# Conformational Studies. Part 6.[1] *X*-Ray Crystal Structure of 3,3-Dimethoxy-19-norandrosta-5(10),6-dien-17-one: an Exception to the Diene Helicity Rule

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The crystal structure of the title compound (1d) has been unequivocally defined by *X*-ray crystallography. Crystals are orthorhombic, space group $P2_12_12_1$, with $Z = 4$ in a unit cell of dimensions $a = 6.042(1)$, $b = 13.469(3)$, $c = 21.634(5)$ Å. The structure was solved by direct methods and refined to a final $R$ of 0.036 for 845 unique observed reflections.

The cisoid diene system in this compound is right-handed, but the c.d. curve is *negative*: the diene, and two cognate derivatives, thus constitute exceptions to the diene helicity rule.

As a result of our interest in conformational problems (see *e.g.* ref. 1) and in the diene helicity rule [2,3] we noted the report [4] that 19-norandrosta-5(10),6-diene-3α,17β-diol (1a) exhibits a negative Cotton effect. A model of this steroid clearly show that if the structure be correct,

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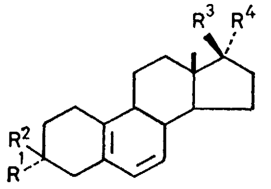
[1] Part 5. J. M. Midgley, J. Parkin, and W. B. Whalley, *J.C.S. Perkin I*, 1977, 834.

[2] A. Moscowitz, E. Charney, U. Weiss, and H. Ziffer, *J. Amer. Chem. Soc.*, 1961, **83**, 4661.

[3] *E.g.* U. Weiss, W. B. Whalley, and I. L. Karle, *J.C.S. Chem. Comm.*, 1972, 16.

[4] F. S. Alvarez and A. N. Watt, *J. Org. Chem.*, 1972, **37**, 3725.

then the cisoid diene system must be rigid and right-handed: hence, if the diene rule be applicable in this case the Cotton and/or c.d. curve(s) should be positive. To resolve this dubiety and the uncertainty, we believed, in the definition of structure (1a) we have repeated the synthesis[4] of (1b) and cognate derivatives, with minor experimental modifications.



(1a) $R^1 = R^3 = OH$, $R^2 = R^4 = H$
(1b) $R^1 = R^4 = H$, $R^2 = R^3 = OH$
(1c) $R^1R^2 = O$, $R^3 = OH$, $R^4 = H$
(1d) $R^1 = R^2 = OMe$, $R^3R^4 = O$

In the absence of a direct comparison, our products (1b—d) appeared to be identical with those previously reported;[4,5] furthermore they exhibited negative c.d. curves of similar amplitude (see Experimental section).

Thus, to define unequivocally the structures of these compounds, the acetal (1d) was subjected to *X*-ray crystallographic analysis. Details are described in the Experimental section. A view of the molecule is given in Figure 1. All bond lengths and angles (Tables 1 and 2) have values close to those generally expected and clearly establish that the molecule (Figure 1) has the double bonds at the 5,10 and 6,7-positions [C=C 1.345(7) and 1.330(7) Å respectively] with the hydrogen atoms at C(8) and C(9), β and α respectively.

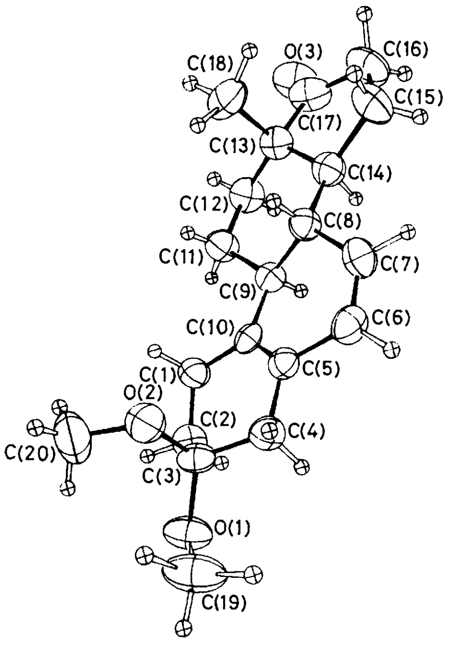


FIGURE 1 A view of the molecule of (1d) viewed down *a* and showing the crystallographic numbering scheme

Torsion angles for the ring system are shown in Figure 2. Ring A has a half-chair conformation. The torsion angles in the sequence of ring B atoms C(9), C(10), C(5)—(8) conform to a right-handed spiral. Ring C has a normal chair conformation, with ring D close to a C(14) envelope.

The crystal structure (Figure 3) consists of discrete molecules separated by normal van der Waals contacts (Table 3).

TABLE 1

Bond lengths (Å) with standard deviations in parentheses

| | | | |
|---|---|---|---|
| C(1)–C(2) | 1.528(7) | C(1)–H(1B) | 0.98(3) |
| C(1)–C(10) | 1.499(6) | C(2)–H(2A) | 0.96(3) |
| C(2)–C(3) | 1.522(7) | C(2)–H(2B) | 1.03(4) |
| C(3)–C(4) | 1.500(7) | C(4)–H(4A) | 1.01(3) |
| C(3)–O(1) | 1.415(6) | C(4)–H(4B) | 1.00(3) |
| C(3)–O(2) | 1.412(6) | C(6)–H(6) | 1.00(4) |
| C(4)–C(5) | 1.521(7) | C(7)–H(7) | 0.94(4) |
| C(5)–C(6) | 1.459(7) | C(8)–H(8) | 1.05(4) |
| C(5)–C(10) | 1.345(7) | C(9)–H(9) | 1.01(3) |
| C(6)–C(7) | 1.330(7) | C(11)–H(11A) | 1.01(3) |
| C(7)–C(8) | 1.499(7) | C(11)–H(11B) | 0.97(4) |
| C(8)–C(9) | 1.549(6) | C(12)–H(12A) | 1.00(4) |
| C(8)–C(14) | 1.541(6) | C(12)–H(12B) | 0.98(4) |
| C(9)–C(10) | 1.506(6) | C(14)–H(14) | 0.98(4) |
| C(9)–C(11) | 1.536(6) | C(15)–H(15A) | 0.94(4) |
| C(11)–C(12) | 1.527(7) | C(15)–H(15B) | 0.98(4) |
| C(12)–C(13) | 1.523(7) | C(16)–H(16A) | 1.07(4) |
| C(13)–C(14) | 1.521(6) | C(16)–H(16B) | 0.98(4) |
| C(13)–C(17) | 1.508(7) | C(18)–H(18A) | 0.99(4) |
| C(13)–C(18) | 1.541(7) | C(18)–H(18B) | 0.91(5) |
| C(14)–C(15) | 1.531(7) | C(18)–H(18C) | 1.08(5) |
| C(15)–C(16) | 1.533(8) | C(19)–H(19A) | 1.07(5) |
| C(16)–C(17) | 1.523(8) | C(19)–H(19B) | 1.07(5) |
| C(17)–O(3) | 1.204(8) | C(19)–H(19C) | 1.05(5) |
| O(1)–C(19) | 1.429(7) | C(20)–H(20A) | 0.97(5) |
| O(2)–C(20) | 1.426(7) | C(20)–H(20B) | 0.98(4) |
| C(1)–H(1A) | 1.00(3) | C(20)–H(20C) | 1.16(5) |

TABLE 2

Valency angles (°), with standard deviations in parentheses

| | | | |
|---|---|---|---|
| C(2)–C(1)–C(10) | 112.8(4) | C(1)–C(10)–C(9) | 118.6(4) |
| C(1)–C(2)–C(3) | 112.0(4) | C(5)–C(10)–C(9) | 119.1(4) |
| C(2)–C(3)–C(4) | 109.6(4) | C(9)–C(11)–C(12) | 113.1(4) |
| C(2)–C(3)–O(1) | 104.8(4) | C(11)–C(12)–C(13) | 111.4(4) |
| C(2)–C(3)–O(2) | 113.1(4) | C(12)–C(13)–C(14) | 109.6(4) |
| C(4)–C(3)–O(1) | 113.1(4) | C(12)–C(13)–C(17) | 115.9(4) |
| C(4)–C(3)–O(2) | 105.2(4) | C(12)–C(13)–C(18) | 111.4(4) |
| O(1)–C(3)–O(2) | 111.2(4) | C(14)–C(13)–C(17) | 100.4(4) |
| C(3)–C(4)–C(5) | 114.1(4) | C(14)–C(13)–C(18) | 114.2(4) |
| C(4)–C(5)–C(6) | 117.6(4) | C(17)–C(13)–C(18) | 105.0(4) |
| C(4)–C(5)–C(10) | 122.8(4) | C(13)–C(14)–C(15) | 105.0(4) |
| C(6)–C(5)–C(10) | 119.6(4) | C(13)–C(14)–C(8) | 111.6(3) |
| C(5)–C(6)–C(7) | 122.1(5) | C(8)–C(14)–C(15) | 121.6(4) |
| C(6)–C(7)–C(8) | 119.2(4) | C(14)–C(15)–C(16) | 101.0(5) |
| C(7)–C(8)–C(9) | 109.6(4) | C(15)–C(16)–C(17) | 106.3(4) |
| C(7)–C(8)–C(14) | 115.0(4) | C(16)–C(17)–C(13) | 108.0(5) |
| C(9)–C(8)–C(14) | 107.9(4) | C(16)–C(17)–O(3) | 126.1(5) |
| C(8)–C(9)–C(10) | 111.2(4) | C(13)–C(17)–O(3) | 125.9(5) |
| C(8)–C(9)–C(11) | 110.8(3) | C(3)–O(1)–C(19) | 115.9(4) |
| C(10)–C(9)–C(11) | 114.8(4) | C(3)–O(2)–C(20) | 116.1(4) |
| C(1)–C(10)–C(5) | 121.9(4) | | |

The *X*-ray examination confirmed the previously assigned structures,[4,5] and the right-handed chiralty of the cisoid diene and thus that the three derivatives (1a), (1c), and (1d) violate the diene helicity rule,[2] at least in its simple form. During the course of this work the preparation and *X*-ray crystallographic examination

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[5] J. Kalvoda and G. Anner, *Helv. Chim. Acta*, 1967, **50**, 260.

of the closely related diene (2) were reported.[6] It too exhibited a negative c.d. curve.

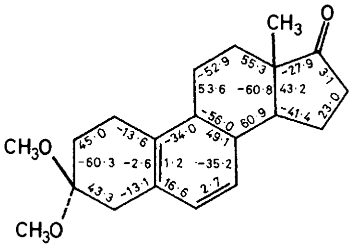


FIGURE 2 Torsion angles in the steroid ring system of (1d)

TABLE 3

Intermolecular contacts $<3$ Å

| | |
|---|---|
| H(1A) ··· O($3^{\mathrm{II}}$) | 2.63 |
| H(4A) ··· H($9^{\mathrm{IV}}$) | 2.58 |
| H(6) ··· C($5^{\mathrm{IV}}$) | 2.73 |
| H(6) ··· C($10^{\mathrm{IV}}$) | 2.98 |
| H(11B) ··· H($16\mathrm{A}^{\mathrm{II}}$) | 2.34 |
| H(12A) ··· H($19\mathrm{B}^{\mathrm{VI}}$) | 2.31 |
| H(15A) ··· H($18\mathrm{A}^{\mathrm{III}}$) | 2.62 |
| H(16A) ··· C($11^{\mathrm{V}}$) | 2.93 |
| H(16B) ··· O($2^{\mathrm{III}}$) | 2.91 |
| H(18B) ··· O($1^{\mathrm{VI}}$) | 2.89 |
| H(19B) ··· C($18^{\mathrm{I}}$) | 2.92 |
| H(19B) ··· H($18\mathrm{C}^{\mathrm{I}}$) | 2.43 |

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

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

A theoretical rationalisation of these observations has been derived by Charney and Rosenfeld[7] and will be published elsewhere. We will comment upon this and similar phenomena elsewhere.[8]

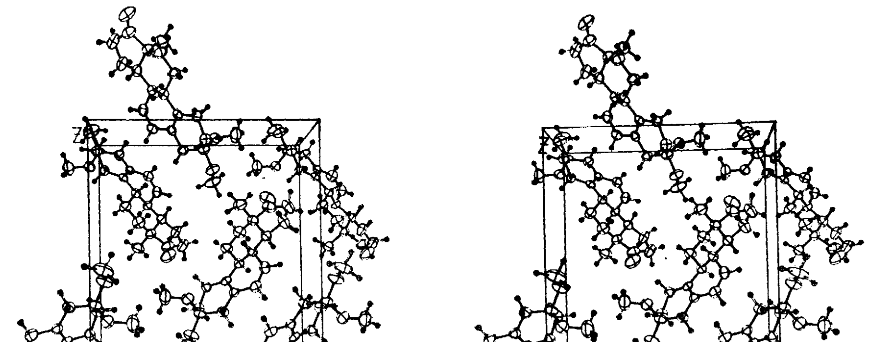
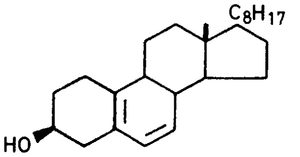


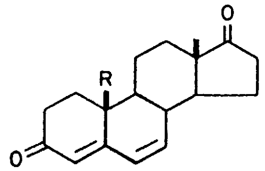
FIGURE 3 A stereoscopic view of the crystal structure of (1d)

During the preparation of (1c) it was observed that oxidation[4] of 19-hydroxyandrosta-4,6-diene-3,17-dione (3a) under controlled conditions furnished the corresponding aldehyde (3b), as an intermediate *en route* to the acid (3c).

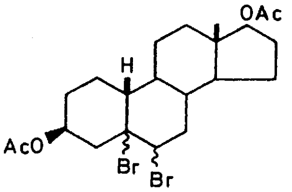
In the expectation that dehydrobromination of (4)



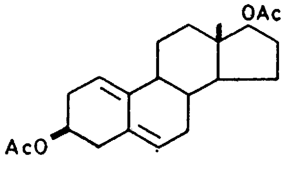
(2)



(3a) R = CH$_2$OH
(3b) R = CHO
(3c) R = CO$_2$H



(4)



(5)

might furnish an alternative pathway to the 5(10),6-diene, type (1), (4) was treated with 1,5-diazabicyclo-[4,3,0]non-5-ene;[9] in the sequel the product was the isomeric 1(10),5-diene (5).[10]

## EXPERIMENTAL

Optical rotations were determined for solutions in chloroform; c.d. measurements were carried out for methanol solutions.

*3,17-Dioxoandrosta*-4,6-*dien*-19-*al* (3b).—A solution of 19-hydroxyandrosta-4,6-diene-3,17-dione[4] (1 g) in acetone (50 ml) at 5 °C was oxidised by the gradual addition of an excess of Jones' reagent. Dilution with water (100 ml), followed by extraction with methylene chloride gave (3b)

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[6] H. Paaren, R. M. Moriarty, and J. Flippen, *J.C.S. Chem. Comm.*, 1976, 114.

[7] E. Charney, personal communication.

[8] W. B. Whalley, unpublished observations.

[9] A. B. Garry, J. M. Midgley, W. B. Whalley, and B. J. Wilkins, *J.C.S. Chem. Comm.*, 1972, 167.

[10] R. Mickova and K. Syhora, *Coll. Czech. Chem. Comm.*, 1969, 458.

(0.5 g) as *needles*, m.p. 145 °C from acetone–light petroleum (b.p. 60—80 °C), $\nu_{\text{max.}}$ 1 730 (17-ketone), 1 750 (19-aldehyde), and 1 660 cm$^{-1}$ (3-ketone); $\tau$ 0.2 (s, C*H*O, H), 3.70 (s, C-6*H*, C-7*H*, 2 H), 4.0 (s, C4-*H*, H), and 9.05 (s, C-18 methyl, 3 H) (Found: C, 76.2; H, 7.4. $C_{19}H_{22}O_3$ requires C, 76.5; H, 7.4%).

19-Norandrosta-5(10),6-diene-3,17-dione formed needles, m.p. 108—110 °C from acetone–n-hexane (lit.[5] m.p. 113—114 °C); c.d. $\Delta\varepsilon$ −5.19 ($\lambda_{\text{max.}}$ 262 nm) (*c* 0.040) $\nu_{\text{max.}}$ 1 740 (C-17 > C=O) and 1 730 cm$^{-1}$ (C-3 > C=O); $\tau$ 9.1 (s, C-18 methyl, 3 H), 7.05 (s, C-4$H_2$, 2 H), and 4.15 (s, C-6-*H*, C-7-*H*, 2 H) (Found: C, 80.0; H, 8.1. Calc. for $C_{18}H_{22}O_2$: C, 80.0; H, 8.2%).

The 3,3-dimethyl acetal formed needles, m.p. 119—121 °C, from methanol (lit.,[5] m.p. 122—125 °C); c.d. $\Delta\varepsilon$ −5.51 ($\lambda_{\text{max.}}$ 262 nm) (*c*, 0.043); $\nu_{\text{max.}}$ 1 740 (C-17 C=O); $\tau$ 9.1 (s, C-18 Me, 3 H), 7.78 (s, C-3-($CH_3)_2$, 6 H), and 4.24 (s, C-6-*H*, C-7-*H*, 2 H) (Found: C, 76.1; H, 9.1. Calc. for $C_{20}H_{28}O_3$: C, 75.9; H, 8.9%).

*Crystal Data for* (1d).—$C_{20}H_{28}O_3$, $M = 316.4$, Orthorhombic, $a = 6.042(1)$, $b = 13.469(3)$, $c = 21.634(5)$ Å, $U = 1\,760.6$ Å$^3$, $Z = 4$, $D_m = 1.19$ g cm$^{-3}$, $F(000) = 688$. $\lambda$(Mo-$K_\alpha$) = 0.710 69 Å, $\mu$(Mo-$K_\alpha$) = 0.44 cm$^{-1}$. Space group $P2_12_12_1$ ($D_2^4$, No. 19) from systematic absences.

Space group and unit cell information were obtained from Weissenberg (Cu-$K_\alpha$, $\lambda = 1.541\,8$ Å) and precession (Mo-$K_\alpha$, $\lambda = 0.710\,69$ Å) photographs. The unit cell dimensions and crystal orientations were refined by least-squares treatment of the diffractometer co-ordinates of 12 reflections. Three-dimensional intensity data for all reflections with $\theta$(Mo-$K_\alpha$) $\leqslant 20°$ were collected on a computer-controlled Hilger and Watts Y 290 four-circle diffractometer with graphite-monochromated Mo-$K_\alpha$ radiation. A $\theta$—$\omega$ step scan technique was employed using 60 steps of 0.01° ($\theta$) per step and a counting time of 1 s per step. Background counts of 15 s were made at the beginning and end of each scan. The standard deviation ($\sigma$) of the intensity was calculated from $\sigma^2(I) = S + 4B + (0.05S)^2$ where $S$ is the scan count, $B$ is the sum of the two backgrounds and $I = S - 2B$. A total of 845 independent reflections had $I \geqslant 3\sigma(I)$ and were retained as the observed data. Lorentz and polarization factors were applied and the normalised structure factors ($E$ values) calculated.

*Structure Solution and Refinement.*—Considerable difficulty was experienced in solving the structure by direct methods because of the preponderance of reflections with $h = 0$ among those with high $E$ values. This was finally circumvented by choosing a very large starting set shown and setting out to refine all $2^{11}$ permutations of allowed phases. This would have meant a total of 16 computer jobs each of 11 m execution time (using SHELX[11] on an IBM 370/155). Very fortunately the first such job produced a solution from which the $E$ map revealed all but one of the methoxy-carbon atoms. This atom was located on a Fourier map and the entire structure was routinely refined by full-matrix techniques using weights derived from the counting statistics. The carbon and oxygen atoms were refined with anisotropic temperature factors using the scattering curves of ref. 12 whereas hydrogen atoms were treated isotropically with the scattering factors of ref. 13. Final values of $R$ and $R'$ were 0.036 and 0.042 respectively [$R^1 = (\Sigma w\Delta^2/\Sigma wF_o^2)^{\frac{1}{2}}$]. A list of calculated and observed structure factors, an analysis of variance calculated after the final refinement cycle, atom thermal parameters, and the starting set of reflections for tangent formula refinement have been deposited as Supplementary Publication No. 22163 (11 pp.).* A final difference map was featureless. Atom positional co-ordinates are given in Table 4 with their standard deviations from the least-squares refinement. Standard deviations in bond lengths and angles contain a contribution from the covariance matrix.

TABLE 4

Final fractional co-ordinates (H × $10^3$, others × $10^4$)

| | *x*/*a* | *y*/*b* | *z*/*c* |
|---|---|---|---|
| C(1) | 1 906(8) | 5 186(3) | 5 653(2) |
| C(2) | 2 371(8) | 4 800(4) | 5 001(2) |
| C(3) | 4 835(8) | 4 786(4) | 4 856(2) |
| C(4) | 5 751(8) | 5 819(4) | 4 902(2) |
| C(5) | 4 932(9) | 6 399(3) | 5 460(2) |
| C(6) | 5 025(8) | 7 338(4) | 5 600(2) |
| C(7) | 5 760(8) | 7 797(3) | 6 140(2) |
| C(8) | 4 377(7) | 7 316(3) | 6 631(2) |
| C(9) | 2 424(7) | 6 752(3) | 6 328(2) |
| C(10) | 3 213(8) | 6 099(3) | 5 807(2) |
| C(11) | 1 021(8) | 6 222(4) | 6 819(2) |
| C(12) | 234(9) | 6 913(4) | 7 333(2) |
| C(13) | 2 158(8) | 7 481(3) | 7 619(2) |
| C(14) | 3 413(8) | 8 034(3) | 7 116(2) |
| C(15) | 4 879(10) | 8 775(3) | 7 462(2) |
| C(16) | 3 280(11) | 9 141(4) | 7 963(3) |
| C(17) | 1 541(11) | 8 332(4) | 8 038(2) |
| C(18) | 3 616(9) | 6 796(4) | 8 019(2) |
| C(19) | 7 157(9) | 4 318(5) | 3 999(2) |
| C(20) | 5 416(13) | 3 210(4) | 5 357(3) |
| O(1) | 4 980(6) | 4 383(2) | 4 253(1) |
| O(2) | 5 077(6) | 4 219(2) | 5 282(2) |
| O(3) | −66(8) | 8 370(3) | 8 367(2) |
| H(1A) | 227(6) | 468(3) | 597(2) |
| H(1B) | 31(5) | 532(2) | 569(1) |
| H(2A) | 169(6) | 523(2) | 471(2) |
| H(2B) | 177(7) | 409(3) | 497(2) |
| H(4A) | 538(6) | 619(2) | 451(1) |
| H(4B) | 741(6) | 583(2) | 491(1) |
| H(6) | 694(7) | 763(5) | 526(2) |
| H(7) | 647(7) | 840(3) | 622(2) |
| H(8) | 527(6) | 679(3) | 688(2) |
| H(9) | 142(6) | 728(2) | 615(1) |
| H(11A) | 200(5) | 569(2) | 699(1) |
| H(11B) | −25(7) | 593(3) | 662(2) |
| H(12A) | −55(6) | 652(3) | 765(2) |
| H(12B) | −76(6) | 743(3) | 718(2) |
| H(14) | 230(7) | 842(3) | 689(2) |
| H(15A) | 527(7) | 931(3) | 720(2) |
| H(15B) | 617(6) | 848(3) | 767(2) |
| H(16A) | 244(7) | 981(3) | 783(2) |
| H(18B) | 392(7) | 921(3) | 837(2) |
| H(18A) | 428(7) | 624(3) | 778(2) |
| H(18B) | 288(8) | 653(3) | 835(2) |
| H(18C) | 493(8) | 724(3) | 822(2) |
| H(19A) | 822(8) | 389(3) | 429(2) |
| H(19B) | 727(9) | 394(4) | 356(2) |
| H(19C) | 793(9) | 498(4) | 387(2) |
| H(20A) | 662(8) | 284(3) | 553(2) |
| H(20B) | 540(8) | 289(3) | 495(2) |
| H(20C) | 389(8) | 308(3) | 567(2) |

17$\beta$-*Hydroxy*-19-*norandrosta*-5(10),6-*dien*-3-*one*(1c).—This formed needles, m.p. 134—136 °C (lit.,[5] m.p. 133—135 °C) from acetone–hexane; c.d. $\Delta\varepsilon$ −6.13 ($\lambda_{\text{max.}}$268 nm) (*c*, 0.06); $\nu_{\text{max.}}$ 3 420 (17$\beta$-OH) and 1 720 cm$^{-1}$ (C-3 > C=O); $\tau$ 9.2 (s, C-18 methyl, 3 H), 7.09 (s, C-4-H's, 2 H), 6.30 (m,

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

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C-17α-*H*, H), and 4.26 (s, C-6-*H*, C-7-*H*, 2 H) (Found: C, 79.2; H, 8.9. Calc. for $C_{18}H_{24}O_2$: C, 79.4; H, 8.9%).

3β,17β-*Diacetoxy*-19-*norandrosta*-5(10),6-*diene*.—A solution of 3β,17β-diacetoxy-19-norandrost-5-ene (0.5 g) in acetic acid (9 ml) was mixed with a saturated solution (9 ml) of sodium acetate in acetic acid. A solution of bromine (0.25 g) in acetic acid (2.5 ml) was added with stirring during 20 min. The resultant *needles* of (4) 3β,17β-diacetoxy-5ζ,6ζ-dibromo-19-norandrostane (0.63 g) had m.p. 216—218 °C from acetone: $[\alpha]_D^{23}$ −70° (*c* 2.1); $\nu_{max.}$ 1 740, 1 730 (3β,17β-acetates); τ 9.15 (s, C-18 Me, 3 H), 7.95 (3β,-17β-OCOC*H*$_3$, 6 H), 5.3 (m, C-3*H*, C-17*H*, 2 H), and 4.7 (s, C-6H, H) (Found: C, 50.4; H, 6.2; Br, 29.7. $C_{22}H_{32}Br_2O_4$ requires C, 50.3; H, 6.2; Br, 30.7%).

When a solution of this dibromide (4) (0.5 g) in toluene (30 ml) containing 1,5-diazabicyclo[4.3.0]non-5-ene (0.5 ml) was heated under reflux during 18 h,[9] (nitrogen), 3β,17β-diacetoxy-19-norandrosta-1(10),5-diene (5) (0.1 g), m.p. 139—143 °C identical with an authentic specimen,[10] was produced.

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