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20-Methyl-14β,17α-pregn-4-en-3-one

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Abstract. $C_{22}H_{34}O$, orthorhombic, $P2_12_12_1$, $a = 7{\cdot}950\,(2)$, $b = 32{\cdot}237\,(10)$, $c = 7{\cdot}281\,(1)$ Å, $M_r = 314{\cdot}5$, $Z = 4$, $D_x = 1{\cdot}12$ g cm^{-3}. The ring junction *C*/*D* is *cis*, while ring junctions *A*/*B* and *B*/*C* are both *trans*. Ring conformations are: *A* 1α,2β half chair; *B*,*C* chair; *D* 14β envelope.

Introduction. Cell dimensions were obtained from a least-squares fit to the settings of 15 reflexions ($\pm hkl$) on a Syntex $P2_1$ diffractometer (Mo $K\alpha$ 0·71069 Å). Intensity measurements were carried out in the θ–$2\theta'$ mode ($3{\cdot}0 \leq 2\theta \leq 50{\cdot}0°$) with graphite-monochromated Mo $K\alpha$ radiation, at scan speeds varying linearly between 2·93° min^{-1} (150 c.p.s. and below) and 19·53° min^{-1} (5000 c.p.s. and above). Scan and background times were equal. Lorentz and polarization but no absorption [μ(Mo $K\alpha$) = 0·34 cm^{-1}] corrections were applied. After application of the acceptance criterion $I \geq 1{\cdot}5\sigma(I)$, 1040 unique

Table 1. *Atom positional parameters* ($\times 10^4$) *and anisotropic temperature factors* (Å^2 $\times 10^3$)

$$T = \exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{23}klb^*c^* + 2U_{13}lhc^*a^* + 2U_{12}hka^*b^*)].$$

	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C(1)	−128 (10)	2337 (2)	6717 (10)	62 (5)	48 (5)	66 (6)	1 (5)	3 (5)	−5 (5)
C(2)	761 (12)	2727 (3)	7566 (16)	73 (7)	58 (7)	145 (10)	33 (7)	−22 (8)	−2 (5)
C(3)	782 (10)	2699 (3)	9639 (17)	44 (6)	50 (6)	137 (11)	−18 (8)	−8 (7)	−7 (5)
C(3)	684 (8)	3010 (2)	589 (10)	103 (5)	70 (4)	166 (7)	−59 (5)	6 (6)	−9 (4)
C(4)	999 (10)	2289 (3)	387 (11)	74 (6)	99 (8)	42 (6)	−13 (6)	7 (5)	−30 (6)
C(5)	1052 (10)	1939 (3)	9390 (12)	46 (5)	59 (6)	56 (6)	−10 (5)	6 (5)	−18 (5)
C(6)	1563 (13)	1521 (3)	176 (10)	144 (9)	80 (6)	46 (6)	10 (5)	−44 (6)	−36 (7)
C(7)	160 (12)	1206 (2)	9918 (11)	93 (7)	53 (5)	58 (6)	14 (5)	−4 (6)	−20 (5)
C(8)	−265 (10)	1158 (2)	7886 (9)	48 (5)	48 (5)	35 (5)	17 (4)	−7 (4)	3 (4)
C(9)	−669 (8)	1574 (2)	7008 (9)	41 (5)	41 (4)	27 (4)	−1 (4)	7 (4)	1 (4)
C(10)	665 (9)	1926 (2)	7350 (10)	55 (5)	36 (5)	40 (5)	7 (4)	11 (5)	0 (4)
C(11)	−1061 (10)	1500 (2)	4965 (9)	53 (5)	48 (5)	41 (5)	11 (4)	5 (5)	−12 (4)
C(12)	−2539 (10)	1210 (2)	4716 (9)	55 (5)	57 (5)	31 (5)	4 (4)	−2 (4)	−3 (4)
C(13)	−2274 (8)	774 (2)	5620 (10)	31 (4)	43 (5)	42 (5)	−10 (4)	10 (4)	6 (4)
C(14)	−1679 (10)	844 (2)	7618 (10)	69 (5)	23 (4)	40 (5)	9 (4)	−12 (5)	−1 (4)
C(15)	−3317 (10)	929 (2)	8691 (10)	55 (5)	82 (6)	31 (5)	−4 (4)	27 (5)	−23 (5)
C(16)	−4726 (9)	727 (3)	7563 (12)	45 (5)	80 (6)	73 (6)	−5 (6)	−2 (5)	−8 (5)
C(17)	−3901 (8)	528 (2)	5904 (10)	39 (4)	39 (4)	48 (5)	−3 (4)	9 (4)	0 (4)
C(18)	−1014 (12)	529 (3)	4503 (14)	55 (6)	70 (6)	55 (6)	1 (6)	1 (6)	−10 (5)
C(19)	2313 (13)	1841 (3)	6288 (11)	57 (6)	81 (7)	53 (6)	1 (6)	10 (6)	−4 (5)
C(20)	−5029 (9)	420 (3)	4255 (11)	40 (5)	65 (6)	45 (6)	−5 (5)	9 (5)	−7 (5)
C(21)	−6260 (11)	70 (3)	4794 (16)	59 (7)	57 (6)	104 (10)	7 (6)	−33 (7)	−20 (5)
C(22)	−6030 (12)	772 (3)	3349 (14)	68 (7)	81 (7)	71 (7)	14 (6)	−21 (6)	−12 (6)

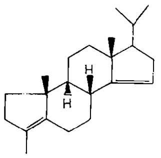
reflexions were retained for use in the structure analysis.

The structure was solved by direct methods (*SHELX*-76 by G. M. Sheldrick). Refinement with anisotropic temperature factors for all the non-hydrogen atoms was by blocked full-matrix least squares, $\Sigma w\Delta^2$ being minimized. The H positional parameters were freely refined with group isotropic temperature factors. The terminal value of $R_G = [\Sigma w\Delta^2/\Sigma wF_o^2]^{1/2}$ was 0·077, with $R_w = [\Sigma w^{1/2}\Delta/\Sigma w^{1/2}|F_o|] = 0{\cdot}062$ and $R = 0{\cdot}061$. The weights were $w = k/[\delta^2(F_o) + gF_o^2]$, where k and g refined to 1·9016 and 0·000433. Complex neutral-atom scattering factors were employed (Cromer & Waber, 1965; Cromer & Liberman, 1970). Tables 1 and 2 list the final atom coordinates and temperature factors. Table 3 gives the bond lengths.*

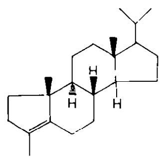
Table 2. *Hydrogen atom positional parameters* ($\times 10^3$) *with isotropic temperature factors* (Å^2 $\times 10^3$)

	x	y	z	U
H(11)	11 (6)	235 (2)	536 (7)	37 (4)
H(12)	−122 (6)	237 (2)	716 (7)	37 (4)
H(21)	17 (6)	297 (2)	704 (7)	37 (4)
H(22)	200 (6)	268 (2)	772 (7)	37 (4)
H(41)	110 (6)	231 (2)	149 (7)	37 (4)
H(61)	133 (6)	158 (2)	77 (9)	37 (4)
H(62)	207 (7)	155 (2)	120 (8)	37 (4)
H(71)	−81 (7)	128 (1)	34 (7)	37 (4)
H(72)	48 (6)	96 (2)	59 (7)	37 (4)
H(81)	84 (6)	104 (2)	747 (7)	37 (4)
H(91)	−165 (6)	168 (1)	756 (7)	37 (4)
H(111)	−6 (6)	140 (1)	419 (7)	37 (4)
H(112)	−123 (6)	180 (2)	441 (7)	37 (4)
H(121)	−280 (7)	115 (2)	355 (7)	37 (4)
H(122)	−334 (7)	135 (2)	513 (7)	37 (4)
H(141)	−132 (7)	60 (2)	793 (7)	37 (4)
H(151)	−360 (6)	85 (1)	983 (7)	37 (4)
H(161)	−546 (6)	86 (1)	737 (7)	37 (4)
H(162)	−557 (7)	48 (2)	834 (7)	37 (4)
H(171)	−344 (6)	25 (1)	647 (7)	37 (4)
H(181)	−86 (9)	25 (2)	516 (9)	63 (7)
H(182)	−123 (10)	53 (2)	332 (11)	63 (7)
H(183)	−6 (8)	68 (2)	429 (11)	63 (7)
H(191)	233 (11)	189 (3)	524 (9)	63 (7)
H(192)	303 (7)	154 (2)	630 (9)	63 (7)
H(193)	324 (9)	200 (2)	699 (8)	63 (7)
H(201)	−442 (7)	34 (2)	331 (8)	37 (4)
H(211)	−708 (9)	24 (2)	550 (10)	63 (7)
H(212)	−571 (9)	−12 (2)	537 (10)	63 (7)
H(213)	−693 (8)	0 (2)	362 (9)	63 (7)
H(221)	−529 (9)	104 (2)	279 (9)	63 (7)
H(222)	−699 (8)	73 (2)	262 (10)	63 (7)
H(223)	−669 (8)	90 (2)	480 (10)	63 (7)

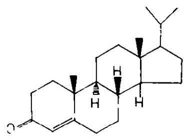
Discussion. It has been demonstrated (Brunke, Böhm & Wolf, 1976) that the HBr-catalysed double-bond isomerization of 3,20-dimethyl-*A*-norpregna-3(5),8(14)-diene can be performed regioselectively [$\Delta^{8(14)} \rightarrow \Delta^{14}$], and, depending on the reaction conditions, with retention or inversion of the configuration at C(17). The 17-epimeric dienes 1(*a*), 1(*b*) yield the monoenes 2(*a*), 2(*b*) upon regioselective (Δ^{14}) and stereospecific hydrogenation, from which the diastereomeric 14α,17β and 14β,17α configurated Δ^4-steroid-3-ketones 3(*a*), 3(*b*) may be produced. 3(*a*) is identical with the Δ^4-steroid-3-ketone which may be synthesized from pregnenolone and which has a known 8β,14α,17β absolute configuration (Brunke, 1974).



1(*a*): 17β
1(*b*): 17α



2(*a*): 14α, 17β
2(*b*): 14β, 17α



3(*a*): 14α, 17β
3(*b*): 14β, 17α

This structural analysis of 3(*b*) confirms the postulated 14β,17α configuration. The ring junction *C*/*D* is *cis* while ring junctions *A*/*B* and *B*/*C* are both *trans*. Ring conformations are as follows, with distances from the least-squares planes through the atoms cited. Ring *A*: 1α,2β half chair; plane (3,4,5,10): C(1) − 0·309, C(2) 0·279, C(3) −0·076, C(4) −0·098, C(5) 0·071, C(10) 0·133 Å. Ring *B*: chair; plane (6,7,9,10): C(5) −0·655,

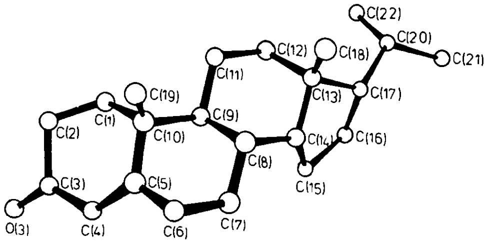


Fig. 1. Molecule 3(*b*) in perspective with the numbering system.

Table 3. *Bond lengths* (Å)

C(1)–C(2)	1·569 (12)	C(1)–C(10)	1·538 (10)
C(2)–C(3)	1·512 (17)	C(3)–O(3)	1·221 (13)
C(3)–C(4)	1·440 (15)	C(4)–C(5)	1·343 (13)
C(5)–C(10)	1·517 (11)	C(5)–C(6)	1·518 (12)
C(6)–C(7)	1·520 (13)	C(7)–C(8)	1·525 (11)
C(8)–C(9)	1·520 (9)	C(8)–C(14)	1·524 (10)
C(9)–C(10)	1·575 (10)	C(10)–C(19)	1·546 (12)
C(9)–C(11)	1·537 (9)	C(11)–C(12)	1·515 (11)
C(12)–C(13)	1·564 (10)	C(13)–C(14)	1·547 (10)
C(13)–C(18)	1·513 (12)	C(13)–C(17)	1·531 (9)
C(14)–C(15)	1·543 (11)	C(15)–C(16)	1·535 (11)
C(16)–C(17)	1·517 (11)	C(17)–C(20)	1·539 (11)
C(20)–C(21)	1·543 (12)	C(20)–C(22)	1·536 (13)

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32025 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 4. *Torsion angles* (°)

Ring *A*	
C(2)–C(1)–C(10)–C(5)	42·5
C(10)–C(1)–C(2)–C(3)	−55·4
C(1)–C(2)–C(3)–C(3)	35·8
C(2)–C(3)–C(4)–C(5)	−5·2
C(3)–C(4)–C(5)–C(10)	−8·1
C(4)–C(5)–C(10)–C(1)	−11·7
Ring *B*	
C(6)–C(5)–C(10)–C(9)	53·0
C(10)–C(5)–C(6)–C(7)	−60·2
C(5)–C(6)–C(7)–C(8)	58·6
C(6)–C(7)–C(8)–C(9)	−54·2
C(7)–C(8)–C(9)–C(10)	50·8
C(8)–C(9)–C(10)–C(15)	−49·0
Ring *C*	
C(14)–C(8)–C(9)–C(11)	−55·9
C(8)–C(9)–C(11)–C(12)	59·6
C(9)–C(11)–C(12)–C(13)	−58·7
C(11)–C(12)–C(13)–C(14)	49·8
C(12)–C(13)–C(14)–C(8)	−47·4
C(9)–C(8)–C(14)–C(13)	53·2
Ring *D*	
C(17)–C(13)–C(14)–C(15)	−38·8
C(13)–C(14)–C(15)–C(16)	23·7
C(14)–C(15)–C(16)–C(17)	0·7
C(15)–C(16)–C(17)–C(13)	−25·1
C(14)–C(13)–C(17)–C(16)	39·4

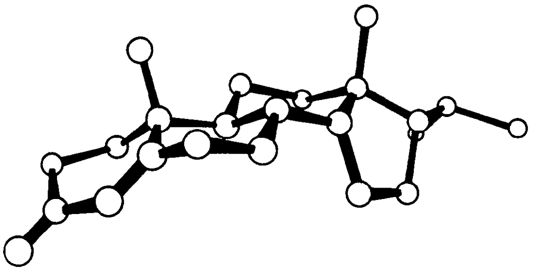

Fig. 2. The ring conformation in molecule 3(*b*).

C(6) 0·034, C(7) −0·034, C(8) 0·627, C(9) 0·033, C(10) −0·033 Å. Ring *C*: chair; plane (8,14,12,11): C(9) −0·704, C(8) −0·021, C(14) 0·021, C(13) 0·625, C(12) −0·021, C(11) 0·022 Å. Ring *D*: 14β envelope; plane (15,16,17,13): C(14) 0·505, C(15) 0·090, C(16) −0·146, C(17) 0·145, C(13) −0·089 Å. Figs. 1 and 2 show molecule 3(*b*) and its ring conformation.

Torsion angles are listed in Table 4.

I am indebted to Professor H. Wolf for suggesting the problem and to Frau A. Borkenstein for technical assistance.

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Tris(triphenylphosphine)(trifluorophosphine)rhodium(I) Hydride Benzene Solvate

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Abstract. $RhP_4F_3C_{54}H_{46}\cdot\frac{3}{2}C_6H_6$. Orthorhombic, *Pbca*; $a = 21\cdot98$ (4), $b = 39\cdot80$ (9), $c = 12\cdot39$ (2) Å, $U = 10842\cdot4$ Å^3; $Z = 8$, $D_x = 1\cdot34$, $D_m = 1\cdot34$ g cm^{-3}. Mo $K\alpha$ radiation, $\lambda = 0\cdot7107$ Å, $\mu = 4\cdot8$ cm^{-1}. The structure has been refined to $R = 0\cdot074$ based on 1668 significant reflexions. The Rh atom has trigonal-bipyramidal coordination with the trifluorophosphine and hydride ligands occupying the axial positions.

Introduction. The crystals rapidly lose solvent on standing and the crystal used for data collection, $0\cdot3 \times 0\cdot3 \times 0\cdot2$ mm, was sealed in a capillary tube under dry nitrogen. Cell dimensions and diffraction data were measured on a Hilger & Watts Y290 four-circle diffractometer. Intensities were collected by the $\omega/2\theta$ step-scan technique with Mo $K\alpha$ radiation (graphite crystal monochromator). Three standard reflexions remeasured periodically showed considerable crystal deterioration and because of this only the 2479 reflexions below $\theta = 15°$ were considered reliable. The data were corrected for Lorentz and polarization effects but not for absorption, and the 1668 reflexions