C(3)—P(1)—C(1)	109.2 (2)	C(14)—C(13)—C(12)	120.9 (5)
C(9)—P(1)—C(1)	107.7 (2)	C(13)—C(14)—C(9)	119.7 (5)
C(9)—P(1)—C(3)	109.3 (2)	C(16)—C(15)—P(1)	120.5 (3)
C(15)—P(1)—C(1)	106.9 (2)	C(20)—C(15)—P(1)	120.2 (3)
C(15)—P(1)—C(3)	113.7 (2)	C(20)—C(15)—C(16)	119.0 (4)
C(15)—P(1)—C(9)	109.8 (2)	C(17)—C(16)—C(15)	120.1 (4)
C(2)—C(1)—P(1)	120.2 (3)	C(18)—C(17)—C(16)	120.6 (4)
C(1)—C(2)—C(1)^{i}	174.7 (7)	C(19)—C(18)—C(17)	119.8 (4)
C(4)—C(3)—P(1)	116.7 (3)	C(20)—C(19)—C(18)	120.3 (5)
C(8)—C(3)—P(1)	123.8 (4)	C(19)—C(20)—C(15)	120.2 (4)
C(8)—C(3)—C(4)	119.5 (4)	O(2)—S(1)—O(1)	114.0 (2)
C(5)—C(4)—C(3)	120.6 (5)	O(3)—S(1)—O(1)	115.8 (2)
C(6)—C(5)—C(4)	119.7 (5)	O(3)—S(1)—O(2)	114.4 (2)
C(7)—C(6)—C(5)	120.3 (5)	C(21)—S(1)—O(1)	103.9 (3)
C(8)—C(7)—C(6)	121.0 (5)	C(21)—S(1)—O(2)	101.9 (3)
C(7)—C(8)—C(3)	118.9 (5)	C(21)—S(1)—O(3)	104.7 (3)
C(10)—C(9)—P(1)	121.8 (3)	F(1)—C(21)—S(1)	111.5 (4)
C(14)—C(9)—P(1)	119.5 (4)	F(2)—C(21)—S(1)	110.4 (5)
C(14)—C(9)—C(10)	118.7 (4)	F(2)—C(21)—F(1)	107.1 (6)
C(11)—C(10)—C(9)	121.0 (5)	F(3)—C(21)—S(1)	111.0 (5)
C(12)—C(11)—C(10)	120.3 (5)	F(3)—C(21)—F(1)	108.8 (6)
C(13)—C(12)—C(11)	119.3 (5)	F(3)—C(21)—F(2)	108.0 (6)

Symmetry code: (i) $-x, y, -z$.

Trifluoromethanesulfonic acid anhydride was dissolved in benzol. An equimolar quantity of 1,3-bis(triphenylphoshoranylidene)acetone (Bestmann & Schlosser, 1979) in benzolic solution was added dropwise. The precipitate was then filtered and recrystallized in a (1:1) mixture of dichloromethane and diethyl ether.

One common isotropic displacement parameter was refined for all the H atoms. Although all the H-atom positions could be recognized in the difference Fourier maps, their free parameters were fixed at calculated positions (C—H 0.95 Å). The polar y direction was fixed by keeping $\Sigma f_i y_i$ constant. The absolute configuration was determined by measuring the Friedel pairs with k indices between −4 and 4 and by refinement of the Flack parameter.

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55215 (14 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: SH1002]

References

Behl, H. (1990). Dissertation. Univ. of Erlangen-Nürnberg, Erlangen, Germany.

Bestmann, H. J. & Behl, H. (1989). *Angew. Chem.* **101**, 1303-1304; *Angew. Chem. Int. Ed. Engl.* **28**, 1219-1220.

Bestmann, H. J. & Schlosser, W. (1979). *Synthesis*, pp. 201-202.

Burla, M. C., Camalli, M., Cascarano, G., Giacovazzo, C., Polidori, G., Spagna, R. & Viterbo, D. (1989). *J. Appl. Cryst.* **22**, 389-393.

Burzlaff, H. & Rothammel, W. (1988). *Proceedings of CIC Meeting*, Tübingen, pp. 415-421. Berlin: Ihringer Verlag.

Busing, W. R. & Levy, H. A. (1957). *Acta Cryst.* **10**, 180-182.

Gomm, M. (1991). Private communication.

Watkin, D. J., Carruthers, J. R. & Betteridge, P. W. (1985). *Crystals User Guide*. Chemical Crystallography Laboratory, Univ. of Oxford, England.

Acta Cryst. (1992). C**48**, 1906–1908

{2*S*-[2*α*,3*α*,3a*β*,6*β*(*R**),7*α*,7a*α*]}-6-(3-Benzyloxy-2-propyl)-2-hydroxy-2,3,7-trimethylhexahydro-4*H*-furo[3,2-*c*]pyran-4-one, a Rearrangement Product of Pyranone Derivatives in the Tirandamycin A Series

MASOOD PARVEZ† AND MING-TEH LIN

Department of Chemistry, The Pennsylvania State University, University Park, PA 16802, USA

PHILIP DESHONG

Department of Chemistry and Biochemistry, University of Maryland, College Park, MD 20742, USA

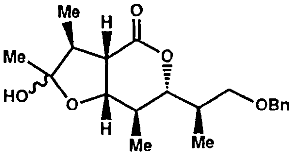
(*Received* 27 *January* 1992; *accepted* 27 *May* 1992)

Abstract

The six- and five-membered heterocyclic rings are *cis*-fused and adopt twist-boat and half-chair conformations, respectively. The average bond distances are: Csp^3—Csp^3 1.520 (6), Csp^3—Csp^2 1.494 (6), C—$C_{\rm benz}$ 1.360 (10) and Csp^3—O 1.425 (5) Å; the C=O and Csp^2—O bond lengths are 1.214 (5) and 1.324 (5) Å, respectively.

Comment

During studies for the total synthesis of tirandamycin A (DeShong, Ramesh, Elango & Perez, 1985) and the pheromone of the male swift moth *Hepialus hecta* L. (DeShong, Lin & Perez, 1986), it was demonstrated that pyranones derived from oxidation of furfuryl alcohols rearranged during treatment with HF yielding lactone (1). Confirmation of the structure of lactone (1) was made using the single-crystal X-ray analysis described in this report.



(1)

The structure consists of discrete molecules separated by normal van der Waals distances. The molecules

---

† Current address: Department of Chemistry, The University of Calgary, 2500 University Drive NW, Calgary, Alberta, Canada T2N 1N4.

0108-2701/92/101906-03$06.00

are linked by an O—H···O hydrogen bond between the hydroxy group and carbonyl O atom with O(4)···O(2) 2.85 Å.

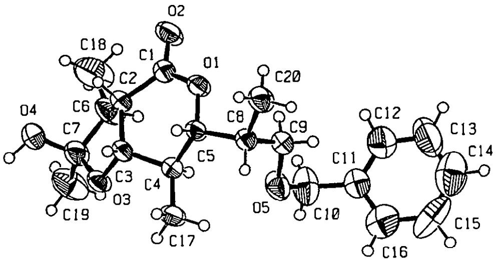


Fig. 1. *ORTEP* drawing of the title compound. H atoms are assigned arbitrary radii; C and O atoms are shown with 50% probability ellipsoids.

Experimental

Crystal data

$C_{20}H_{28}O_5$
M_r = 348.44
Triclinic
$P\bar{1}$
a = 11.157 (2) Å
b = 11.873 (4) Å
c = 7.703 (1) Å
α = 94.54 (2)°
β = 106.08 (2)°
γ = 72.84 (2)°
V = 937 (1) Å^3
Z = 2

D_x = 1.235 Mg m^{-3}
Mo $K\alpha$ radiation
λ = 0.71069 Å
Cell parameters from 25 reflections
θ = 10–15°
μ = 0.082 mm^{-1}
T = 293 (1) K
Prism
0.43 × 0.37 × 0.25 mm
Colourless

Data collection

Enraf-Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
3662 measured reflections
3290 independent reflections
1670 observed reflections [$I>3\sigma(I)$]

$R_{\rm int}$ = 0.017
$\theta_{\rm max}$ = 25°
$h = -13 \rightarrow 13$
$k = -14 \rightarrow 14$
$l = 0 \rightarrow 9$
3 standard reflections
frequency: 120 min
intensity variation: <0.5%

Refinement

Refinement on F
Final R = 0.0628
wR = 0.0708
1670 reflections
223 parameters

Only H-atom U's refined
$w = 1/[\sigma^2(F_o)+0.0015(F_o)^2]$
$(\Delta/\sigma)_{\rm max} < 0.02$
$\Delta\rho_{\rm max}$ = 0.53 e Å^{-3}
$\Delta\rho_{\rm min}$ = −0.26 e Å^{-3}

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å^2)

$$U_{\rm eq} = \tfrac{1}{3}\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
O(1)	0.0985 (3)	0.6161 (2)	0.5291 (3)	0.052 (2)
O(2)	0.1992 (4)	0.4299 (3)	0.5413 (4)	0.075 (2)
O(3)	0.1915 (3)	0.6232 (2)	1.0858 (3)	0.049 (2)
O(4)	0.1974 (4)	0.4397 (3)	1.1720 (4)	0.085 (2)
O(5)	0.2159 (3)	0.8781 (3)	0.5978 (4)	0.071 (2)
C(1)	0.1528 (5)	0.5164 (4)	0.6221 (6)	0.053 (3)
C(2)	0.1547 (4)	0.5123 (4)	0.8173 (5)	0.050 (3)
C(3)	0.1065 (4)	0.6319 (3)	0.9056 (5)	0.043 (3)
C(4)	0.1127 (4)	0.7334 (3)	0.8063 (5)	0.042 (2)
C(5)	0.0358 (4)	0.7259 (3)	0.6106 (5)	0.041 (2)
C(6)	0.2923 (6)	0.4600 (4)	0.9426 (6)	0.064 (3)
C(7)	0.2684 (5)	0.5052 (4)	1.1244 (6)	0.054 (3)
C(8)	0.0175 (4)	0.8228 (4)	0.4788 (5)	0.043 (3)
C(9)	0.1420 (4)	0.8312 (4)	0.4450 (6)	0.053 (3)
C(10)	0.3424 (5)	0.8690 (6)	0.5823 (7)	0.085 (4)
C(11)	0.3438 (4)	0.9358 (5)	0.4284 (6)	0.057 (3)
C(12)	0.3627 (6)	0.8831 (6)	0.2709 (8)	0.093 (5)
C(13)	0.3643 (8)	0.9383 (10)	0.1282 (9)	0.131 (7)
C(14)	0.3444 (7)	1.0524 (10)	0.1373 (12)	0.113 (7)
C(15)	0.3233 (6)	1.1180 (6)	0.2845 (15)	0.106 (6)
C(16)	0.3244 (5)	1.0560 (6)	0.4363 (9)	0.087 (4)
C(17)	0.0576 (4)	0.8520 (4)	0.8912 (5)	0.053 (3)
C(18)	0.3590 (7)	0.3352 (6)	0.9319 (8)	0.103 (5)
C(19)	0.3867 (6)	0.5088 (5)	1.2757 (7)	0.080 (4)
C(20)	−0.0740 (5)	0.8041 (4)	0.2954 (5)	0.058 (3)

Table 2. *Geometric parameters* (Å, °)

C(1)—O(1)	1.324 (5)	C(8)—C(5)	1.526 (5)
C(5)—O(1)	1.469 (4)	C(7)—C(6)	1.524 (6)
C(1)—O(2)	1.214 (5)	C(18)—C(6)	1.456 (7)
C(3)—O(3)	1.440 (4)	C(19)—C(7)	1.509 (7)
C(7)—O(3)	1.415 (5)	C(9)—C(8)	1.515 (6)
C(7)—O(4)	1.392 (6)	C(20)—C(8)	1.540 (5)
C(9)—O(5)	1.415 (5)	C(11)—C(10)	1.484 (7)
C(10)—O(5)	1.421 (5)	C(12)—C(11)	1.361 (7)
C(2)—C(1)	1.503 (5)	C(16)—C(11)	1.378 (7)
C(3)—C(2)	1.538 (5)	C(13)—C(12)	1.330 (8)
C(6)—C(2)	1.545 (6)	C(14)—C(13)	1.306 (17)
C(4)—C(3)	1.506 (5)	C(15)—C(14)	1.359 (14)
C(5)—C(4)	1.525 (5)	C(16)—C(15)	1.426 (13)
C(17)—C(4)	1.535 (5)		
C(5)—O(1)—C(1)	121.7 (3)	C(18)—C(6)—C(7)	116.8 (4)
C(7)—O(3)—C(3)	110.1 (3)	O(4)—C(7)—O(3)	110.4 (4)
C(10)—O(5)—C(9)	111.9 (4)	C(6)—C(7)—O(3)	103.1 (3)
O(2)—C(1)—O(1)	116.7 (4)	C(6)—C(7)—O(4)	107.8 (4)
C(2)—C(1)—O(1)	120.8 (4)	C(19)—C(7)—O(3)	107.1 (4)
C(2)—C(1)—O(2)	122.5 (4)	C(19)—C(7)—O(4)	111.5 (4)
C(3)—C(2)—C(1)	116.0 (3)	C(19)—C(7)—C(6)	116.6 (4)
C(6)—C(2)—C(1)	113.3 (4)	C(9)—C(8)—C(5)	114.8 (3)
C(6)—C(2)—C(3)	102.9 (3)	C(20)—C(8)—C(5)	109.8 (3)
C(2)—C(3)—O(3)	105.2 (3)	C(20)—C(8)—C(9)	107.9 (3)
C(4)—C(3)—O(3)	110.2 (3)	C(8)—C(9)—O(5)	110.6 (3)
C(4)—C(3)—C(2)	112.5 (3)	C(11)—C(10)—O(5)	114.4 (4)
C(5)—C(4)—C(3)	106.8 (3)	C(12)—C(11)—C(10)	122.4 (5)
C(17)—C(4)—C(3)	111.4 (3)	C(16)—C(11)—C(10)	121.6 (5)
C(17)—C(4)—C(5)	111.4 (3)	C(16)—C(11)—C(12)	116.0 (5)
C(4)—C(5)—O(1)	109.7 (3)	C(13)—C(12)—C(11)	125.1 (7)
C(8)—C(5)—O(1)	104.9 (3)	C(14)—C(13)—C(12)	118.1 (8)
C(8)—C(5)—C(4)	118.8 (3)	C(15)—C(14)—C(13)	123.9 (8)
C(7)—C(6)—C(2)	99.9 (4)	C(16)—C(15)—C(14)	116.7 (7)
C(18)—C(6)—C(2)	119.9 (5)	C(15)—C(16)—C(11)	120.2 (6)

Space group $P\bar{1}$ or $P1$; $P\bar{1}$ assumed and confirmed by analysis. Lorentz-polarization corrections but no absorption or extinction corrections were applied. The structure was solved by direct methods using *MULTAN*82 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982). Refinement by full-matrix least-squares calculations; C and O anisotropic. H atoms were located from ΔF map. H atoms were included at geometrically idealized positions (C—H and O—H 0.95 Å) and overall isotropic temperature factors applied for different types. Scattering factors were those of Cromer & Mann (1968) and Stewart, Davidson & Simpson (1965). Computer programs used were *SHELX*76 (Sheldrick, 1976) and *ORTEP*II (Johnson, 1976).

PD acknowledges the generous financial support of the National Institutes of Health.

Lists of structure factors, anisotropic temperature factors, calculated coordinates of H atoms, mean-planes data and important torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55195 (15 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: BR1004]

References

Cromer, D. T. & Mann, J. B. (1968). *Acta Cryst.* **A24**, 321–324.
DeShong, P., Lin, M.-T. & Perez, J. J. (1986). *Tetrahedron Lett.* **27**, 2091–2094.
DeShong, P., Ramesh, S., Elango, V. & Perez, J. J. (1985). *J. Am. Chem. Soc.* **107**, 5219–5224.
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. (1982). *MULTAN82. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.
Sheldrick, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.
Stewart, R. F., Davidson, E. R. & Simpson, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

Acta Cryst. (1992). **C48**, 1908–1909

1,8-Dichloro-5-oxa-10-azatricyclo[5.3.1.$0^{3,8}$]-undecan-9-one: Structure of a Hydrolysed Diels–Alder Addition Product

M. G. Barlow, R. G. Pritchard, L. Sibous and A. E. Tipping

Department of Chemistry, University of Manchester Institute of Science and Technology, PO Box 88, Manchester M60 1QD, England

(*Received* 7 *May* 1992; *accepted* 6 *July* 1992)

Abstract

The title molecule is bisected by a crystallographic mirror plane which contains the Cl, O and N atoms. Pairs of molecules are linked across an inversion centre by a strong hydrogen bond between the amine H and ketonic O atoms [NH···O 2.05(4) Å, N—H···O 167(3)°].

Comment

The structure determination reported herein forms part of an investigation into the Diels–Alder addition of diolefins to trichloro-1,2,4-triazine. In contrast to mono-olefins where a second addition occurs only to a very limited extent (Barlow, Haszeldine & Simpkin, 1982), the title molecule [(1), major product] results from a regioselective Diels–Alder addition to diallyl ether (see scheme below) followed by a second intramolecular addition. A minor isomer (2) is formed by competing [1,5] sigmatropic shift of hydrogen and intramolecular addition.

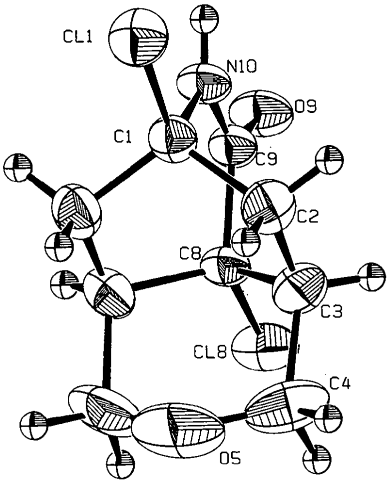
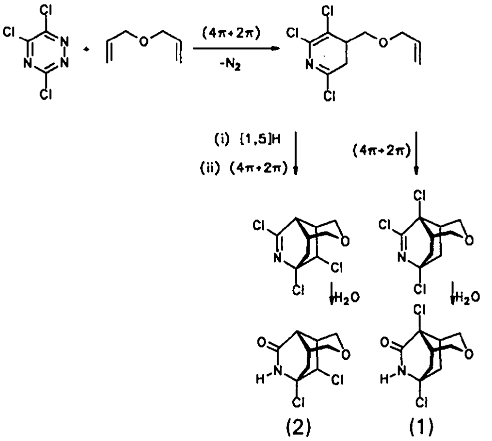


Fig. 1. *ORTEP*II drawing of the title molecule showing atom-numbering scheme.



Experimental

Crystal data

$C_9H_{11}Cl_2NO_2$
$M_r = 236.1$
Monoclinic
$C2/m$
$a = 12.669\ (5)$ Å
$b = 8.760\ (2)$ Å
$c = 9.475\ (5)$ Å
$\beta = 107.38\ (3)°$
$V = 1003.6\ (7)$ Å^3
$Z = 4$
$D_x = 1.562$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 20 reflections
$\theta = 7.1–22.2°$
$\mu = 0.62$ mm^{-1}
$T = 293$ K
Block
0.3 × 0.3 × 0.2 mm
Colourless