Compound (3*b*)

Crystal data

$C_{27}H_{25}ClN_4O_2$
$M_r = 472.98$
Monoclinic
$P2_1/c$
$a = 12.985$ (1) Å
$b = 14.036$ (2) Å
$c = 13.314$ (3) Å
$\beta = 102.7$ (3)°
$V = 2368$ (4) Å^3
$Z = 4$
$D_x = 1.33$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 11$–16°
$\mu = 0.190$ mm^{-1}
$T = 294$ K
Prism
0.60 × 0.50 × 0.30 mm
Yellow

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: none
5058 measured reflections
4847 independent reflections
2659 reflections with $I > 2.5\sigma(I)$

$R_{\rm int} = 0.026$
$\theta_{\rm max} = 26°$
$h = -15 \rightarrow 15$
$k = 0 \rightarrow 17$
$l = 0 \rightarrow 16$
3 standard reflections
frequency: 120 min
intensity decay: 0.2%

Refinement

Refinement on F
$R = 0.049$
$wR = 0.065$
$S = 1.877$
2659 reflections
308 parameters
H atoms not refined
$w = 4F_o^2/[\sigma^2(F_o^2) + 0.0025F_o^4]$
$(\Delta/\sigma)_{\rm max} = 0.006$

$\Delta\rho_{\rm max} = 0.331$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.301$ e Å^{-3}
Extinction correction: isotropic (Zachariasen, 1963)
Extinction coefficient: 0.48×10^{-6}
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 2. *Selected geometric parameters (Å, °) for (3b)*

N2—N3	1.387 (4)	N11—C3a	1.481 (4)
N2—C1	1.275 (4)	N11—C10a	1.448 (4)
N3—C3a	1.501 (4)	C3a—C4	1.542 (4)
N6—C5	1.281 (4)	C4—C5	1.510 (4)
N6—C6a	1.409 (4)	C6a—C10a	1.384 (4)
N11—C1	1.387 (4)		
N3—N2—C1	107.2 (2)	N3—C3a—N11	98.7 (2)
N2—N3—C3a	110.8 (2)	N3—C3a—C4	113.0 (2)
C5—N6—C6a	118.9 (3)	N11—C3a—C4	111.6 (2)
C1—N11—C3a	107.3 (2)	C3a—C4—C5	111.2 (2)
C1—N11—C10a	122.9 (3)	N6—C5—C4	121.7 (3)
C3a—N11—C10a	117.1 (2)	N6—C6a—C10a	123.2 (3)
N2—C1—N11	114.6 (3)	N11—C10a—C6a	120.0 (3)

For both compounds, data collection: *CAD*-4 *Operations Manual* (Enraf–Nonius, 1989); cell refinement: *CAD*-4 *Operations Manual*; data reduction: *BEGIN* in *SDP-Plus* (Frenz, 1985); program(s) used to solve structures: *MULTAN*80 (Main *et al.*, 1980); program(s) used to refine structures: *LSFM* in *SDP-Plus*; molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *CIF VAX* in *MolEN* (Fair, 1990).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: CF1173). Services for accessing these data are described at the back of the journal.

References

Baouid, A., Hasnaoui, A. & Lavergne, J. P. (1996). *Bull. Soc. Chim. Belg.* **105**, 339–344.
Barltrop, J. A., Richards, C. G., Russel, D. M. & Ryback, G. (1959). *J. Chem. Soc.* pp. 1132–1142.
El Messaoudi, M., Hasnaoui, A., El Mouhtadi, M. & Lavergne, J. P. (1992). *Bull. Soc. Chim. Belg.* **101**, 977–985.
El Messaoudi, M., Hasnaoui, A. & Lavergne, J. P. (1994). *Synth. Commun.* **24**, 513–520.
Enraf–Nonius (1989). *CAD*-4 *Operations Manual.* Enraf–Nonius, Delft, The Netherlands.
Fair, C. K. (1990). *MolEN. An Interactive Intelligent System for Crystal Structure Analysis.* Enraf–Nonius, Delft, The Netherlands.
Frenz, B. A. (1985). *Enraf–Nonius SDP-Plus Structure Determination Package.* Version 1.1. Enraf–Nonius, Delft, The Netherlands.
Hasnaoui, A., Baouid, A. & Lavergne, J. P. (1991). *J. Heterocycl. Chem.* **28**, 73–76.
Huisgen, R. & Koch, H. J. (1955). *Ann. Chem.* **591**, 200–231.
Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Main, P., Fiske, S. J., Hull, S. E., Lessinger, L., Germain, G., Declercq, J.-P. & Woolfson, M. M. (1980). *MULTAN*80. *A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Universities of York, England, and Louvain, Belgium.
Sharp, R. & Hamilton, C. S. (1946). *J. Am. Chem. Soc.* **68**, 588–591.
Zachariasen, W. H. (1963). *Acta Cryst.* **16**, 1139–1144.

Acta Cryst. (1998). C**54**, 521–523

17α-(4-Chlorobenzoyloxy)-3-methoxy-13α-gona-1,3,5(10)-triene†

ALEXANDER KUHL,[a] DIETER SCHOLLMEYER,[b] MARKUS SCHÜRMANN,[a] HANS PREUT[a] AND WOLFGANG KREISER[a]

[a]*Fachbereich Chemie, Universität Dortmund, Otto-Hahn-Straße 6, 44221 Dortmund, Germany, and* [b]*Institut für Organische Chemie, Universität Mainz, Saarstraße 21, 55099 Mainz, Germany. E-mail: uch002@uxp1.hrz.uni-dortmund.de*

(*Received 20 May 1997; accepted 19 November 1997*)

Abstract

The hydroboration of 3-methoxy-18-norestra-1,3,5(10),-13(18)-tetraene in an anti-Markovnikov sense leads to the formation of two diastereomeric alcohols which have been separated by high-performance liquid chromatography or fractional crystallization of their 17-*p*-chlorobenzoates. The assignment of the absolute configuration of the title compound, $C_{25}H_{27}ClO_3$, has been carried out by X-ray analysis.

---

† IUPAC name: 3-methoxy-13α-gona-1,3,5(10)-trien-17α-yl 4-chlorobenzoate.

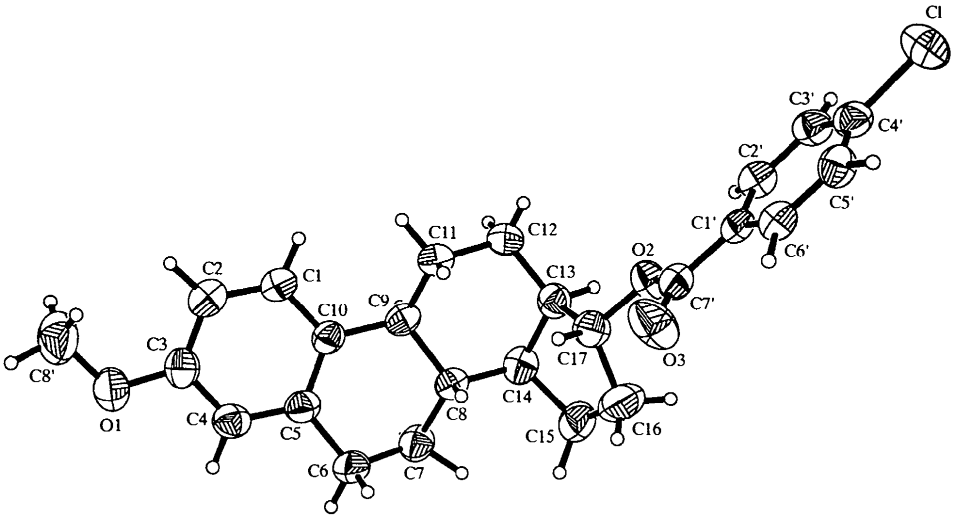
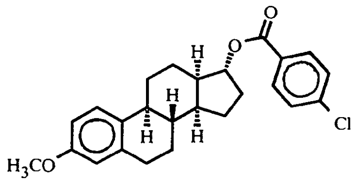


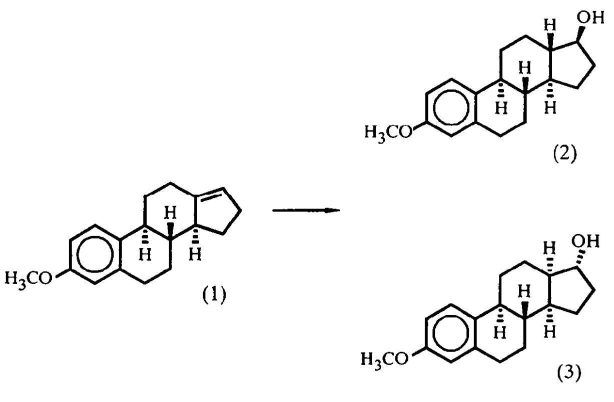
Fig. 1. View of the title compound showing the labelling of all non-H atoms. Displacement ellipsoids are shown at 50% probability levels. H atoms are drawn as circles of arbitrary radii.

Comment

In an attempted synthesis of 18-norestradiol, the diastereomeric alcohols (2) and (3) were produced in ten steps starting from estrone (Kuhl *et al.*, 1998). In order to determine the molecular structure of these alcohols, an X-ray analysis was required, since the unambiguous identification of each diastereomer using NMR techniques failed. With their 17-*p*-chlorobenzoates, modified derivatives were found which allow separation, as well as satisfying crystallization, resulting in the title compound, (I).



(I)



The structure of (I) (Fig. 1) displays a *cis* annulation of the *D* ring, indicated by a surprisingly large H13—C13—C14—H14 torsion angle of −45.7° and an α configuration at the oxygenated C17 atom, which is secured through an O2—C17—C13—H13 torsion angle of 43.2°, demonstrating a *cis* relationship. The dihedral angle between the best planes [maximum deviation from planarity of 0.015 (4) Å] through the steroidal phenyl ring and the phenyl ring of the benzoyloxy moiety is 88.1 (1)°. There are no hydrogen bonds.

Experimental

The hydroboration was accomplished by refluxing a solution of tetraene (1) in benzene with two equivalents of neat catecholborane (Brown & Gupta, 1971) under promotion of 10 mol% of $LiBH_4$ (Arase *et al.*, 1991). Thereafter, oxidative work-up with alkaline H_2O_2 solution (Brown & Gupta, 1975) and column chromatography provided alcohols (2) and (3), which were separated by high-performance liquid chromatography or derivatization. Esterification with *p*-chlorobenzoyl chloride and repeated crystallization from methanol and once from diethyl ether at room temperature gave the pure title compound (m.p. 440–441 K). The second isomer, with 13β-H and 17β-chlorobenzoyloxy-, could not be crystallized, even though the latter material appears of higher interest because of its putative biological activity.

Crystal data

$C_{25}H_{27}ClO_3$
$M_r = 410.92$
Orthorhombic
$P2_12_12_1$
$a = 5.4759\ (7)$ Å
$b = 7.4682\ (6)$ Å
$c = 50.997\ (5)$ Å
$V = 2085.5\ (4)$ Å^3
$Z = 4$
$D_x = 1.309$ Mg m^{-3}
D_m not measured

Cu $K\alpha$ radiation
$\lambda = 1.54178$ Å
Cell parameters from 25 reflections
$\theta = 35$–$44°$
$\mu = 1.806$ mm^{-1}
$T = 298\ (2)$ K
Plate
0.51 × 0.16 × 0.03 mm
Colourless

Data collection

Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: none
3143 measured reflections
2862 independent reflections
2281 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.059$
$\theta_{\rm max} = 74.91°$
$h = -4 \rightarrow 6$
$k = -5 \rightarrow 9$
$l = -37 \rightarrow 63$
3 standard reflections
frequency: 60 min
intensity decay: 5%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.060$
$wR(F^2) = 0.175$
$S = 1.044$
2860 reflections
282 parameters
Only H-atom U's refined
$w = 1/[\sigma^2(F_o^2) + (0.1106P)^2 + 0.4663P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = -0.004$
$\Delta\rho_{\rm max} = 0.390$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.338$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute structure: Flack (1983)
Flack parameter = 0.01 (4)

Table 1. *Selected torsion angles (°)*

C10—C5—C6—C7	−21.5 (6)	C11—C12—C13—C14	45.9 (5)
C5—C6—C7—C8	50.2 (5)	C12—C13—C14—C8	−45.4 (5)
C6—C7—C8—C9	−63.9 (5)	C17—C13—C14—C15	−40.5 (4)
C7—C8—C9—C10	47.4 (5)	C9—C8—C14—C13	52.3 (4)
C14—C8—C9—C11	−60.8 (5)	C13—C14—C15—C16	27.8 (6)
C6—C5—C10—C9	5.9 (6)	C14—C15—C16—C17	−4.5 (7)
C8—C9—C10—C5	−19.2 (6)	C14—C13—C17—C16	38.6 (5)
C8—C9—C11—C12	60.8 (5)	C15—C16—C17—C13	−21.0 (6)
C9—C11—C12—C13	−53.0 (5)		

Since μx had a value of 0.29, an absorption correction was not considered necessary. H atoms were located from difference Fourier syntheses and refined with a riding model (including free rotation about O—C).

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CELSIUS* (Svenson, 1974). Data reduction: *CORINC* (Dräger & Gattow, 1971). Program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1994). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL-Plus* (Sheldrick, 1991). Software used to prepare material for publication: *SHELXL*93 and *PARST*95 (Nardelli, 1995).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1312). Services for accessing these data are described at the back of the journal.

References

Altomare, A., Cascarano, G., Giacovazzo, C., Guagliardi, A., Burla, M. C., Polidori, G. & Camalli, M. (1994). *J. Appl. Cryst.* **27**, 435.
Arase, A., Nunokawa, Y., Masuda, Y. & Hoshi, M. (1991). *J. Chem. Soc. Chem. Commun.* pp. 205–206.
Brown, H. C. & Gupta, S. K. (1971). *J. Am. Chem. Soc.* **93**, 1816–1818.
Brown, H. C. & Gupta, S. K. (1975). *J. Am. Chem. Soc.* **97**, 5249–5255.
Dräger, M. & Gattow, G. (1971). *Acta Chem. Scand.* **25**, 761. Revised by L. Wiehl & D. Schollmeyer (1994). University of Mainz, Germany.
Enraf–Nonius (1989). *CAD*-4 *Software*. Version 5.0. Enraf–Nonius, Delft, The Netherlands.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
Kuhl, A., Karels, H. & Kreiser, W. (1998). In preparation.
Nardelli, M. (1995). *J. Appl. Cryst.* **28**, 659.
Sheldrick, G. M. (1991). *SHELXTL-Plus*. Release 4.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures.* University of Göttingen, Germany.
Svenson, C. (1974). *CELSIUS. Program for Refinement of Lattice Parameters.* Lund, Sweden.

Acta Cryst. (1998). **C54**, 523–525

P,*P*-Dichloro-*N*-(dichlorophosphinoyl)-*P*-(diisopropylamino)monophosphazene

TUNCER HÖKELEK,[a]* ZEYNEL KILIÇ[b] AND HAKAN DAL[b]

[a]*Hacettepe University, Department of Physics, 06532 Beytepe, Ankara, Turkey, and* [b]*Ankara University, Department of Chemistry, 06100 Tandoğan, Ankara, Turkey. E-mail: merzifon@eti.cc.hun.edu.tr*

(Received 11 July 1997; accepted 17 November 1997)

Abstract

The title compound, $C_6H_{14}Cl_4N_2OP_2$, has an acyclic monophosphazene skeleton and a bulky diisopropylamino side group. The bulky substituent is instrumental in determining the molecular geometry. The P—N bonds have neither single- nor double-bond character and are substantially shorter than the ideal P—N single bond. The P—N—P angle [134.0 (2)°] is similar to the angle found in cyclotetraphosphazenes, but wider than that in cyclotriphosphazenes.

Comment

Over the past decade, the reactions of *P*,*P*,*P*-trichloro-*N*-(dichlorophosphinoyl)monophosphazene, $Cl_2P(O)N{=}PCl_3$, (1), with amines have been investigated extensively (Kılıç *et al.*, 1989, 1991, 1994; Bulloch & Keat, 1979). Thermolysis of compound (1) leads to the elimination of phosphorus oxychloride, $P(O)Cl_3$, and polydichlorophosphazene, $(NPCl_2)_n$ (D'halluin *et al.*, 1992). Polydichlorophosphazene is used to obtain linear polyorganophosphazenes. The reaction of (1) with bulky diisopropylamine yield partial aminolysis products $Cl_2P(O)N{=}PCl_2\{N[CH(CH_3)_2]_2\}$, (2), and $Cl_2P(O)N{=}PCl\{N[CH(CH_3)_2]_2\}_2$, (3). The X-ray crystal structure of (3) has been determined previously, confirming the geminal structure (Kılıç *et al.*, 1994). The structure determination of compound (2) was undertaken in order to understand the effect of a single bulky diisopropylamino group on the P=N double bond and also to compare the obtained results with those of compounds