Mikes, F., Boshart, G. & Gil-av, E. (1976). *J. Chromatogr.* **122**, 205–221.
Sakurai, T. & Kobayashi, K. (1978). *Rikagaku Kenkyusho Hokoku*, **55**, 69–77.
Schaffrin, R. M. & Trotter, J. (1970). *J. Chem. Soc. A*, pp. 1561–1565.
Yamada, K., Tanaka, H., Nakagawa, H., Ogashiwa, S. & Kawazura, H. (1982). *Bull. Chem. Soc. Jpn*, **55**, 500–504.

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The Structures of 9-Hydroxy-10-methyl-*cis*-2-decalone,* $C_{11}H_{18}O_2$ (I), and 11-Oxatricyclo[4.4.3.$0^{1,6}$]tridecane-3,12-dione, $C_{12}H_{16}O_3$ (II)

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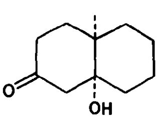
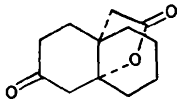
Abstract. (I): $M_r = 182{\cdot}3$, monoclinic, $P2_1/a$, $a = 13{\cdot}643\,(4)$, $b = 5{\cdot}989\,(1)$, $c = 12{\cdot}265\,(3)$ Å, $\beta = 93{\cdot}62\,(2)°$, $U = 1000{\cdot}2$ Å^3, $Z = 4$, D_m (flotation) = 1·20, $D_x = 1{\cdot}210$ g cm^{-3}, μ(Cu $K\alpha$) = 6·52 cm^{-1}, $F(000) = 400$, room temperature, final $R = 0{\cdot}037$ over 1181 reflections. (II): $M_r = 208{\cdot}3$, monoclinic, $P2_1$, $a = 7{\cdot}565\,(2)$, $b = 10{\cdot}585\,(3)$, $c = 7{\cdot}422\,(2)$ Å, $\beta = 117{\cdot}62\,(2)°$, $U = 527$ Å^3, $Z = 2$, D_m (flotation) = 1·30, $D_x = 1{\cdot}312$ g cm^{-3}, μ(Cu $K\alpha$) = 7·70 cm^{-1}, $F(000) = 224$, room temperature, final $R = 0{\cdot}033$ over 750 reflections. Both molecules adopt chair–chair conformations in which the oxygen ring substituent is axial in the ring containing the carbonyl group. The presence of a γ-lactone which incorporates the atoms of the ring junction significantly flattens the entire decalone system of (II). All intermolecular separations for (I) and (II) are normal van der Waals contacts except for an O···O hydrogen bond of 2·837 (2) Å in (I).

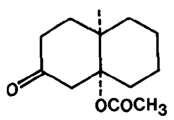
Introduction. In connection with a study of the relative β-elimination reactivities of 11-oxatricyclo[4.4.3.$0^{1,6}$]-tridecane-3,12-dione (II) and 9-acetoxy-10-methyl-*cis*-2-decalone (III) (Mayer, Spencer & Onan, 1984), we wished to determine if the greatly enhanced reactivity of (II) is associated with an elongated C(sp^3)—O bond length, as previously found to be the case in the hydrolysis of a series of acetals (Jones & Kirby, 1979). Direct comparison of the C(sp^3)—O bond lengths of these two compounds proved impossible because suitable crystals of (III) could not be obtained. Because 9-hydroxy-10-methyl-*cis*-2-decalone (I), 9-hydroxy-10-methyl-*trans*-2-decalone, and 9-acetoxy-10-methyl-*trans*-2-decalone all crystallize well, it was decided to use the observed C(sp^3)—O bond lengths for these three compounds to estimate the C(sp^3)—O bond length for (III). Here we report the structures of the *cis*-fused lactone (II) and β-ketol (I).



(I)



(II)



(III)

Experimental. Lath-like crystals of (I) were grown from isopentane, chunky crystals of (II) were grown from ether, crystal dimensions *ca* 0·12 × 0·20 × 0·40 mm (I) and 0·20 × 0·20 × 0·32 mm (II); Syntex $P2_1$ automated diffractometer, Cu $K\alpha$ radiation, cell dimensions for each by least-squares refinement of 2θ values of 15 reflections with $60 \le 2\theta \le 80°$, $\theta/2\theta$ scans, variable-speed scan, $4 \le 2\theta \le 115°$, 1591 (I) and 832 (II) independent reflections collected, 1181 with $I > 2\sigma(I)$ considered observed for (I), 750 for (II); two check reflections measured every 48 reflections showed a maximum variation in intensity of 6% for (I), 4% for (II); Lorentz–polarization and empirical absorption corrections applied, scattering factors for C and O from Cromer & Waber (1965), for H from Stewart, Davidson & Simpson (1965); structures solved by direct methods [*MULTAN*80 (Germain, Main & Woolfson, 1971)], full-matrix least-squares refinement minimizing $\sum w\,||F_o| - |F_c||^2$ with weights $w^{1/2} = 1$ for $|F_o| \le 7{\cdot}0$ and $w^{1/2} = 7{\cdot}0/|F_o|$ for $|F_o| > 7{\cdot}0$ (program based on *FMLS* by P. K. Gantzel, R. A. Sparks and K. N. Trueblood, modified by A. T. McPhail); all H atoms located in difference syntheses,

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* 8a-Hydroxy-4a-methyl-*cis*-decahydro-2-naphthalenone.

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anisotropic temperature factors for non-hydrogen atoms, isotropic factors for H atoms; inspection of F_o *vs* F_c values for low-angle reflections of high intensity indicated secondary extinction in (II) and the 020 reflection was removed from this data set; convergence for (I) at $R = 0{\cdot}037$, $wR = 0{\cdot}038$, $S = 0{\cdot}314$, $\Delta_{\text{mean}}/\sigma_{\text{max}} = 0{\cdot}070$ for non-hydrogen atoms, maximum $\Delta\rho$ peak 0·15 e Å^{-3}; convergence for (II) at $R = 0{\cdot}033$, $wR = 0{\cdot}033$, $S = 0{\cdot}245$, $\Delta_{\text{mean}}/\sigma_{\text{max}} = 0{\cdot}015$ for non-hydrogen atoms, maximum $\Delta\rho$ peak 0·10 e Å^{-3};[*] *ORTEP* (Johnson, 1965) was used for drawings of single molecules.

Discussion. Final atomic parameters for the non-hydrogen atoms of (I) and (II) are listed in Table 1. Views of the molecular conformations of these *cis*-fused molecules are shown in Figs. 1 and 2, each with the crystallographic numbering scheme employed. Bond lengths and angles are compared in Table 2.

(I) adopts a double-chair conformation. The mean endocyclic torsion angle for the cyclohexanone ring, 51·0 (21)°,[†] shows the ring to be flatter than the accepted norm for unsubstituted cyclohexanone (Bucourt, 1974). The greatest flattening occurs about C(3) which is flanked by torsion angles of 48·3 (2) and −48·6 (2)°. The mean torsion angle in the cyclohexane ring is a slightly flattened 54·5 (10)° (Buys & Geise, 1970). The transannular interactions involving the methyl and hydroxyl groups are not large enough to necessitate flattening at the ring junction but the C(9)—C(10) bond length is slightly longer than the mean C(sp^3)—C(sp^3) length [1·552 (2) *vs* 1·535 Å, respectively]. In the molecule 9-carboxy-*cis*-2-decalone (IV) (Chadwick & Dunitz, 1979), the carboxyl group is oriented in such a manner as to engender transannular interactions which substantially flatten the cyclohexanone ring (mean endocyclic torsion angle 47·1°). However, the bond lengths and angles are quite similar to those in (I), except that, as expected, the mean valency angle in the cyclohexanone ring of (IV) is slightly larger than that in (I). The parameters defining (I) are very similar to those describing 9-hydroxy-10-methyl-*trans*-2-decalone (V) (Onan, Mayer & Spencer, 1984). The rings in the latter are slightly less symmetrical but the bond lengths and angles are nearly identical.

Table 1. *Fractional atomic coordinates of the non-hydrogen atoms* (×10^4) *and equivalent isotropic temperature factors* (Å^2) *for* (I) *and* (II), *with estimated standard deviations in parentheses*

$$U_{\text{eq}} = \tfrac{1}{3}(U_{11} + U_{22} + U_{33} + 2U_{13}\cos\beta).$$

Compound I

	x	y	z	$U_{\text{eq}}(\times 10^4)$
C(1)	4610 (1)	2259 (3)	3703 (1)	401
C(2)	3893 (1)	2808 (3)	4536 (1)	412
C(3)	2888 (1)	3458 (3)	4087 (2)	475
C(4)	2490 (1)	1815 (3)	3215 (2)	446
C(5)	3344 (1)	3269 (3)	1586 (2)	471
C(6)	4086 (2)	2861 (3)	729 (2)	599
C(7)	5071 (2)	2110 (3)	1258 (2)	586
C(8)	4954 (1)	104 (3)	2008 (2)	476
C(9)	4204 (1)	513 (3)	2866 (1)	358
C(10)	3194 (1)	1236 (3)	2328 (1)	374
O(11)	4117 (1)	2769 (3)	5515 (1)	555
O(12)	4046 (1)	−1515 (2)	3452 (1)	447
C(15)	2714 (1)	−670 (3)	1649 (2)	526

Compound II

	x	y	z	$U_{\text{eq}}(\times 10^3)$
C(1)	6140 (6)	1665 (5)	−916 (7)	35
C(2)	5073 (6)	2478	−2772 (7)	37
C(3)	5048 (7)	3864 (6)	−2383 (7)	44
C(4)	7164 (6)	4340 (6)	−1034 (7)	52
C(5)	7644 (7)	4003 (6)	2544 (7)	52
C(6)	8515 (8)	3206 (7)	4466 (7)	64
C(7)	8115 (8)	1792 (7)	3962 (7)	62
C(8)	9000 (6)	1382 (5)	2582 (7)	48
C(9)	8176 (5)	2155 (5)	617 (6)	45
C(10)	8328 (5)	3607 (5)	978 (6)	53
O(11)	4228 (6)	2003 (6)	−4472 (6)	79
O(12)	9533 (4)	1952 (4)	−296 (4)	42
C(13)	10963 (6)	2855 (6)	384 (7)	45
O(14)	12303 (4)	2833 (5)	−66 (5)	66
C(15)	10555 (6)	3803 (5)	1656 (7)	43

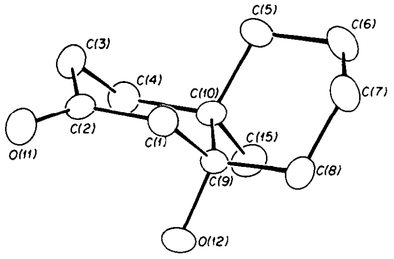

Fig. 1. View of 9-hydroxy-10-methyl-*cis*-2-decalone with the atom-numbering scheme.

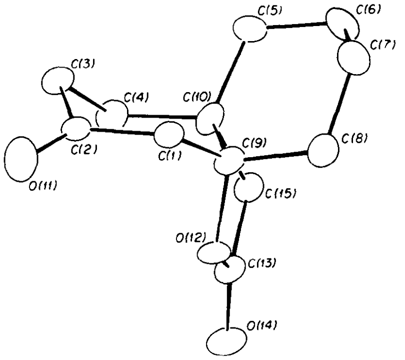

Fig. 2. View of 11-oxatricyclo[4.4.3.0^{1,6}]tridecane-3,12-dione with the atom-numbering scheme.

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[*] Lists of structure factors, anisotropic thermal parameters and hydrogen-atom parameters and a complete table of torsion angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39228 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

[†] Standard deviations quoted for means are sample standard deviations, estimated standard deviations for individual torsion angles in (I) are *ca* 0·2° and in (II), *ca* 0·4°.

Table 2. *Interatomic distances* (Å) *and valency angles* (°) *for* (I) *and* (II), *with estimated standard deviations in parentheses*

	(I)	(II)
C(1)–C(2)	1·495 (2)	1·505 (7)
C(1)–C(9)	1·543 (2)	1·520 (6)
C(2)–C(3)	1·497 (3)	1·498 (6)
C(2)–O(11)	1·220 (2)	1·228 (7)
C(3)–C(4)	1·527 (3)	1·527 (7)
C(4)–C(10)	1·537 (3)	1·547 (7)
C(5)–C(6)	1·524 (3)	1·521 (8)
C(5)–C(10)	1·541 (3)	1·535 (7)
C(6)–C(7)	1·524 (3)	1·540 (10)
C(7)–C(8)	1·528 (3)	1·526 (8)
C(8)–C(9)	1·533 (3)	1·531 (7)
C(9)–C(10)	1·552 (2)	1·557 (7)
C(9)–O(12)	1·434 (2)	1·486 (5)
C(10)–C(15)	1·536 (3)	1·532 (6)
O(12)–C(13)		1·355 (6)
C(13)–O(14)		1·206 (5)
C(13)–C(15)		1·506 (7)
C(2)–C(1)–C(9)	112·4 (1)	114·7 (4)
C(1)–C(2)–C(3)	115·4 (1)	115·7 (4)
C(1)–C(2)–O(11)	122·3 (2)	120·7 (3)
C(3)–C(2)–O(11)	122·2 (2)	123·6 (5)
C(2)–C(3)–C(4)	111·6 (2)	110·3 (5)
C(3)–C(4)–C(10)	115·5 (1)	115·0 (4)
C(6)–C(5)–C(10)	113·5 (2)	114·1 (5)
C(5)–C(6)–C(7)	111·1 (2)	111·2 (4)
C(6)–C(7)–C(8)	111·5 (2)	110·0 (5)
C(7)–C(8)–C(9)	112·8 (2)	112·2 (4)
C(1)–C(9)–C(8)	109·7 (1)	110·8 (4)
C(1)–C(9)–C(10)	111·5 (1)	115·8 (4)
C(1)–C(9)–O(12)	107·4 (1)	106·5 (3)
C(8)–C(9)–C(10)	111·5 (1)	113·5 (4)
C(8)–C(9)–O(12)	109·7 (1)	107·2 (3)
C(10)–C(9)–O(12)	106·9 (1)	102·1 (3)
C(4)–C(10)–C(5)	110·6 (1)	110·7 (4)
C(4)–C(10)–C(9)	109·9 (1)	111·5 (4)
C(4)–C(10)–C(15)	106·7 (1)	107·2 (4)
C(5)–C(10)–C(9)	109·0 (1)	112·1 (4)
C(5)–C(10)–C(15)	109·5 (1)	114·8 (4)
C(9)–C(10)–C(15)	111·1 (1)	99·9 (3)
C(9)–O(12)–C(13)		109·2 (4)
O(12)–C(13)–O(14)		120·7 (5)
O(12)–C(13)–C(15)		110·1 (4)
O(14)–C(13)–C(15)		129·1 (5)
C(10)–C(15)–C(13)		102·6 (4)

Formation of a *γ*-lactone across the 9,10 positions of a *cis*-fused decalone system effects a closing of the torsion angle analogous to the O(12)–C(9)–C(10)–C(15) angle. From a comparison of Newman projections about the C(9)–C(10) bonds in (I) and in (II) (Fig. 3) it is also apparent that each ring in the decalone system is significantly flattened; for (II) the mean endocyclic torsion angle in the cyclohexanone ring is 46·9 (56)° and that in the cyclohexane ring is 52·3 (52)°. The cyclohexanone ring in (II) is very symmetrical with the C_s axis running through C(3) and C(9). In contrast to what is seen for (I) the manifestation of flattening is greatest at the C(9) end (dihedral angles *ca* 40°) and is almost non-existent at the C(3) end (dihedral angles *ca* 53°). The cyclohexane ring is also quite symmetrical with the C_s axis running through C(7) and C(10). The flattening again occurs at the ring junction but there is ring puckering at the C(7) end of the chair (dihedral angles *ca* 57·7°). This conformation allows reasonable H···H transannular interactions involving H atoms on carbons 1, 5 and 7 (> 2·35 Å) while still keeping H(6*B*) 2·27 Å from H(15*A*).

The butyrolactone moiety adopts the usual envelope conformation with the *β* carbon lying out of the plane of the other ring atoms (Jeffrey, Rosenstein & Vlasse, 1967; Harlow & Simonsen, 1976; Jones & Karle, 1974); in particular, C(10) lies 0·59 Å out of the C—O—(CO)—C plane. The *γ*-lactone is more puckered than the less substituted 4-benzyl-4-phenyl-1,4-butyrolactone (Harlow & Simonsen, 1976) [sum of endocyclic dihedral angles 127·4 (4) and 94·6°, respectively] but adopts a conformation strikingly similar to that adopted by the tetrahydrofuran-like ring in 19*R*-methoxy-5,19-methyleneoxido-17*β*-acetoxy-5*β*-androstan-3-one (Jones & Karle, 1974). In this latter case, a five-membered oxygen heterocycle is formed across the ring junction of a *cis*-2-decalone-type system and in it, too, C(10) lies 0·60 Å out of the plane of the C—C—O—C plane.

There are two possible chair–chair conformations accessible to (I) and (II), these being related by ring inversion. In both (I) and (II) the conformation which is observed is the one in which O(12) is axial to the cyclohexanone ring and the C(9)—C(1)—C(2)—O(11) torsion angle is positive [C(9)—C(1)—C(2)—O(11) 129·3 (2)° (I), 135·8 (5)° (II)]. The adoption of this conformation places the C(9)—O(12) bond in a *trans*-diaxial orientation relative to the axial C(1) proton. This is the orientation which would be required if (II) were to undergo a concerted elimination to 2-(2′-oxo-1′,9′-octalin-10-yl)ethanoic acid as recently proposed (Mayer, Spencer & Onan, 1984). The solid-state conformation of (II) therefore lends additional support to the proposal of an *E*2 mechanism.

The C(9)—O(12) bond lengths in (I) and (V) are very similar [1·434 (2) and 1·439 (3)°, respectively] and both are much shorter than that for 9-acetoxy-10-methyl-*trans*-2-decalone [1·478 (3) Å]. This length, in

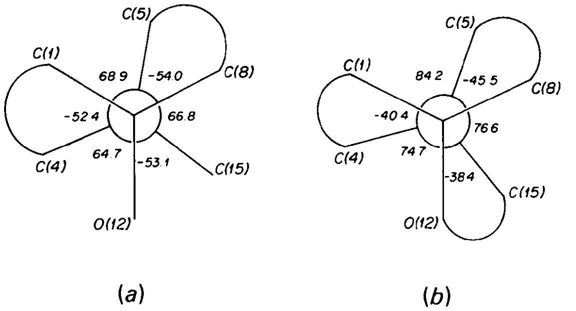

Fig. 3. Newman projections down the C(9)—C(10) bond for (*a*) (I) and (*b*) (II). Estimted standard deviations are *ca* 0·2° in (I) and *ca* 0·4° in (II).

turn, is slightly shorter (though not significantly) than that in (II) [1·486 (5) Å]. Allen & Kirby (unpublished results) have determined that the average length for a C(sp^3)—O bond of the type R_3C—OC(=O)— is 1·473 (2) Å so it can only be stated that the C(sp^3)—O length in (II) may be sufficiently elongated to be consistent with the reactivity of (II).

Molecule (I) packs as hydrogen-bonded dimers around centers of symmetry with O(11) to O(12) separations of 2·837 (2) Å (the molecule at x,y,z is hydrogen bonded to the molecule at $1-x$, $-y$, $1-z$). All other intermolecular distances in (I) and all in (II) correspond to normal van der Waals contacts.

References

Bucourt, R. (1974). *Topics in Stereochemistry*, edited by E. L. Eliel & N. L. Allinger, pp. 159–224. New York: John Wiley.

Buys, H. R. & Geise, H. J. (1970). *Tetrahedron Lett.* pp. 2991–2992.

Chadwick, D. J. & Dunitz, J. D. (1979). *J. Chem. Soc. Perkin Trans.* 2, pp. 276–284.

Cromer, D. T. & Waber, J. T. (1965). *Acta Cryst.* **18**, 104–109.

Germain, G., Main, P. & Woolfson, M. M. (1971). *Acta Cryst.* A**27**, 368–376.

Harlow, R. L. & Simonsen, S. H. (1976). *Acta Cryst.* B**32**, 2137–2144.

Jeffrey, G. A., Rosenstein, R. D. & Vlasse, M. (1967). *Acta Cryst.* **22**, 725–733.

Johnson, C. K. (1965). *ORTEP*. Report ORNL-3974. Oak Ridge National Laboratory, Tennessee.

Jones, D. S. & Karle, I. L. (1974). *Acta Cryst.* B**30**, 624–627.

Jones, P. G. & Kirby, A. J. (1979). *J. Chem. Soc. Chem. Commun.* pp. 288–289.

Mayer, B. J., Spencer, T. A. & Onan, K. D. (1984). *J. Am. Chem. Soc.* In the press.

Onan, K. D., Mayer, B. J. & Spencer, T. A. (1984). *Acta Cryst.* C**40**, 1044–1047.

Stewart, R. F., Davidson, E. R. & Simpson, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

Acta Cryst. (1984). C**40**, 1044–1047

The Structures of 9-Hydroxy-10-methyl-*trans*-2-decalone, $C_{11}H_{18}O_2$ (I), and 9-Acetoxy-10-methyl-*trans*-2-decalone, $C_{13}H_{20}O_3$ (II)*

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Abstract. (I): $M_r = 182·3$, monoclinic, $P2_1/c$, $a = 12·325$ (1), $b = 6·357$ (1), $c = 14·400$ (1) Å, $\beta = 116·70$ (8)°, $U = 1008$ Å^3, $Z = 4$, D_m(flotation) = 1·19, $D_x = 1·201$ g cm^{-3}, μ(Cu $K\alpha$) = 6·48 cm^{-1}, $F(000) = 400$, room temperature, final $R = 0·059$ for 1199 reflections. (II): $M_r = 224·3$, monoclinic, $P2_1/n$, $a = 7·822$ (1), $b = 10·731$ (1), $c = 15·052$ (2) Å, $\beta = 101·02$ (1)°, $U = 1240$ Å^3, $Z = 4$, D_m(flotation) = 1·19, $D_x = 1·201$ g cm^{-3}, μ(Cu $K\alpha$) = 6·85 cm^{-1}, $F(000) = 488$, room temperature, final $R = 0·069$ over 1424 reflections. Both molecules adopt relatively undistorted chair–chair conformations. In (II) the ester carbonyl group is synplanar to the C(sp^3)—O bond. All intermolecular separations for (I) and (II) appear to be normal van der Waals contacts apart from a weak O···O hydrogen bond of 2·938 (3) Å in (I).

Introduction. In the preceding communication (Onan, Mayer & Spencer, 1984) the structures of two *cis* decalones were described. This communication reports the structures of two *trans* decalones, 9-hydroxy-10-methyl-*trans*-2-decalone (I) and 9-acetoxy-10-methyl-*trans*-2-decalone (II), which were needed for comparison with the structures of the aforementioned *cis* decalones and for a projected comparison with the structures of *trans* decalones bearing an additional axial substituent at C(6). The latter compounds are being used in studies of intramolecular α-proton transfer (Jacobs, Nelson & Spencer, 1980; Gula, Vitale & Spencer, unpublished results).

Experimental. Pastille-shaped crystals of (I) were obtained by slow evaporation from a solution of ether and methanol, chunky crystals of (II) were grown from ether, crystal dimensions *ca* 0·16 × 0·24 × 0·40 mm (I) and 0·20 × 0·20 × 0·25 mm (II); Syntex $P2_1$ automated diffractometer, Cu $K\alpha$ radiation, cell

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* 8a-Hydroxy-4a-methyl-*trans*-decahydro-2-naphthalenone and 4a-methyl-2-oxo-*trans*-decahydro-8a-naphthyl acetate, respectively.

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