Jauch, D. A., Sethy, V. H., Weick, B. G., Chase, T. N. & Schwarcz, R. (1993). *Neuropharmacology*, **32**, 467–472.

Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Kapoor, V., Kapoor, R. & Chalmers, J. (1994). *Clin. Exp. Pharmacol. Physiol.* **21**, 891–896.

Kvick, A., Koetzle, T. F., Thomas, R. & Takusagawa, F. (1974). *J. Chem. Phys.* **60**, 3866–3874.

Martin, D. W., Mayes, P. A. & Rodwell, V. W. (1983). *Harper's Review of Biochemistry*, pp. 464–479. Tokyo: Maruzen Asia.

Molecular Structure Corporation (1985). *TEXSAN. TEXRAY Structure Analysis Package*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

Molecular Structure Corporation (1988). *MSC/AFC Diffractometer Control Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

Sheldrick, G. M. (1985). *SHELXS86. Crystallographic Computing 3*, edited by G. M. Sheldrick, C. Krüger & R. Goddard, pp. 175–189. Oxford University Press.

Stone, T. W. (1993). *Pharmacol. Rev.* **45**, 309–379.

Takusagawa, F., Hirotsu, K. & Shimada, A. (1973). *Bull. Chem. Soc. Jpn*, **46**, 2372–2380.

Takusagawa, F. & Koetzle, T. F. (1978). *Acta Cryst.* B**34**, 1149–1154.

Takusagawa, F. & Shimada, A. (1973). *Chem. Lett.* pp. 1089–1090.

A *cis*-Fused Decalone and a Bicyclo[4.3.1]-decanone Ring System

Khalil A. Abboud, Yongping Xie and Eric J. Enholm

Department of Chemistry, University of Florida, PO Box 117200, Gainesville, Florida 32611-7200, USA. E-mail: kaabboud@pine.circa.ufl.edu

Abstract

The crystal structures of $(4a\alpha,8\alpha,8a\alpha)$-($\pm$)-1-oxoperhydro-8-naphthyl p-bromobenzoate, $C_{17}H_{19}BrO_3$, (2), and ($\pm$)-*endo*-5-hydroxy-1-methylbicyclo[4.3.1.]decan-7-one, $C_{11}H_{18}O_2$, (3), were determined in order to ascertain their relative configurations. Compound (2) has two *cis*-fused six-membered rings which both adopt chair conformations. Compound (3) has a bridged bicyclic ring system consisting of a six- and a seven-membered ring which both adopt chair conformations. Molecules of (3) are linked about inversion centers into dimers by O—H···O hydrogen bonds [O···O 2.844 (3) Å] involving the hydroxy and carbonyl groups.

Comment

Many of the sophisticated organic molecules found in nature, such as carbohydrates, steroids and some terpenes, possess the common feature of cyclic components

(Thebtaranonth & Thebtaranonth, 1994). Cyclization reactions, especially those promoted by free radicals, are therefore particularly valuable in the synthesis and modification of these complex molecules (Giese, 1986). The application of free radicals to synthesis, in general, permits neutral reaction conditions and alleviates the need for protecting groups (Curran, 1988).

As part of a plan to develop and exploit free-radical reactions, unsaturated ketones were subjected to treatment with tri-*n*-butyltin hydride, which led to the formation of *O*-stannyl ketyls. The title molecules, (2) and (3), were prepared by a new *O*-stannyl ketyl reaction which promoted an aldol-like cyclization (Enholm, Xie & Abboud, 1995). This contrasts with most aldol reactions which require strong bases or dissolving metal conditions. Three new stereocenters were formed in compound (2) and two in compound (3) in the free-radical annulation reaction. Since it was not clear what relative stereochemistry would prevail in compounds (2) and (3), we undertook X-ray studies to ascertain these details. The results of these studies are described herein.

(1)   (2)

(3)
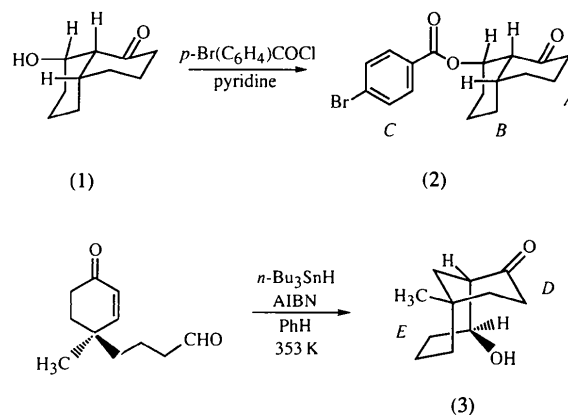
Displacement ellipsoid drawings of compounds (2) and (3) with the atom-labeling schemes are shown in Figs. 1 and 2, respectively. All bond lengths and angles of both molecules are normal. Compound (2) has two six-membered rings (A and B), which are fused together along the C5—C10 bond, and a phenyl ring (C). Ring A exhibits a $^{1}C_{4}$ conformation (Boeyens, 1978), with atoms C1 and C4 at distances of 0.60 (1) and −0.66 (1) Å, respectively, from the plane composed of atoms C2, C3, C5 and C10. Ring B exhibits a $^{6}C_{9}$ inverted chair conformation, with atoms C6 and C9 at distances of 0.66 (1) and −0.61 (1) Å, respectively, from the plane containing atoms C5, C7, C8 and C10. The planes of rings A and B form an angle of 126.4 (2)° with one another. The plane of the carboxy group (C11, O11*a* and O11*b*) is slightly skewed from the plane of the bromophenyl ring, with a dihedral angle of 12.1 (2)°. Phenyl ring C is planar, with the largest deviation from the least-squares plane being 0.002 (4) Å and the average bond length 1.382 (6) Å.
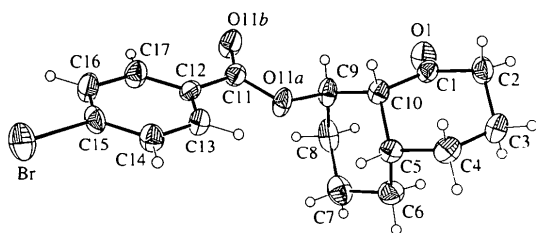
Fig. 1. The molecular structure of compound (2), showing 50% probability ellipsoids for the non-H atoms and the atom-numbering scheme.
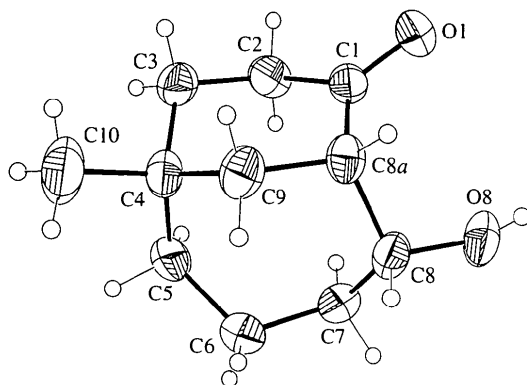

Fig. 2. The molecular structure of compound (3), showing 50% probability ellipsoids for the non-H atoms and the atom-numbering scheme.

Compound (3) consists of a six-membered (D) and a seven-membered ring (E). The six-membered ring adopts a $^1C_4$ chair conformation, with atoms C1 and C4 at distances of 0.43 (1) and −0.68 (1) Å from the plane of the ring containing atoms C2, C3, C8a and C9. The seven-membered ring also exhibits a chair conformation (Boessenkool & Boeyens, 1980), with the C8 atom and the C4—C5 bond, respectively, above and below the plane containing atoms C6, C7, C8a and C9. Atoms C8, C4 and C5 are at distances of 0.63 (1), 1.14 (1) and 1.13 (1) Å, respectively, from the same plane. The seven-membered ring has internal torsion angles consistent with a chair conformation, alternating + and − around the ring, with that at C4—C5 being closest to zero [−1.1 (3)°]. The planes of the chair form an angle of 95.89 (7)° with one another.

Compound (3) has one hydrogen bond involving the O8—H8a hydroxyl group and the carbonyl O1 atom; O8—H8a 0.87 (3), H8a···O1^i 2.001 (3), O8···O1^i 2.844 (3) Å and O8—H8a···O1^i 162 (2)° [symmetry code: (i) 1 − x, 1 − y, 2 − z].

Experimental

Compounds (2) and (3) were crystallized by slow evaporation from a 2-propanol/hexane mixture and ethanol, respectively.

Compound (2)

Crystal data

$C_{17}H_{19}BrO_3$	Mo $K\alpha$ radiation
$M_r = 351.23$	$\lambda = 0.71073$ Å
Triclinic	Cell parameters from 50
$P\bar{1}$	reflections
$a = 7.851$ (1) Å	$\theta = 10–11°$
$b = 10.239$ (2) Å	$\mu = 2.68$ mm^{-1}
$c = 10.869$ (2) Å	$T = 298$ K
$\alpha = 63.03$ (1)°	Plate
$\beta = 80.85$ (1)°	$0.48 \times 0.38 \times 0.19$ mm
$\gamma = 85.97$ (1)°	Colorless
$V = 768.8$ (2) Å^3	
$Z = 2$	
$D_x = 1.517$ Mg m^{-3}	

Data collection

Siemens $P3m/V$ diffractometer	1992 observed reflections [$I_{net} > 2\sigma(I_{net})$]
ω scans	$R_{int} = 0.0192$
Absorption correction: from measured crystal faces (*SHELXTL-Plus*; Sheldrick, 1991)	$\theta_{max} = 27.5°$ $h = 0 \rightarrow 10$ $k = -13 \rightarrow 13$ $l = -14 \rightarrow 14$
$T_{min} = 0.321$, $T_{max} = 0.615$	4 standard reflections monitored every 100
3784 measured reflections	reflections
3527 independent reflections	intensity decay: 1%

Refinement

Refinement on F	$(\Delta/\sigma)_{max} = 0.001$
$R = 0.069$	$\Delta\rho_{max} = 0.50$ e Å^{-3}
$wR = 0.0476$	$\Delta\rho_{min} = -0.55$ e Å^{-3}
$S = 1.41$	Extinction correction: none
1992 reflections	Atomic scattering factors
190 parameters	from *International Tables*
H atoms riding (C—H = 0.96 Å)	*for X-ray Crystallography* (1974, Vol. IV)
$w = 1/[\sigma^2(F) + 0.0004F^2]$	

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

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

	x	y	z	U_{eq}
Br	−0.18966 (8)	−0.22301 (6)	−0.09793 (6)	0.0645 (3)
O1	−0.5184 (4)	0.5961 (3)	0.2803 (3)	0.057 (2)
O11a	−0.3313 (4)	0.2754 (3)	0.1544 (3)	0.048 (1)
O11b	−0.2096 (4)	0.4302 (3)	−0.0605 (3)	0.056 (2)
C1	−0.5969 (6)	0.4827 (4)	0.3234 (4)	0.038 (2)
C2	−0.7685 (6)	0.4551 (5)	0.4141 (5)	0.047 (2)
C3	−0.7707 (6)	0.3105 (5)	0.5464 (5)	0.050 (2)
C4	−0.7101 (6)	0.1853 (4)	0.5113 (5)	0.048 (2)
C5	−0.5318 (5)	0.2121 (4)	0.4248 (4)	0.039 (2)
C6	−0.3862 (6)	0.2113 (5)	0.5030 (5)	0.052 (2)
C7	−0.2117 (6)	0.2394 (6)	0.4118 (6)	0.060 (3)
C8	−0.2096 (6)	0.3826 (5)	0.2781 (6)	0.058 (3)
C9	−0.3552 (6)	0.3908 (4)	0.1989 (5)	0.044 (2)
C10	−0.5314 (6)	0.3585 (4)	0.2894 (4)	0.038 (2)
C11	−0.2594 (6)	0.3087 (5)	0.0239 (5)	0.039 (2)
C12	−0.2436 (5)	0.1789 (4)	−0.0022 (4)	0.034 (2)
C13	−0.3292 (5)	0.0481 (4)	0.0891 (4)	0.040 (2)
C14	−0.3134 (6)	−0.0717 (4)	0.0618 (5)	0.044 (2)

C15	-0.2126 (6)	-0.0596 (4)	-0.0585 (5)	0.042 (2)
C16	-0.1260 (6)	0.0690 (5)	-0.1516 (5)	0.049 (2)
C17	-0.1430 (6)	0.1871 (5)	-0.1221 (5)	0.047 (2)

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

C15—Br	1.897 (6)	C5—C4	1.523 (6)
C1—O1	1.209 (5)	C6—C5	1.527 (7)
C9—O11a	1.457 (7)	C10—C5	1.552 (5)
C11—O11a	1.334 (6)	C7—C6	1.518 (6)
C11—O11b	1.209 (5)	C8—C7	1.525 (6)
C2—C1	1.499 (6)	C9—C8	1.513 (8)
C10—C1	1.514 (7)	C10—C9	1.525 (6)
C3—C2	1.525 (5)	C12—C11	1.473 (7)
C4—C3	1.521 (8)		
C9—O11a—C11	119.1 (3)	C8—C7—C6	111.8 (4)
C2—C1—C10	114.7 (4)	C9—C8—C7	112.2 (4)
C2—C1—O1	122.2 (5)	C10—C9—O11a	104.4 (4)
C10—C1—O1	123.1 (4)	C10—C9—C8	113.0 (4)
C3—C2—C1	111.7 (4)	O11a—C9—C8	108.6 (4)
C4—C3—C2	110.8 (4)	C1—C10—C5	110.7 (4)
C5—C4—C3	112.8 (4)	C1—C10—C9	112.7 (4)
C6—C5—C10	110.3 (4)	C5—C10—C9	111.9 (3)
C6—C5—C4	114.1 (4)	C12—C11—O11a	111.7 (3)
C10—C5—C4	109.7 (3)	C12—C11—O11b	124.7 (4)
C7—C6—C5	111.9 (4)	O11a—C11—O11b	123.6 (5)

Compound (3)

Crystal data

$C_{11}H_{18}O_2$	Mo $K\alpha$ radiation
$M_r = 182.25$	$\lambda = 0.71073$ Å
Monoclinic	Cell parameters from 40
$P2_1/c$	reflections
$a = 12.010$ Å	$\theta = 10\text{--}11°$
$b = 7.553$ Å	$\mu = 0.08$ mm^{-1}
$c = 12.134$ Å	$T = 298$ K
$\beta = 110.34°$	Needle
$V = 1032.1$ (3) Å^3	$0.34 \times 0.28 \times 0.28$ mm
$Z = 4$	Colorless
$D_x = 1.173$ Mg m^{-3}	

Data collection

Siemens $P3m/V$ diffractom-	1380 observed reflections
eter	$[I_{net} > 2\sigma(I_{net})]$
ω scans	$R_{int} = 0.010$
Absorption correction:	$\theta_{max} = 27.5°$
from measured crystal	$h = 0 \rightarrow 15$
faces (*SHELXTL-Plus*;	$k = 0 \rightarrow 9$
Sheldrick, 1991)	$l = -15 \rightarrow 15$
$T_{min} = 0.967$, $T_{max} =$	4 standard reflections
0.983	monitored every 100
2676 measured reflections	reflections
2374 independent reflections	intensity decay: 1%

Refinement

Refinement on F	$w = 1/[\sigma^2(F) + 0.0004F^2]$
$R = 0.0463$	$(\Delta/\sigma)_{max} = 0.001$
$wR = 0.0526$	$\Delta\rho_{max} = 0.15$ e Å^{-3}
$S = 1.55$	$\Delta\rho_{min} = -0.15$ e Å^{-3}
1380 reflections	Extinction correction: none
122 parameters	Atomic scattering factors
H atoms riding (C—H =	from *International Tables*
0.96 Å), except for the	*for X-ray Crystallography*
hydroxyl H atom	(1974, Vol. IV)

Table 3. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for (3)*

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

	x	*y*	*z*	U_{eq}
O1	0.4552 (1)	0.4714 (2)	0.8126 (1)	0.0637 (7)
O8	0.6174 (2)	0.6958 (3)	1.0135 (1)	0.0697 (8)
C1	0.5548 (2)	0.4712 (3)	0.8071 (2)	0.0443 (8)
C2	0.5729 (2)	0.5054 (3)	0.6932 (2)	0.0532 (8)
C3	0.6679 (2)	0.3886 (3)	0.6754 (2)	0.0545 (9)
C4	0.7856 (2)	0.3917 (3)	0.7790 (2)	0.0519 (8)
C5	0.8435 (2)	0.5773 (3)	0.7890 (2)	0.0652 (10)
C6	0.8713 (2)	0.6834 (3)	0.9020 (2)	0.0616 (9)
C7	0.7648 (2)	0.7450 (3)	0.9314 (2)	0.0546 (8)
C8	0.7092 (2)	0.6083 (3)	0.9865 (2)	0.0508 (8)
C8a	0.6622 (2)	0.4372 (3)	0.9152 (2)	0.0449 (8)
C9	0.7592 (2)	0.3337 (3)	0.8881 (2)	0.0536 (9)
C10	0.8685 (2)	0.2535 (4)	0.7569 (2)	0.0922 (14)

Table 4. *Selected geometric parameters (Å, °) for (3)*

C1—O1	1.220 (3)	C9—C4	1.529 (3)
C8—O8	1.417 (3)	C10—C4	1.529 (4)
C2—C1	1.494 (3)	C6—C5	1.522 (3)
C8a—C1	1.508 (2)	C7—C6	1.515 (3)
C3—C2	1.517 (3)	C8—C7	1.506 (3)
C4—C3	1.531 (2)	C8a—C8	1.548 (3)
C5—C4	1.550 (3)	C9—C8a	1.531 (3)
C2—C1—C8a	118.6 (2)	C6—C5—C4	119.9 (2)
C2—C1—O1	120.7 (2)	C7—C6—C5	115.8 (2)
C8a—C1—O1	120.7 (2)	C8—C7—C6	115.7 (2)
C3—C2—C1	113.0 (2)	C8a—C8—O8	110.9 (2)
C4—C3—C2	113.6 (2)	C8a—C8—C7	117.2 (2)
C5—C4—C9	114.4 (2)	O8—C8—C7	106.5 (2)
C5—C4—C10	109.2 (2)	C9—C8a—C1	112.6 (2)
C5—C4—C3	109.8 (2)	C9—C8a—C8	112.9 (2)
C9—C4—C10	107.4 (2)	C1—C8a—C8	112.3 (2)
C9—C4—C3	107.2 (2)	C4—C9—C8a	116.3 (2)
C10—C4—C3	108.5 (2)		

For both compounds, *SHELXTL-Plus* (Sheldrick, 1991) was used for data collection, cell refinement, data reduction, structure solution and refinement, molecular graphics and preparation of material for publication.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: FG1079). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Boessenkool, I. K. & Boeyens, J. C. A. (1980). *J. Cryst. Mol. Struct.* **10**, 11–18.
Boeyens, J. C. A. (1978). *J. Cryst. Mol. Struct.* **8**, 317–320.
Curran, D. P. (1988). *Synthesis*, pp. 417–439, 489–513.
Enholm, E. J., Xie, Y. & Abboud, K. A. (1995). *J. Org. Chem.* **60**, 1112–1113.
Giese, B. (1986). In *Radicals in Organic Synthesis: Formation of Carbon–Carbon Bonds*. New York: Pergammon.
Sheldrick, G. M. (1991). *SHELXTL-Plus*. Release 4.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Thebtaranonth, C. & Thebtaranonth, Y. (1994). In *Cyclization Reactions*. Boca Raton, Florida: CRC Press.