

4-Chloromercurioandrosta-4,6-diene-3,17-dione: Preparation, X-Ray Structure Determination, and Potential Utility

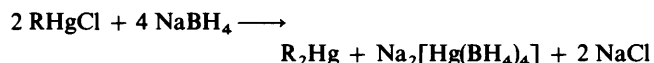
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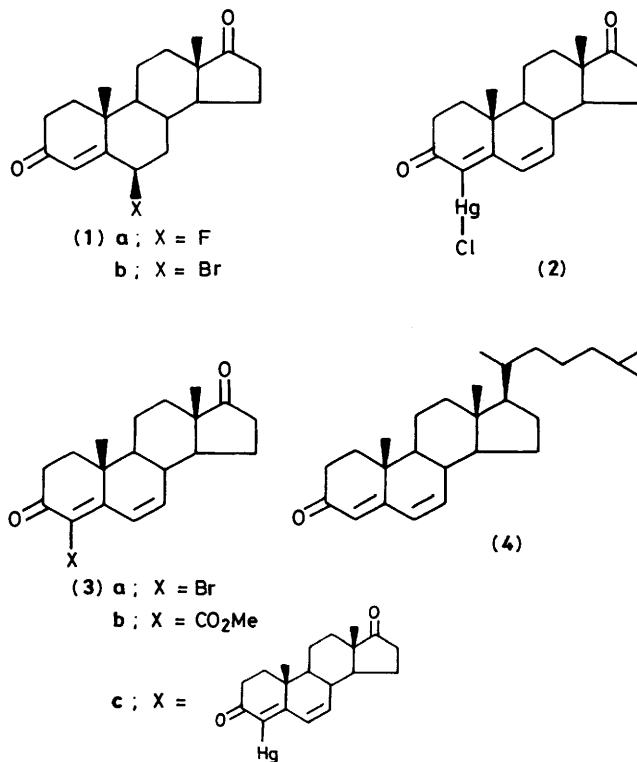
The novel steroid 4-chloromercurioandrosta-4,6-diene-3,17-dione (**2**) was obtained as a major side-product during conversions of 6 β -bromoandrost-4-ene-3,17-dione (**1b**) into its 6 β -fluoro derivative (**1a**) using HF(pyridine)_n and mercuric oxide. Compound (**2**) was successfully converted into various 4-substituted steroids (using standard vinyl-mercury methodology), including the disteroidal mercury compound (**3c**). Crystals of the acetone solvate of (**2**), 2(HgClC₁₉H₄₀O₂)·acetone, were monoclinic, space group *P*2₁, *Z* = 2 with dimensions *a* = 7.295(8), *b* = 24.12(1), *c* = 12.215(12) Å, β = 108.0(1)°. The two independent molecules have equivalent structures with the mercury atoms strongly bound to a chlorine atom and to carbon atom C(4) of the steroid. The acetone molecule forms a weak bridge between the two mercury atoms.

In our earlier paper¹ we reported two new syntheses of 6 β -fluoroandrost-4-ene-3,17-dione (**1a**) as part of our programme to produce novel aromatase inhibitors for the treatment of breast cancer. During attempts to prepare larger quantities of compound (**1a**) by one of these routes, we obtained the novel vinyl mercury side-product (**2**). The synthesis involved treatment of 6 β -bromoandrost-4-ene-3,17-dione (**1b**) with a mixture of yellow mercuric oxide and pyridinium poly(hydrogen fluoride). This method,² for the conversion of α -halogeno ketones into α -fluoro ketones, provided reasonable yields of compound (**1a**) (40%) after extensive chromatography; however, compound (**2**) was easily obtained (*ca.* 40%) after simple chromatography and recrystallisation from acetone-hexane mixtures. We first suspected that the compound contained mercury when the mass spectrum proved to be excessively complex; in addition the C-3 carbonyl signal was shifted to 1642 cm⁻¹ in the i.r. spectrum (1660 cm⁻¹ for androsta-4,6-diene-3,17-dione), and ¹⁹⁹Hg satellites were visible in the ¹³C n.m.r. spectrum. Finally, an X-ray structure determination (*vide infra*) provided final proof of the structure (**2**). The chlorine atom is apparently derived from the dichloromethane used for extraction.

Methods for the preparation of 4-substituted steroids are not common, and compound (**2**) should, in principle, allow access to such compounds. In practice it was possible to prepare 4-bromoandrost-4,6-diene-3,17-dione (**3a**) (Br₂ in CCl₄) and 4-methoxycarbonylandrost-4,6-diene-3,17-dione (**3b**) (PdCl₂, LiCl, CO) by standard methods.^{3,4} Finally, the mercury chloride was treated with sodium borohydride in an attempt to prepare androsta-4,6-diene-3,17-dione. This would have allowed access to 4-deuterio- and 4-tritio-steroids by use of the corresponding borohydrides. However, the reaction provided a mixture of alcohols which upon oxidation yielded the symmetrical di-steroidal mercury compound (**3c**). That a symmetrical product had been obtained was clear from the 400 MHz ¹H n.m.r. spectrum, which showed two clear singlets for the two sets of methyl protons. The exact mechanism of this reaction is not clear, but it is an example of the relatively common process of 'symmetrisation' (ref. 5), and a possible equation is given below:



Discussion of X-Ray Structure.—The asymmetric unit contains two molecules of HgCl(C₁₉H₄₀O₂) and one molecule of



solvent acetone. The two independent molecules (A and B) have similar geometries (see later, and Tables 1 and 2) and the conformation of molecule A is shown in Figure 1 together with the atomic numbering scheme.

The mercury atoms are two co-ordinate being strongly bonded to a chlorine atom [A 2.372(7), B 2.379(12) Å] and to C(4) of the steroid [A 2.00(3), B 2.11(3) Å]. The C(4)–Hg–Cl angles are close to linear, being 177.0(10), 174.5(10)°. A search of the Cambridge Data Centre files established that this is the first crystal structure which contains a mercury atom bonded directly to a steroid. Bis(testosterone)mercury(II) chloride⁶ contains mercury at 2.46 Å from an oxygen bonded to C(17) and is therefore not a direct comparison.

A search of the data files for mercury bonded to two fused six-membered rings, gave just one example, *viz* α -naphthylmercury iodide.⁷ However there are numerous examples of

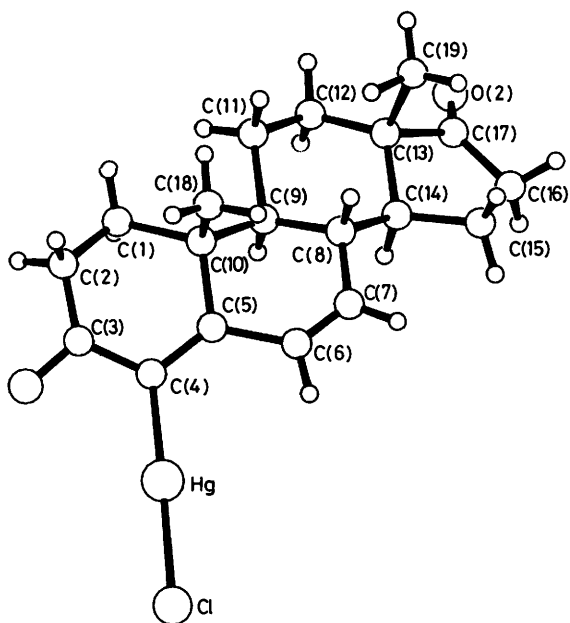


Figure 1. The conformation of $\text{HgCl}(\text{C}_{19}\text{H}_{40}\text{O}_2)$, molecule A

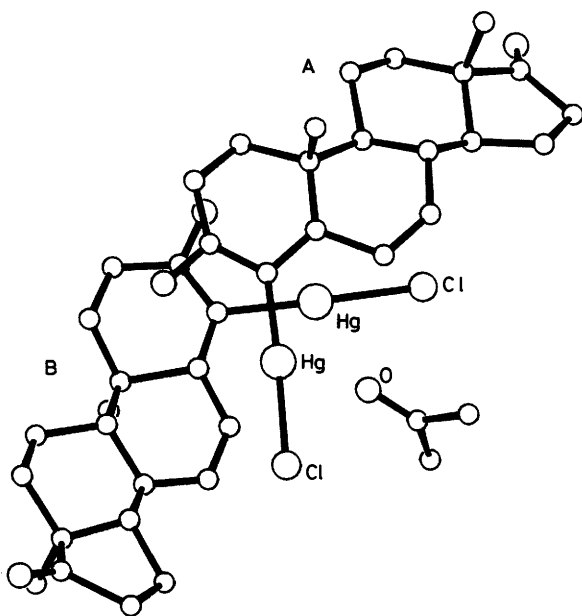


Figure 2. Two molecules A and B weakly bridged by an acetone molecule. (Hydrogen atoms omitted for clarity)

Hg–C bonds in other cyclic systems and the present Hg–C bond lengths are typical. In view of the standard deviations we do not believe the difference in Hg–Cl bond lengths to be significant.

There are 12 examples in the Cambridge Data Centre files of structures containing this type of steroid (with four fused 6 + 6 + 6 + 5 rings) with double bonds at C(4)–C(5) and C(6)–C(7), but most have different conformations at one or other of the asymmetric carbon atoms or have several side chains. The compound that is closest to the present molecule is cholesta-4,6-dien-3-one⁸ which differs only in the absence of mercury and the side chain on C(17). In Table 3, the conformations of molecules A and B are compared with that of this molecule (4).

As can be seen the variations in the torsion angles are small

Table 1. Atomic co-ordinates ($\times 10^4$) of compound (2)•acetone with e.s.d.s in parentheses

	x	y	z
Hg(1)	9 552(2)	5 000(0)	–1 323(1)
Cl(1)	9 483(10)	5 077(5)	600(6)
C(1A)	9 485(50)	4 661(22)	–5 294(29)
C(2A)	8 871(89)	4 261(23)	–4 643(54)
C(3A)	9 162(57)	4 375(20)	–3 470(54)
C(4A)	9 479(55)	4 912(13)	–2 965(27)
C(5A)	9 273(67)	5 364(19)	–3 685(43)
C(6A)	9 381(56)	5 987(20)	–3 441(44)
C(7A)	9 331(46)	6 375(19)	–4 045(34)
C(8A)	9 580(60)	6 311(16)	–5 159(40)
C(9A)	10 219(44)	5 743(15)	–5 339(37)
C(10A)	8 929(48)	5 279(14)	–5 003(33)
C(11A)	10 334(77)	5 659(18)	–6 658(32)
C(12A)	11 678(68)	6 083(19)	–6 957(35)
C(13A)	11 041(50)	6 640(15)	–6 669(38)
C(14A)	10 984(54)	6 728(14)	–5 411(33)
C(15A)	10 777(60)	7 346(17)	–5 296(40)
C(16A)	12 219(65)	7 566(23)	–5 862(43)
C(17A)	12 481(57)	7 142(18)	–6 690(36)
C(18A)	9 149(62)	6 841(28)	–7 592(33)
C(19A)	6 664(39)	5 331(21)	–5 557(41)
O(1A)	9 318(36)	3 980(17)	–2 769(25)
O(2A)	13 580(74)	7 117(16)	–7 276(37)
Hg(2)	4 604(2)	5 329(1)	–2 435(2)
Cl(2)	5 005(13)	6 294(5)	–2 694(11)
C(1B)	3 991(54)	3 345(16)	–2 089(35)
C(2B)	4 718(70)	3 551(28)	–3 088(34)
C(3B)	4 709(75)	4 154(29)	–3 105(60)
C(4B)	4 540(53)	4 469(11)	–2 147(40)
C(5B)	4 458(41)	4 281(15)	–1 180(34)
C(6B)	4 783(63)	4 612(17)	–105(37)
C(7B)	4 524(64)	4 406(12)	771(34)
C(8B)	4 275(55)	3 816(15)	966(33)
C(9B)	3 603(41)	3 483(14)	–159(28)
C(10B)	4 737(41)	3 626(17)	–968(31)
C(11B)	3 462(53)	2 846(16)	118(40)
C(12B)	2 195(45)	2 728(14)	801(36)
C(13B)	2 699(56)	3 101(17)	1 961(39)
C(14B)	2 647(62)	3 703(16)	1 638(32)
C(15B)	2 863(82)	3 963(21)	2 769(33)
C(16B)	1 305(58)	3 671(25)	3 193(35)
C(17B)	1 179(82)	3 085(23)	2 587(46)
C(18B)	4 515(74)	2 849(23)	2 766(41)
C(19B)	6 899(49)	3 502(22)	–407(37)
O(1B)	4 533(63)	4 370(18)	–4 070(36)
O(2B)	124(60)	2 709(18)	2 626(33)
O	2 486(40)	5 809(14)	–782(28)
C(2C)	2 967(92)	6 244(24)	–233(38)
C(3C)	1 549(78)	6 702(21)	–411(58)
C(4C)	4 861(92)	6 357(34)	540(75)

suggesting that the mercury atom has had little immediate effect on the steroid geometry, although there are naturally differences in the conformations of the five-membered rings.

In the present structure, the two molecules are connected *via* a solvent acetone molecule and this is illustrated in Figure 2. The two mercury atoms are weakly bonded to the oxygen atom of the acetone [2.85(3), 3.13(4) Å]. The Hg...Hg distance is 3.530(2) Å, well outside the limits of a bonded distance. The dimercury acetone group is almost planar. A least-squares plane calculation through Hg(1)–Hg(2)–O–C(1C) shows the four atoms coplanar to within 0.08 Å. The carbon atoms C(3C) and C(4C) are respectively 0.20 and 0.10 Å from this plane. The Hg...O vectors are approximately perpendicular to the C(4)–Hg–Cl moiety, the O–Hg–Cl angles being 87.7, 80.1° for A and 95.2, 102.5° for B. This type of bonding (two-co-ordinate

Table 2. Molecular dimensions in molecules A and B of compound (2)-acetone; bond lengths (Å) and bond angles (°)

	A	B
Hg(1)-Cl(1)	2.372(7)	2.379(12)
Hg(1)-C(4)	2.002(35)	2.106(27)
C(1)-C(2)	1.41(8)	1.56(6)
C(1)-C(10)	1.61(6)	1.47(5)
C(2)-C(3)	1.41(9)	1.46(9)
C(3)-C(4)	1.42(6)	1.43(8)
C(3)-O(1)	1.26(6)	1.26(8)
C(4)-C(5)	1.38(5)	1.28(6)
C(5)-C(6)	1.53(6)	1.49(5)
C(5)-C(10)	1.56(6)	1.60(5)
C(6)-C(7)	1.19(6)	1.25(6)
C(7)-C(8)	1.44(6)	1.46(5)
C(8)-C(9)	1.49(5)	1.53(5)
C(8)-C(14)	1.53(6)	1.66(6)
C(9)-C(10)	1.59(5)	1.51(5)
C(9)-C(11)	1.65(6)	1.58(5)
C(10)-C(19)	1.58(4)	1.54(4)
C(11)-C(12)	1.54(7)	1.45(6)
C(12)-C(13)	1.50(6)	1.62(6)
C(13)-C(14)	1.56(6)	1.50(5)
C(13)-C(17)	1.61(5)	1.53(9)
C(13)-C(18)	1.56(5)	1.51(5)
C(14)-C(15)	1.51(5)	1.48(5)
C(15)-C(16)	1.52(8)	1.56(7)
C(16)-C(17)	1.49(7)	1.58(8)
C(17)-O(2)	1.23(7)	1.20(8)
Cl(1)-Hg(1)-C(4)	177.0(10)	174.5(10)
C(2)-C(1)-C(10)	111(4)	117(3)
C(1)-C(2)-C(3)	117(5)	109(5)
C(2)-C(3)-C(4)	125(5)	121(5)
C(2)-C(3)-O(1)	120(5)	115(5)
C(4)-C(3)-O(1)	115(5)	122(5)
Hg(1)-C(4)-C(3)	118.7(33)	112.0(38)
Hg(1)-C(4)-C(5)	121.3(29)	120.8(29)
C(3)-C(4)-C(5)	118(4)	127(4)
C(4)-C(5)-C(6)	132(4)	125(3)
C(4)-C(5)-C(10)	120(4)	117(3)
C(6)-C(5)-C(10)	108(4)	114(3)
C(5)-C(6)-C(7)	132(5)	121(4)
C(6)-C(7)-C(8)	121(5)	126(4)
C(7)-C(8)-C(9)	112(4)	112(3)
C(7)-C(8)-C(14)	114(3)	113(3)
C(9)-C(8)-C(14)	108(4)	106(3)
C(8)-C(9)-C(10)	112(3)	112(3)
C(8)-C(9)-C(11)	112(3)	110(3)
C(10)-C(9)-C(11)	112(3)	116(3)
C(1)-C(10)-C(5)	112(3)	108(3)
C(1)-C(10)-C(9)	112(3)	113(3)
C(5)-C(10)-C(9)	105(3)	105(3)
C(1)-C(10)-C(19)	106(3)	111(3)
C(5)-C(10)-C(19)	104(3)	109(3)
C(9)-C(10)-C(19)	117(3)	111(3)
C(9)-C(11)-C(12)	112(3)	114(3)
C(11)-C(12)-C(13)	106(4)	112(3)
C(12)-C(13)-C(14)	117(3)	109(3)
C(12)-C(13)-C(17)	115(4)	115(3)
C(14)-C(13)-C(17)	97(3)	101(4)
C(12)-C(13)-C(18)	112(3)	105(3)
C(14)-C(13)-C(18)	112(3)	120(4)
C(17)-C(13)-C(18)	101(3)	107(4)
C(8)-C(14)-C(13)	109(3)	109(3)
C(8)-C(14)-C(15)	122(4)	120(4)
C(13)-C(14)-C(15)	105(3)	100(3)
C(14)-C(15)-C(16)	101(4)	104(4)
C(15)-C(16)-C(17)	109(4)	101(4)
C(13)-C(17)-C(16)	106(4)	105(4)
C(13)-C(17)-O(2)	121(4)	128(5)
C(16)-C(17)-O(2)	132(5)	127(6)

Solvent acetone dimensions

OC-C(2C)	1.24(6)
C(2C)-C(3C)	1.48(8)
C(2C)-C(4C)	1.44(8)
OC-C(2C)-C(3C)	119(5)
OC-C(2C)-C(4C)	125(5)
C(3C)-C(2C)-C(4C)	116(5)

but with weak perpendicular interactions) is well known for mercury.

Experimental

I.r. spectra were recorded with a Perkin-Elmer 157 double-beam grating spectrophotometer (solution spectra using chloroform as solvent); ^1H n.m.r. spectra were recorded with a Varian T-60 (60 MHz) or a Varian HA 100 (100 MHz) instrument (tetramethylsilane as internal standard); ^{13}C n.m.r. spectra were recorded by Dr. Brian Wood at the City of London Polytechnic on a Jeol FX90Q (90 MHz) instrument; and mass spectra were recorded on an A.E.I. MS12 spectrometer. Kieselgel GF₂₅₄+₃₅₄(Merck) was used for analytical t.l.c., and flash chromatography was performed with Merck silica gel (230–400 mesh). Organic solvents were distilled from calcium hydride when required anhydrous. Light petroleum refers to that fraction boiling in the range 40–60 °C.

4-Chloromercurioandrosta-4,6-diene-3,17-dione (2).—6 β -Bromoandrost-4-ene-3,17-dione¹ (**1a**) (4.0 g, 0.13 mmol) was added to a vigorously stirred suspension of yellow mercuric oxide (4.74 g, 0.26 mmol) in pyridinium poly(hydrogen fluoride) (70%; 40 ml) at room temperature. After 4 h, the mixture was poured onto crushed ice (*ca.* 300 g) and extracted into dichloromethane (5 \times 50 ml), and the extracts were washed in turn with water (3 \times 50 ml) and brine (50 ml), then dried. Removal of the solvent afforded a pale yellow gum (3.79 g) which was shown by ^1H n.m.r. (250 MHz) to comprise 4-chloromercurioandrosta-4,6-diene-3,17-dione (**2**), 6 β -fluoroandrost-4-ene-3,17-dione, and androsta-4,6-diene-3,17-dione in an approximate ratio of 4.6:3.6:1. Flash chromatography of the mixture using diethyl ether–dichloromethane (5:1) as eluant afforded a fraction enriched in the chloromercury compound and crystallisation from acetone–*n*-hexane gave pale yellow needles (0.96 g) of the pure compound, m.p. 102–104 °C (decomp.); $[\alpha]_{\text{D}}^{20} + 71^\circ$ (*c* 3.1, CHCl_3); ν_{max} , 3 030 and 3 003 (both olefin), 2 945, 2 920, 2 865, 1 740 (C-17 ketone), 1 642 (C-3 ketone), 1 613, 1 550, 1 295, and 1 270 cm^{-1} ; δ_{H} (CDCl_3 ; 250 MHz) 1.0 (3 H, s, 18- H_3), 1.2 (3 H, s, 19- H_3), 6.33 (1 H, dd, *J* 10 and 2.5 Hz, 7-H), and 6.38 (1 H, dd, *J* 10 and 1.5 Hz, 6-H); δ_{C} (CDCl_3 ; 22.5 MHz) 135.329 (C-6), 141.418 (C-7), 152.627 (C-4), 168.267 (C-5), 200.003 (C-3), and 219.089 (C-17).

4-Bromoandrosta-4,6-diene-3,17-dione (3a).—A solution of bromine in chloroform (0.3M; 0.75 ml) was added dropwise to a stirred solution at room temperature of 4-chloromercurioandrosta-4,6-diene-3,17-dione (**2**) (0.37 g, 0.71 mmol) in chloroform (5 ml). After 15 min, the reaction mixture was filtered and the filtrate flash chromatographed using diethyl ether–tetrachloromethane (4:1) as eluant. Repeated recrystallization of the crude bromo compound (**3a**) (0.13 g, 50%) from diethyl ether–dichloromethane gave colourless crystals, m.p. 149–150 °C (decomp.); ν_{max} , 3 040 (olefin), 2 955, 2 870, 1 740 (C-17 ketone), 1 675 (C-3 ketone), 1 615, 1 550, 1 293, 1 270,

Table 3. Dihedral angles (°) in molecules A and B of compound (2)-acetone compared to those in compound (4)

	A	B	(4)
Cl-Hg-C(4)-C(3)	-49.4	-85.6	
Cl-Hg-C(4)-C(5)	115.1	91.1	
C(10)-C(1)-C(2)-C(3)	-42.8	-44.1	-51.4
C(2)-C(1)-C(10)-C(5)	41.1	51.1	48.5
C(2)-C(1)-C(10)-C(9)	158.8	166.8	167.1
C(2)-C(1)-C(10)-C(19)	-71.9	-68.3	-69.5
C(1)-C(2)-C(3)-C(4)	19.8	14.9	28.4
C(1)-C(2)-C(3)-O(1)	-154.1	-153.8	-153.8
C(2)-C(3)-C(4)-Hg(1)	172.8	179.3	
C(2)-C(3)-C(4)-C(5)	7.8	3.0	-2.7
O(1)-C(3)-C(4)-Hg(1)	-13.0	-12.8	
O(1)-C(3)-C(4)-C(5)	-178.0	170.8	179.5
Hg(1)-C(4)-C(5)-C(6)	11.0	-12.6	
Hg(1)-C(4)-C(5)-C(10)	-171.3	-171.0	
C(3)-C(4)-C(5)-C(6)	175.6	163.5	-179.5
C(3)-C(4)-C(5)-C(10)	-6.7	5.1	0.2
C(4)-C(5)-C(6)-C(7)	174.2	174.2	171.0
C(10)-C(5)-C(6)-C(7)	-3.6	-26.9	-8.5
C(4)-C(5)-C(10)-C(1)	-17.1	-30.8	-23.2
C(4)-C(5)-C(10)-C(9)	-139.3	-151.3	-142.9
C(4)-C(5)-C(10)-C(19)	97.2	89.9	97.2
C(6)-C(5)-C(10)-C(1)	161.1	168.4	156.1
C(6)-C(5)-C(10)-C(9)	38.8	47.9	36.6
C(6)-C(5)-C(10)-C(19)	-84.6	-70.9	-83.3
C(5)-C(6)-C(7)-C(8)	-14.3	13.1	0.5
C(6)-C(7)-C(8)-C(9)	-9.9	-21.7	-22.5
C(6)-C(7)-C(8)-C(14)	-133.5	-141.6	-142.6
C(7)-C(8)-C(9)-C(10)	48.8	46.0	51.5
C(7)-C(8)-C(9)-C(11)	175.5	177.2	179.7
C(14)-C(8)-C(9)-C(10)	175.6	169.5	174.4
C(14)-C(8)-C(9)-C(11)	-57.7	-59.2	-57.4
C(7)-C(8)-C(14)-C(13)	-176.7	-171.5	-176.7
C(7)-C(8)-C(14)-C(15)	-53.5	-56.8	-53.8
C(9)-C(8)-C(14)-C(13)	57.6	64.9	61.9
C(9)-C(8)-C(14)-C(15)	-179.2	179.7	-175.1
C(8)-C(9)-C(10)-C(1)	175.1	-174.9	-178.1
C(8)-C(9)-C(10)-C(5)	-62.9	-57.4	-58.6
C(8)-C(9)-C(10)-C(19)	51.7	60.0	58.5
C(11)-C(9)-C(10)-C(1)	48.7	57.2	56.0
C(11)-C(9)-C(10)-C(5)	175.3	174.7	175.6
C(11)-C(9)-C(10)-C(19)	-74.8	-67.8	-67.6
C(8)-C(9)-C(11)-C(12)	57.2	57.0	78.1
C(10)-C(9)-C(11)-C(12)	-176.4	-173.9	-178.1
C(9)-C(11)-C(12)-C(13)	-51.4	-52.0	-54.9
C(11)-C(12)-C(13)-C(14)	55.8	55.4	53.9
C(11)-C(12)-C(13)-C(17)	169.2	167.9	163.0
C(11)-C(12)-C(13)-C(18)	-76.3	-75.0	-69.1
C(12)-C(13)-C(14)-C(18)	-60.2	-60.3	-59.6
C(12)-C(13)-C(14)-C(15)	166.7	172.4	169.5
C(17)-C(13)-C(14)-C(8)	176.9	178.4	179.0
C(17)-C(13)-C(14)-C(15)	43.8	51.2	48.0
C(18)-C(13)-C(14)-C(8)	71.8	61.2	62.3
C(18)-C(13)-C(14)-C(15)	-61.2	-66.0	-68.6
C(12)-C(13)-C(17)-C(16)	-152.0	-149.8	-155.2
C(12)-C(13)-C(17)-O(2) [or C(20)]	25.0	30.9	80.9
C(14)-C(13)-C(17)-C(16)	-27.4	-32.6	-41.4
C(14)-C(13)-C(17)-O(2) [or C(20)]	149.6	148.1	-165.3
C(18)-C(13)-C(17)-C(16)	87.1	94.1	76.8
C(18)-C(13)-C(17)-O(2) [or C(20)]	-95.8	-85.0	-47.1
C(8)-C(14)-C(15)-C(16)	-169.0	-169.7	-163.3
C(13)-C(14)-C(15)-C(16)	-43.9	-50.5	-35.8
C(14)-C(15)-C(16)-C(17)	25.0	28.9	8.8
C(15)-C(16)-C(17)-C(13)	2.4	2.7	20.9
C(15)-C(16)-C(17)-O(2) [or C(20)]	-174.2	-177.9	149.0

1 200, and 787 cm^{-1} ; δ_{H} (CDCl_3 ; 60 MHz) 1.0 (3 H, s, 18- H_3), 1.15 (3 H, s, 19- H_3), 6.35 (1 H, dd, J 10 and 2 Hz, 6-H), and 6.8 (1 H, dd, J 10 and 3 Hz, 7-H) [Found: M^+ , 362.0870 (89.5%)].

$\text{C}_{19}\text{H}_{23}\text{O}_2^{79}\text{Br}$ requires M , 362.0877; M^+ , 364.0862 (88.5%). $\text{C}_{19}\text{H}_{23}\text{O}_2^{81}\text{Br}$ requires M , 364.0857].

4-Methoxycarbonylandrosta-4,6-diene-3,17-dione (3b).—Dry methanol (7 ml) was added to a mixture of palladium chloride (0.17 g, 0.96 mmol) and lithium chloride (0.08 g, 1.89 mmol) under nitrogen. A slow stream of carbon monoxide was bubbled through the suspension, it was cooled to -78°C , and a solution of 4-chloromercurioandrosta-4,6-diene-3,17-dione (2) (0.50 g, 0.96 mmol) in dry methanol (8 ml) and dry dichloromethane (4 ml) was added with stirring. The reaction mixture was allowed to warm to room temperature during 4 h and stirring, under a constant stream of carbon monoxide, was continued overnight. The mixture was filtered, the residue washed with diethyl ether (3 \times 10 ml), and the combined filtrates diluted with diethyl ether (30 ml). After being washed in turn with saturated aqueous ammonium chloride (20 ml) and brine (20 ml), the solvent was removed and the residue flash chromatographed using diethyl ether-dichloromethane (3:1) as eluant. Recrystallization from diethyl ether gave pale yellow crystals of the methyl ester (3b) (0.07 g, 21%), m.p. 207–209 $^\circ\text{C}$ (decomp.); ν_{max} . 3 007 (olefin), 2 985, 2 965, 2 860, 1 733 (C-17 ketone), 1 657 (C-3 ketone), 1 613, 1 573, and 1 243 cm^{-1} ; δ_{H} (CDCl_3 ; 60 MHz) 1.0 (3 H, s, 18- H_3), 1.2 (3 H, s, 19- H_3), 4.8 (3 H, s, ester Me), and 6.2 (2 H, m, 6- and 7-H); δ_{C} (CDCl_3 ; 22.5 MHz) 52.301 (OMe), 125.070 (C-6), 138.402 (C-4), 141.540 (C-7), 158.740 (C-5), 167.211 (ester carbonyl), 194.849 (C-3), and 219.024 (C-17) [Found: M^+ , 342.1846 (80.65%). $\text{C}_{21}\text{H}_{26}\text{O}_4$ requires M , 342.1831].

Bis(3,17-dioxoandrosta-4,6-dien-4-yl)mercury(II) (3c).—A freshly prepared 11M-solution of sodium borohydride in aqueous THF (2 ml; 3:1 v/v THF- H_2O) was added to 4-chloromercurioandrosta-4,6-diene-3,17-dione (2) (0.32 g, 6.16 mmol) in THF (5 ml), and a grey precipitate was formed immediately. After 30 min, the mixture was filtered, diluted with water (15 ml) and extracted with dichloromethane (5 \times 10 ml). The combined extracts were dried (Na_2SO_4), the solvent removed under reduced pressure and the residue dissolved in AnalaR acetone (5 ml) and treated at 0°C with Jones reagent. The reaction was followed by t.l.c. using diethyl ether-dichloromethane (5:1) as eluant and when this indicated that oxidation was complete the mixture was poured into water (15 ml) and extracted with dichloromethane (5 \times 7 ml). The combined extracts were washed in turn with water (2 \times 7 ml) and brine (7 ml), then dried, the solvent removed, and the residue flash chromatographed using diethyl ether-dichloromethane (5:1). This afforded colourless crystals of bis-(3,17-dioxoandrosta-4,6-dien-4-yl)mercury(II) (3c) (0.0567 g, 24%) which, after recrystallization from diethyl ether, had m.p. 198–200 $^\circ\text{C}$ (decomp.); ν_{max} . 3 030 (olefin), 2 977, 2 950, 2 900, 2 880, 2 870, 1 743 (C-17 ketone), 1 633 (C-3 ketone), 1 615, 1 553, 1 273, and 1 205 cm^{-1} ; δ_{H} (CDCl_3 ; 400 MHz) 0.97 (6 H, s, 2 \times 18- H_3), 1.14 (6 H, s, 2 \times 19- H_3), 6.25 (2 H, dd J 2 and 9.8 Hz, 6-H), and 6.55 (2 H, dd J 2.7 and 9.8 Hz, 7-H) [Found: M^+ , 766.3082 (29.4%). $\text{C}_{38}\text{H}_{46}\text{O}_4$ ^{200}Hg requires 766.3079. Base peak, 283.1702 (100%). $\text{C}_{19}\text{H}_{23}\text{O}_2$ requires 283.1698. Found: C, 58.8; H, 6.1. $\text{C}_{38}\text{H}_{46}\text{O}_4\text{Hg}$ requires C 59.5; H 6.0%].

X-Ray Crystallographic Analysis.—Suitable crystals of $2(\text{HgClC}_{19}\text{H}_{40}\text{O}_2)$: acetone were obtained after recrystallisation from acetone.

Crystal data. $\text{Hg}_2\text{C}_{41}\text{H}_{83}\text{O}_5$, $M = 1 098.5$, monoclinic, space group $P2_1$, $Z = 2$, with cell dimensions $a = 7.295(8)$, $b = 24.12(1)$, $c = 12.215(12)$ Å, $\beta = 108.0(1)^\circ$, $U = 2 044.1$ Å 3 , $D_{\text{m}} = 1.78$, $D_{\text{c}} = 1.78$ g cm^{-3} , $\lambda = 0.7107$ Å, $\mu(\text{cm}^{-1}) 78.2$, $F(000) = 1 068$.

Precession photographs established the preliminary cell constants and space group. The crystal was mounted on a Stoe

STADI2 diffractometer and data was collected *via* a variable width ω scan. Background counts were 20 s and the scan rate of $0.033^\circ \text{ s}^{-1}$ was applied to a width of $(1.5 + \sin\mu/\tan\theta)$. 3854 Independent reflections with $2\theta < 50^\circ$ were measured of which 2 073 with $I > 2.5\sigma(I)$ were used in subsequent calculations. An absorption correction was applied using SHELX 76.⁹

The Patterson function was used to determine the positions of the mercury atoms. The remaining hydrogen atoms were fixed in tetrahedral or trigonal positions. Hydrogen atoms in similar parts of the molecule were given equivalent thermal parameters and just four thermal parameters were refined. Non-hydrogen atoms were refined anisotropically *via* full-matrix least squares and the final *R* value was 0.061 (R_w 0.067). The opposite (assumed to be incorrect) enantiomorph gave *R* 0.064. Scattering factors and dispersion corrections were taken from ref. 10. The final-difference Fourier maps showed no important features and in the final cycles of refinement no shift was greater than 0.1σ . Calculations were carried out using SHELX 76⁹ at the University of Manchester Computer Centre.

Final co-ordinates are given in Table 1, and bond lengths and angles in Table 2. Anisotropic and isotropic thermal parameters and hydrogen atomic co-ordinates are available as a Supplementary publication (SUP. No. 56170, 7 pp.).* Structure factor tables are available on request from the editorial office.

* For details of the Supplementary Publication Scheme see Instructions for Authors (1985) in *J. Chem. Soc., Perkin Trans. 1*, 1985, Issue 1.

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