Acta Cryst. (1990). C46, 937–939

Intramolecular Free-Radical Ring Closures. II. Structures of Two Bicyclic Lactones*

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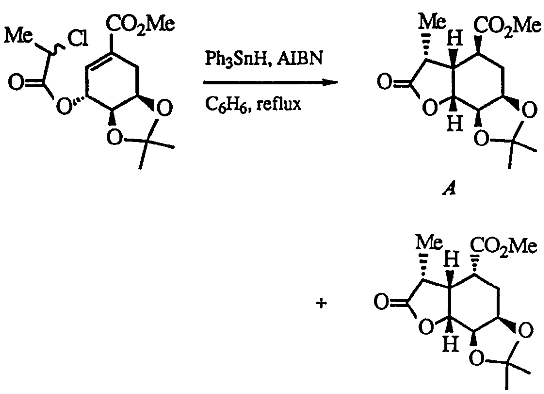
(*Received* 12 *July* 1989; *accepted* 17 *October* 1989)

Abstract. $C_{14}H_{20}O_6$, isomer *A*, $M_r = 284{\cdot}31$, orthorhombic, $P2_12_12_1$, $a = 5{\cdot}537$ (9), $b = 14{\cdot}404$ (4), $c = 18{\cdot}748$ (10) Å, $V = 1495{\cdot}2$ Å^3, $Z = 4$, $D_x = 1{\cdot}263$ Mg m^{-3}, $\lambda(\mathrm{Cu}\ K\alpha) = 1{\cdot}54178$ Å, $\mu = 0{\cdot}79$ mm^{-1}, $F(000) = 608$, $T = 296$ K, $R = 0{\cdot}035$ for 783 observed reflections. $C_{14}H_{20}O_6$, isomer *B*, $M_r = 284{\cdot}31$, monoclinic, $C2$, $a = 21{\cdot}390$ (5), $b = 7{\cdot}991$ (3), $c = 9{\cdot}019$ (2) Å, $\beta = 109{\cdot}43°$, $V = 1453{\cdot}8$ Å^3, $Z = 4$, $D_x = 1{\cdot}299$ Mg m^{-3}, $\lambda(\mathrm{Cu}\ K\alpha) = 1{\cdot}54178$ Å, $\mu = 0{\cdot}82$ mm^{-1}, $F(000) = 608$, $T = 296$ K, $R = 0{\cdot}047$ for 1430 observed reflections. During the course of studies in tin-mediated radical cyclizations, the title lactones were obtained in crystalline form. Although spectroscopic assignment based on ^{1}H NMR and nuclear Overhauser enhancement studies indicated the proposed structures, X-ray analysis was used for confirmation. The five-membered lactone is *cis* fused to a cyclohexane ring in both isomers. In isomer *A* the methyl group α to the lactone carbonyl is *anti* to the ester group, while in isomer *B* it is *syn*.

Experimental. The bicyclic products *A* and *B* are obtained from the reaction shown below in 79% yield in a 1·4 : 1 ratio respectively.



A

B

Isomer *A*, $C_{14}H_{20}O_6$, colorless prism of size 0·16 × 0·20 × 0·42 mm. Unit-cell dimensions from 25 centered reflections in the range $20 < \theta < 25°$. Enraf–Nonius CAD-4 diffractometer, graphite-monochromatized Cu $K\alpha$ radiation, $2\theta_{max} = 100°$. The data were collected in the ω-scan mode, $\Delta\omega = (1{\cdot}00 + 0{\cdot}14 \tan\theta)°$, at a scan speed of 4° min^{-1}. The orientation was checked every 100 measurements. The intensities of seven standards (checked every hour) presented a maximum fluctuation of ±2·4%. 942 measured reflections of which 783 with $I > 3\sigma(I)$. Data corrected for Lp, uncorrected for absorption.

Isomer *B*, $C_{14}H_{20}O_6$, colorless prism of size 0·15 × 0·30 × 0·44 mm. Enraf-Nonius CAD-4 diffractomer, Laue symmetry $2/m$ from 25 centered reflections, $22 < \theta < 25°$ and axial photographs. No systematic absences (besides *hkl*, $h + k \neq 2n$) were found in data set, consistent with space groups $C2$, Cm and $C2/m$. The last two space groups were ruled out by the presence of chiral centers in the compound. Graphite-monchromatized Cu $K\alpha$ radiation was used, $2\theta_{max} = 140°$. The data were collected in the ω-scan mode, $\Delta\omega = (1{\cdot}00 + 0{\cdot}14 \tan\theta)°$ at a scan speed of 4° min^{-1}. The orientation was checked every 100 measurements. The intensities of six standards (checked every hour) presented a maximum fluctuation of ±3·3%. 1480 measured reflections of which 1430 with $I > 3\sigma(I)$. Data corrected for Lp.

The structures were solved using *MULTAN*80,‡ refined on $|F_o|$ by full-matrix least squares. Refinement anisotropic for C, O, isotropic for H atoms, only H(12) in isomer *A* visible on ΔF map used to calculate idealized positions for the methyl H atoms (C—H 0·95 Å, $B_{iso} = 9{\cdot}5$ Å^2), positions recalculated after each least-squares cycle. For both isomers, the absolute configurations of both isomers were deduced from the known chirality of the asymmetric centers present in the starting material.

* *A*: Methyl (1*R*,2*S*,6*R*,9*R*)-4,5-isopropylidenedioxy-9-methyl-8-oxo-*cis*-7-oxabicyclo[4.3.0]nonane-2-carboxylate. *B*: Methyl (1*R*,2*R*,6*R*,9*R*)-4,5-isopropylidenedioxy-9-methyl-8-oxo-*cis*-7-oxabicyclo[4.3.0]nonane-2-carboxylate.

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‡ The programs used here are modified versions of: *NRC*-2, data reduction, *NRC*-10, bond distances and angles, and *NRC*-22, mean planes (Ahmed, Hall, Pippy & Huber, 1973); *FORDAP*, Fourier and Patterson maps (A. Zalkin, unpublished); *MULTAN*80, multisolution program (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980); *NUCLS*, least-squares refinement (Doedens & Ibers, 1967); and *ORTEP* (Johnson, 1965).

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Table 1. *Final atomic coordinates and their e.s.d.'s* (× 10^4) *and* U_{eq} *values* (Å^2 × 10^3)

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

	x	y	z	U_{eq}
Isomer *A*				
O1	9466 (11)	4628 (4)	−1470 (2)	94
O2	6281 (9)	4269 (3)	−2129 (2)	88
O3	2817 (8)	3389 (2)	505 (2)	69
O4	5074 (8)	4552 (2)	994 (2)	63
O5	2884 (8)	6390 (3)	−116 (2)	75
O6	2489 (11)	7449 (3)	−976 (2)	100
C1	5510 (12)	4830 (4)	−981 (3)	54
C2	5052 (15)	3954 (4)	−533 (4)	61
C3	3045 (13)	4126 (4)	0 (3)	60
C4	3531 (14)	4954 (4)	471 (3)	59
C5	4779 (12)	5777 (4)	142 (3)	57
C6	3738 (16)	6876 (5)	−689 (4)	73
C7	6253 (15)	6594 (4)	−854 (3)	62
C8	6401 (13)	5624 (4)	−507 (3)	53
C11	7334 (16)	4583 (4)	−1544 (3)	64
C12	7892 (18)	3977 (5)	−2706 (3)	121
C14	4134 (12)	3638 (4)	1133 (3)	65
C15	2433 (17)	3661 (7)	1760 (4)	84
C16	6203 (18)	2981 (6)	1248 (6)	91
C17	6939 (19)	6701 (6)	−1640 (4)	78
Isomer *B*				
O1	6092 (1)	2592	118 (3)	71
O2	6191 (1)	2662 (5)	2689 (2)	59
O3	8322 (1)	2441 (4)	1354 (2)	50
O4	8675 (1)	1613 (5)	3868 (2)	52
O5	7776 (1)	−2261 (4)	3177 (2)	60
O6	6952 (1)	−4082 (5)	2344 (3)	75
C1	7083 (1)	1557 (5)	2039 (3)	43
C2	7311 (1)	886 (5)	722 (3)	47
C3	8060 (1)	773 (5)	1298 (3)	47
C4	8374 (1)	158 (5)	3021 (3)	50
C5	7892 (1)	−557 (5)	3765 (3)	49
C6	7133 (2)	−2693 (5)	2797 (3)	58
C7	6739 (2)	−1269 (5)	3112 (3)	56
C8	7200 (1)	273 (5)	3379 (3)	46
C11	6396 (1)	2296 (5)	1468 (3)	50
C12	5568 (2)	3537 (9)	2315 (6)	88
C14	8858 (1)	2629 (5)	2777 (3)	53
C15	8896 (2)	4415 (6)	3289 (4)	70
C16	9495 (2)	1986 (8)	2553 (5)	70
C17	6043 (2)	−1222 (6)	1883 (6)	83

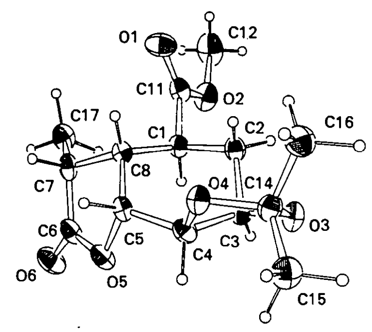

Fig. 1. An *ORTEP* diagram of isomer *A* with the H atoms and the atomic numbering. Ellipsoids represent 30% probability.

For isomer *A*, final $R = 0{\cdot}035$, $wR = 0{\cdot}046$ (weights based on counting statistics), $w = 1/[\sigma^2(F) + 0{\cdot}00005F^2]$, $S = 1{\cdot}73$, (shift/σ) mean 0·020, max. 0·05. The residual electron density fluctuation on final difference Fourier synthesis gave a general background ranging from −0·19 to 0·16 e Å^{-3}.

For isomer *B*, final $R = 0{\cdot}047$, $wR = 0{\cdot}053$ (weights based on counting statistics), $w = 1/[\sigma^2(F) + 0{\cdot}00005F^2]$, $S = 2{\cdot}39$; (shift/σ) mean 0·020, max. 0·04. The residual electron density fluctuation on final difference Fourier synthesis gave a general background ranging from −0·11 to 0·10 e Å^{-3}. The scattering factors were taken from Cromer & Mann (1968) for O and C, and from Stewart, Davidson & Simpson (1965) for H.

Table 2. *Bond distances* (Å), *bond angles and torsion angles* (°) *with their e.s.d.'s for A*, $C_{14}H_{20}O_6$

C1—C2	1·537 (8)	C6—O5	1·367 (8)
C1—C8	1·530 (8)	C6—O6	1·204 (9)
C1—C11	1·504 (9)	C7—C8	1·543 (8)
C2—C3	1·515 (10)	C7—C17	1·530 (9)
C3—C4	1·508 (8)	C11—O1	1·190 (11)
C3—O3	1·428 (7)	C11—O2	1·322 (8)
C4—C5	1·504 (8)	C12—O2	1·464 (9)
C4—O4	1·424 (7)	C14—C15	1·507 (11)
C5—C8	1·528 (8)	C14—C16	1·502 (12)
C5—O5	1·454 (7)	C14—O3	1·431 (7)
C6—C7	1·483 (12)	C14—O4	1·439 (7)
C2—C1—C8	110·5 (5)	C8—C7—C17	119·0 (6)
C2—C1—C11	107·5 (5)	C1—C8—C5	112·4 (5)
C8—C1—C11	111·6 (5)	C1—C8—C7	114·5 (5)
C1—C2—C3	110·3 (5)	C5—C8—C7	100·0 (5)
C2—C3—C4	112·6 (5)	C1—C11—O1	124·9 (6)
C2—C3—O3	112·4 (5)	C1—C11—O2	111·5 (5)
C4—C3—O3	102·4 (5)	O1—C11—O2	123·6 (6)
C3—C4—C5	117·7 (5)	C15—C14—C16	112·3 (7)
C3—C4—O4	100·9 (5)	C15—C14—O3	109·2 (6)
C5—C4—O4	109·1 (5)	C15—C14—O4	110·3 (5)
C4—C5—C8	118·9 (5)	C16—C14—O3	110·4 (6)
C4—C5—O5	106·5 (5)	C16—C14—O4	109·1 (6)
C8—C5—O5	104·3 (4)	O3—C14—O4	105·3 (5)
C7—C6—O5	110·4 (6)	C11—O2—C12	116·3 (5)
C7—C6—O6	129·3 (7)	C3—O3—C14	108·3 (4)
O5—C6—O6	120·2 (6)	C4—O4—C14	106·2 (4)
C6—C7—C8	102·1 (5)	C5—O5—C6	108·8 (5)
C6—C7—C17	114·9 (6)		
C1—C2—C3—O3	−170·4 (5)	C4—C5—C8—C1	32·5 (7)
C1—C2—C3—C4	−55·3 (7)	C4—C5—C8—C7	154·4 (5)
C1—C8—C5—O5	−85·8 (5)	C5—O5—C6—C7	1·3 (7)
C1—C8—C7—C17	−40·6 (8)	C5—C8—C1—C2	−50·9 (7)
C1—C11—O2—C12	−178·0 (5)	C5—C8—C7—C17	−160·9 (6)
C2—C3—C4—C5	36·4 (8)	C7—C8—C1—C2	−164·1 (5)
C3—O3—C14—O4	1·9 (6)	C7—C8—C5—O5	36·1 (5)
C3—O3—C14—C15	120·3 (6)	C8—C1—C11—O1	33·2 (9)
C3—O3—C14—C16	−115·8 (6)	C8—C1—C11—O2	−149·4 (5)
C3—C4—C5—C8	−25·5 (8)	C8—C5—O5—C6	−24·4 (6)
O3—C3—C4—O4	38·9 (6)	C8—C5—C4—O4	88·5 (6)
C4—O4—C14—C15	−93·6 (6)	C8—C7—C6—O5	22·0 (7)
C4—O4—C14—C16	142·7 (6)		

Atomic parameters for isomers *A* and *B* are given in Table 1, selected bond distances and angles in Tables 2 and 3.* Figs. 1 and 2 show thermal-ellipsoid plots with the atom numbering for isomers *A* and *B*, respectively.

Related literature. The synthesis of butyrolactones from a radical-mediated intramolecular cyclization of a chloroester and an olefin has until recently been a preparatively unexplored reaction, see Giese (1986), Surzur & Bertrand (1988), Curran (1988) and Hanessian, Bennani & Di Fabio (1990).

* Lists of structure factors, anisotropic thermal parameters, H-atom coordinates, distances and angles involving the H atoms and a stereoview of the unit cell for both isomers have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52339 (21 pp.). Copies may be obtained through the Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. *Bond angles* (Å), *bond angles and torsion angles* (°) *with their e.s.d.'s for B*, $C_{14}H_{20}O_6$

C1—C2	1·524 (4)	C6—O5	1·347 (4)
C1—C8	1·541 (4)	C6—O6	1·201 (5)
C1—C11	1·507 (4)	C7—C8	1·546 (5)
C2—C3	1·514 (4)	C7—C17	1·532 (6)
C3—C4	1·553 (4)	C11—O1	1·207 (3)
C3—O3	1·440 (5)	C11—O2	1·346 (3)
C4—C5	1·517 (4)	C12—O2	1·442 (6)
C4—O4	1·422 (5)	C14—C15	1·494 (6)
C5—C8	1·552 (4)	C14—C16	1·531 (5)
C5—O5	1·452 (5)	C14—O3	1·416 (3)
C6—C7	1·498 (5)	C14—O4	1·427 (4)
C2—C1—C8	111·5 (2)	C8—C7—C17	120·6 (3)
C2—C1—C11	113·6 (2)	C1—C8—C5	110·8 (2)
C8—C1—C11	114·5 (2)	C1—C8—C7	118·7 (3)
C1—C2—C3	109·3 (2)	C5—C8—C7	101·9 (2)
C2—C3—C4	114·7 (2)	C1—C11—O1	126·1 (3)
C2—C3—O3	108·2 (2)	C1—C11—O2	110·6 (3)
C4—C3—O3	102·9 (2)	O1—C11—O2	123·3 (3)
C3—C4—C5	115·5 (3)	C15—C14—C16	113·7 (3)
C3—C4—O4	104·3 (2)	C15—C14—O3	109·0 (3)
C5—C4—O4	108·9 (3)	C15—C14—O4	109·2 (3)
C4—C5—C8	118·5 (3)	C16—C14—O3	109·4 (3)
C4—C5—O5	104·5 (2)	C16—C14—O4	111·1 (3)
C8—C5—O5	106·5 (2)	O3—C14—O4	103·9 (3)
C7—C6—O5	110·4 (3)	C11—O2—C12	116·2 (3)
C7—C6—O6	128·9 (3)	C3—O3—C14	108·6 (2)
O5—C6—O6	120·6 (3)	C4—O4—C14	105·9 (2)
C6—C7—C8	105·4 (3)	C5—O5—C6	111·7 (3)
C6—C7—C17	110·7 (3)		
C1—C2—C3—O3	−74·9 (3)	C4—C5—C8—C1	9·5 (4)
C1—C2—C3—C4	39·4 (3)	C4—C5—C8—C7	136·7 (3)
C1—C8—C5—O5	−107·8 (3)	C5—C8—C1—C11	173·9 (3)
C1—C8—C7—C17	−23·5 (5)	C5—O5—C6—C7	−0·3 (4)
C1—C11—O2—C1	173·8 (3)	C5—C8—C1—C2	43·2 (3)
C2—C3—C4—C5	11·5 (4)	C5—C8—C7—C17	−145·3 (3)
C3—O3—C14—O4	−33·1 (3)	C7—C8—C1—C2	−74·0 (3)
C3—O3—C14—C15	−149·4 (3)	C7—C8—C5—O5	19·4 (3)
C3—O3—C14—C16	85·6 (3)	C8—C1—C11—O1	−140·4 (3)
C3—C2—C1—C11	159·3 (3)	C8—C1—C11—O2	42·2 (3)
C3—C4—C5—C8	−37·6 (4)	C8—C5—O5—C6	−12·7 (3)
O3—C3—C4—O4	9·4 (3)	C8—C5—C4—O4	79·2 (3)
C4—O4—C14—C15	155·3 (3)	C8—C7—C6—O5	13·1 (4)
C4—O4—C14—C16	−78·4 (3)		

We thank 'Le Ministère de l'Education du Québec' for financial support and Professor A. L. Beauchamp for assistance in the collection of data and help in resolution of the structure.

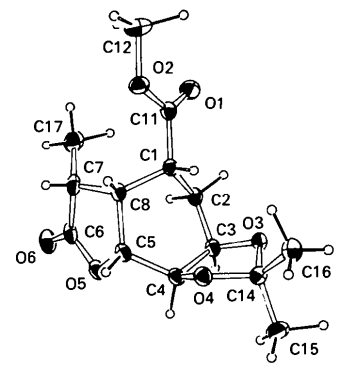

Fig. 2. An *ORTEP* diagram of isomer *B* with the H atoms and the atomic numbering. Ellipsoids represent 30% probability.

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Acta Cryst. (1990). **C46**, 939–941

Intramolecular Free-Radical Ring Closures. III. Structure of a Chiral δ-Lactone*

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(*Received* 12 *July* 1989; *accepted* 17 *October* 1989)

Abstract. $C_{26}H_{34}O_5Si$, orthorhombic, $M_r = 454{\cdot}64$, $P2_12_12_1$, $a = 7{\cdot}425\,(3)$, $b = 10{\cdot}491\,(4)$, $c = 32{\cdot}882\,(12)$ Å, $V = 2561{\cdot}4$ Å^3, $Z = 4$, $D_x = 1{\cdot}179$ Mg m^{-3}, $\lambda(\text{Cu } K\alpha) = 1{\cdot}54178$ Å, $\mu = 1{\cdot}05$ mm^{-1}, $F(000) = 976$, $T = 220$ K, $R = 0{\cdot}052$ for 2075 observed reflections. A triphenyltin hydride-mediated intramolecular cyclization of a chloropropionate ester and an α,β-unsaturated ester gave a crystalline lactone. Although spectroscopic assignment based on ^{1}H NMR and nuclear Overhauser

* Methyl (3*S*,4*R*,6*S*)-6-(*tert*-butyldiphenylsilyloxymethyl)-3-methyl-2-oxo-3,4,5,6-tetrahydro-4-pyranacetate.

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0108-2701/90/050939-03$03.00