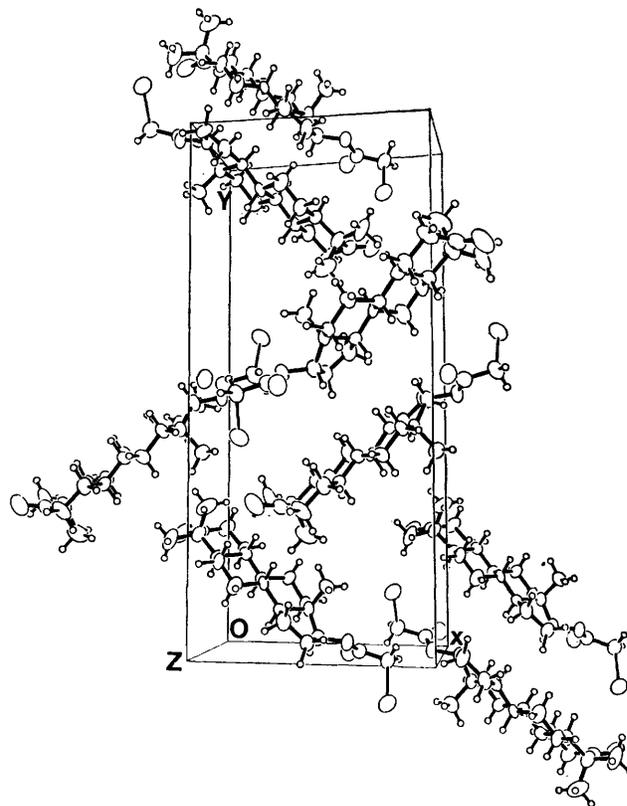
FIGURE 3   General view of the crystal structure of (1)

positions with C–H 0.95 Å) but not refined in subsequent cycles. Refinement converged when R = 0.046 and R' = $(\Sigma w \Delta^2/\Sigma w F_0^2)^{\frac{1}{2}}$ = 0.056 and a final difference synthesis was featureless. The atomic scattering curves used in the calculations were from ref. 9. Both real and imaginary parts of the dispersion curve for iodine [10] were included in

TABLE 3

Final positional parameters (×10^4) for 17β-iodoacetoxy-4,4-dimethyl-19-nor-5α-androstan-3-one with estimated standard deviations in parentheses

Atom	x/a	y/b	z/c
C(1)	4 331(11)	1 852(5)	5 404(15)
C(2)	5 205(12)	2 296(5)	5 715(17)
C(3)	6 224(11)	2 233(5)	4 530(19)
C(4)	5 951(10)	2 207(5)	2 516(16)
C(5)	5 038(10)	1 759(4)	2 249(15)
C(6)	4 639(10)	1 696(5)	311(16)
C(7)	3 867(11)	1 231(5)	27(16)
C(8)	2 789(8)	1 257(4)	1 262(14)
C(9)	3 177(9)	1 311(4)	3 220(15)
C(10)	3 949(9)	1 798(4)	3 519(13)
C(11)	2 083(9)	1 301(4)	4 436(16)
C(12)	1 297(9)	817(4)	4 192(16)
C(13)	907(8)	757(4)	2 240(14)
C(14)	2 031(9)	762(4)	1 062(15)
C(15)	1 594(10)	603(5)	−818(17)
C(16)	648(12)	198(5)	−375(19)
C(17)	418(10)	230(4)	1 614(17)
C(18)	33(10)	1 198(4)	1 707(16)
C(20)	5 483(14)	2 754(5)	1 949(23)
C(21)	7 069(11)	2 092(7)	1 517(20)
C(22)	−1 198(10)	−72(5)	3 436(17)
C(23)	−2 466(13)	−235(4)	3 255(15)
O(1)	7 208(8)	2 188(4)	5 100(12)
O(2)	−609(8)	−141(3)	4 696(12)
O(3)	−838(6)	416(3)	1 885(12)
I	−2 556(1)	−987(1)	1 945(1)

the structure-factor calculation, the absolute configuration being already established. The function minimised was $\Sigma w\Delta^2$ with $w = 1/\{1 + [(|F_o| - 50)/20]^2\}$.

A view of the molecule with the numbering scheme is in Figure 1 and the molecular packing is in Figure 3. Final fractional co-ordinates are in Tables 3 and 4 and main interatomic distances and angles are in Table 2. Thermal parameters and a listing of structure factors have been

TABLE 4

Calculated positional parameters ($\times 10^3$) for the hydrogen atoms in 17β-iodoacetoxy-4,4-dimethyl-19-nor-5α-androstan-3-one (the associated carbon atom is shown in brackets)

Atom	x	y	z
H(1)[C(1)]	472	151	582
H(2)[C(1)]	360	192	623
H(3)[C(2)]	548	231	702
H(4)[C(2)]	479	266	543
H(5)[C(5)]	541	140	263
H(6)[C(6)]	538	166	−51
H(7)[C(6)]	418	203	−6
H(8)[C(7)]	433	89	34
H(9)[C(7)]	360	121	−129
H(10)[C(8)]	231	161	92
H(11)[C(9)]	368	98	350
H(12)[C(10)]	344	213	321
H(13)[C(11)]	158	163	422
H(14)[C(11)]	236	130	576
H(15)[C(12)]	56	86	501
H(16)[C(12)]	176	49	459
H(17)[C(14)]	256	45	143
H(18)[C(15)]	229	44	−159
H(19)[C(15)]	129	92	−155
H(20)[C(16)]	89	−18	−79
H(21)[C(16)]	−14	29	−109
H(22)[C(17)]	86	−8	222
H(23)[C(18)]	−20	117	41
H(24)[C(18)]	44	157	191
H(25)[C(18)]	−65	119	246
H(26)[C(20)]	536	270	60
H(27)[C(20)]	607	305	225
H(28)[C(20)]	469	284	260
H(29)[C(21)]	741	172	189
H(30)[C(21)]	770	237	175
H(31)[C(21)]	690	207	15
H(32)[C(23)]	−289	5	249
H(33)[C(23)]	−286	−25	448

deposited as Supplementary Publication No. SUP 22765 (16 pp.).*

17β-*Iodoacetoxy*-4,4-*dimethyl*-5α-*androstan*-2-*one*　(2).— *Crystal data.* $C_{23}H_{35}O_3I$, $M = 486.4$. Orthorhombic, $a = 14.917(3)$, $b = 19.466(4)$, $c = 7.490(2)$ Å, $U = 2\,174.9$ Å^3, $D_m = 1.50$ g cm^{-3}, $Z = 4$, $D_c = 1.49$, $F(000) = 1\,000$. Space group $P2_12_12_1$ (D_2^4, No. 19) from systematic absences $h00$ if $h = 2n + 1$, $0k0$ if $k = 2n + 1$, $00l$ if $l = 2n + 1$. Mo-K_α radiation, $\lambda = 0.710\,69$ Å; $\mu(\text{Mo-}K_\alpha) = 16.0$ cm^{-1}.

A small crystal ($0.40 \times 0.08 \times 0.08$ mm) was used for the intensity data collection. Intensities were measured on a Hilger and Watts Y290 PDP8I-controlled four-circle diffractometer using graphite-monochromated Mo-K_α radiation as described previously.[11] Data were corrected for Lorentz, polarisation, and absorption effects. Of the 2 217 reflections with $\theta \leqslant 25°$, 1 561 with intensities $>3\sigma(I)$ were employed in structure refinement.

Refinement by full-matrix least-squares calculations, with anisotropic thermal parameters, of the co-ordinates determined previously,[8] proceeded smoothly. When R was

* For details of the Supplementary Publications scheme see Notice to Authors No. 7 in *J.C.S. Perkin II*, 1979, Index issue.

TABLE 5

Final positional parameters ($\times 10^4$) for 17β-iodoacetoxy-4,4-dimethyl-5α-androstan-3-one with estimated standard deviations in parentheses

Atom	x/a	y/b	z/c
C(1)	8 363(8)	1 870(7)	−138(15)
C(2)	8 994(10)	2 489(8)	−288(18)
C(3)	9 254(9)	2 631(6)	−2 202(20)
C(4)	8 513(7)	2 687(6)	−3 550(15)
C(5)	7 840(7)	2 070(5)	−3 291(14)
C(6)	7 056(8)	2 069(5)	−4 584(17)
C(7)	6 556(8)	1 381(6)	−4 547(16)
C(8)	6 268(7)	1 169(6)	−2 684(14)
C(9)	7 065(7)	1 210(5)	−1 364(12)
C(10)	7 528(6)	1 922(5)	−1 347(13)
C(11)	6 796(8)	941(6)	512(15)
C(12)	6 341(7)	236(6)	476(15)
C(13)	5 538(7)	224(5)	−800(15)
C(14)	5 876(6)	446(5)	−2 641(13)
C(15)	5 120(9)	259(6)	−3 893(17)
C(16)	4 766(9)	−423(7)	−3 150(17)
C(17)	5 171(7)	−480(6)	−1 280(14)
C(18)	4 777(8)	675(5)	−83(19)
C(19)	6 882(8)	2 465(6)	−602(20)
C(20)	8 079(8)	3 395(5)	−3 377(19)
C(21)	8 925(10)	2 642(8)	−5 423(18)
C(22)	4 612(10)	−997(7)	1 432(21)
C(23)	3 823(7)	−1 293(6)	2 332(21)
O(1)	10 035(6)	2 701(5)	−2 586(13)
O(2)	5 352(6)	−989(4)	2 127(15)
O(3)	4 434(6)	−755(4)	−168(12)
I	2 876(1)	−529(1)	3 056(2)

0.060, a difference synthesis revealed all the hydrogen atoms. These were allowed for (in idealised positions with C–H 0.95 Å) in subsequent rounds of calculations. One
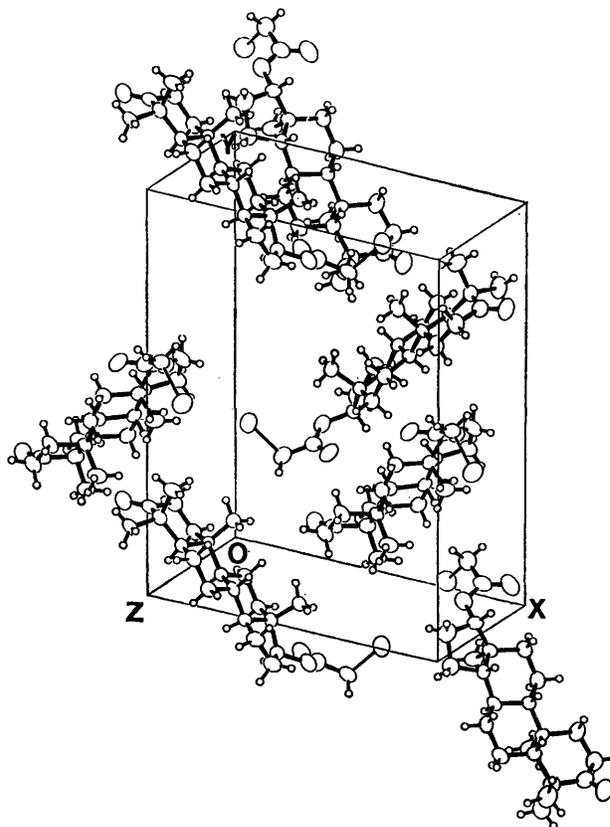
FIGURE 4　General view of the crystal structure of (2)

overall isotropic thermal parameter was refined for the methyl hydrogen atoms, and another for the non-methyl ones. Refinement converged with $R = 0.041$ and $R' =$

TABLE 6

Calculated positional parameters ($\times 10^4$) for the hydrogen atoms in 17β-iodoacetoxy-4,4-dimethyl-5α-androstan-3-one (the associated carbon atom is shown in brackets)

Atom	x	y	z
H(1)[C(1)]	8 165	1 837	1 065
H(2)[C(1)]	8 680	1 464	−450
H(3)[C(2)]	9 526	2 391	362
H(4)[C(2)]	8 710	2 882	207
H(5)[C(5)]	8 204	1 685	−3 573
H(6)[C(6)]	7 265	2 156	−5 761
H(7)[C(6)]	6 658	2 424	−4 230
H(8)[C(7)]	6 944	1 036	−5 001
H(9)[C(7)]	6 038	1 412	−5 279
H(10)[C(8)]	5 823	1 489	−2 319
H(11)[C(9)]	7 509	899	−1 780
H(12)[C(11)]	7 311	914	1 252
H(13)[C(11)]	6 385	1 263	999
H(14)[C(12)]	6 140	115	1 638
H(15)[C(12)]	6 765	−94	74
H(16)[C(14)]	6 389	197	−3 021
H(17)[C(15)]	5 327	216	−5 087
H(18)[C(15)]	4 666	601	−3 839
H(19)[C(16)]	4 130	−425	−3 094
H(20)[C(16)]	4 964	−789	−3 891
H(21)[C(17)]	5 661	−787	−1 136
H(22)[C(18)]	4 266	690	−839
H(23)[C(18)]	4 970	1 130	168
H(24)[C(18)]	4 627	450	1 001
H(25)[C(19)]	6 406	2 500	−1 440
H(26)[C(19)]	7 168	2 899	−485
H(27)[C(19)]	6 649	2 327	522
H(28)[C(20)]	7 620	3 489	−4 180
H(29)[C(20)]	8 598	3 676	−3 667
H(30)[C(20)]	7 910	3 491	−2 190
H(31)[C(21)]	9 136	2 186	−5 586
H(32)[C(21)]	9 414	2 953	−5 496
H(33)[C(21)]	8 500	2 749	−6 325
H(34)[C(23)]	3 547	−1 615	1 553
H(35)[C(23)]	4 017	−1 522	3 385

$(\Sigma w\Delta^2/\Sigma wF_0^2)^{\frac{1}{2}} = 0.039$ and a final difference synthesis had no significant features. The scattering factors for the non-hydrogen atoms were from ref. 12 with allowance for anomalous dispersion of iodine;[10] for hydrogen atoms, scattering factors were obtained from ref. 13. The function mimimized was $\Sigma w\Delta^2$ with $w = 1/\sigma^2(F_0)$ derived from counting statistics.

A view of the molecule with the numbering scheme is shown in Figure 2 and the arrangement of the molecules in the unit cell is in Figure 4. The final fractional co-ordinates are in Tables 5 and 6 and the principal distances and angles are in Table 2. Thermal parameters and a listing of structure factors have been deposited as Supplementary Publication No. SUP 22765.

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