Fig. 1. Atomic numbering of the molecule. The thermal ellipsoids are at 50% probability for O and C, but at 10% probability for H.
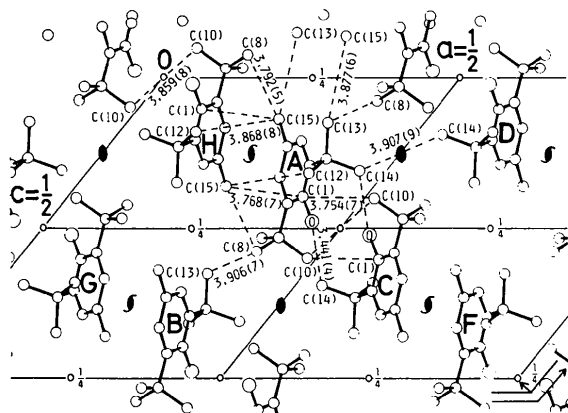

Fig. 2. The crystal structure projected along the *b* axis. Broken lines show the van der Waals contacts of atoms (distances in Å). Symmetry code: (*A*) *x,y,z*; (*B*) $x,-y,\frac{1}{2}+z$,; (*C*) $-x,-y,-z$; (*D*) $-x,y,-\frac{1}{2}-z$; (*E*) $\frac{1}{2}+x, \frac{1}{2}+y, z$; (*F*) $\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$; (*G*) $\frac{1}{2}-x, \frac{1}{2}-y, -z$; (*H*) $\frac{1}{2}-x, \frac{1}{2}+y, -\frac{1}{2}-z$.

situated so that one of the methyl groups is near the benzene plane and the other two face the hydroxy group. A few degrees of rotation are allowed about the bond between a C atom in a benzene ring and the central atom of a *tert*-butyl group. The nearest-neighbor distance between the O atom and the H atoms of *tert*-butyl groups is $O\cdots H(C12,2) = 2\cdot30$ (4) Å. Some of the H coordinates in the Maze-Baudet result are not acceptable. The present analysis gives more reasonable positions. The H atoms belonging to the *tert*-butyl groups are all in $\pm$ *gauche* or *trans* positions. One of the H atoms [H(C15,2)] of the methyl group is near the plane of the benzene ring. The benzene ring is planar within 0·015 (5) Å, and O and C(15) are slightly above (*ca* 0·05 Å) and C(7) and C(11) are slightly below the benzene plane. The crystal structure projected along the *b* axis is shown in Fig. 2. Molecules are arranged in a plane parallel to (101) with normal van der Waals distances.

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Structure of (2R,3S)-3,5-Dimethyl-2-{(S)-1-[(3S,5R,6R)-3,5-dimethyl-2-oxotetrahydro-2H-pyran-6-yl]ethyl}-2,3-dihydro-4-pyranone, $C_{16}H_{24}O_4$

BY RICHARD D. ADAMS AND BRIGITTE E. SEGMULLER

Department of Chemistry, Yale University, New Haven, CT 06511, USA

Abstract. $M_r = 280\cdot4$, monoclinic, $P2_1/n$, $a = 10\cdot191$ (3), $b = 7\cdot621$ (7), $c = 20\cdot354$ (6) Å, $\beta = 94\cdot47$ (2)°, $V = 1576$ (2) Å³, $Z = 4$, $D_x = 1\cdot18$ g cm⁻³, $\lambda(\text{Mo }K\bar{\alpha}) = 0\cdot7107$ Å, $\mu = 0\cdot078$ mm⁻¹, F (000) = 608, $T = 298$ K. Final $R = 0\cdot042$ for 868 independent reflections. The tetrahydropyran-2-one ring has a chair conformation while the dihydropyran-4-one ring is in a twisted half-chair conformation.

Introduction. It has recently been discovered that Lewis acids will catalyze the cyclocondensation of aldehydes with siloxydienes (Danishefsky, Larson & Askin, 1982). The stereochemistry of the addition is dependent on the type of Lewis-acid catalyst. In the presence of zinc chloride the aldehyde (1) adds to the siloxydiene (2) to give the pyranone (3) in 43% yield. The stereochemistry of (3) was established by a single-crystal X-ray diffraction analysis. The dihydropyran-4-one ring in (3) can be opened (Danishefsky *et al.*, 1982) to yield one of the key intermediates in the synthesis of 6-deoxyerythronolide B (Masamune, Hirama, Mori, Ali & Garvey, 1981).

(1)

(2)

(3)

Experimental. Colorless elongated prisms (from hexane), $0.10 \times 0.15 \times 0.55$ mm; Enraf–Nonius CAD-4 diffractometer, graphite-monochromated Mo $K\alpha$; 2498 $hk\pm l$ with $\theta < 23°$; 868 independent, $F^2 > 2\sigma(F^2)$; Lp correction, absorption ignored; direct methods [Enraf–Nonius (1979) *SDP*; *MULTAN* (Main *et al.*, 1980)]; anisotropic full matrix based on F, H (calculated) not refined; final $R = 0.042$, $wR = 0.034$, $S = 1.87$, $w = 1/\sigma^2$; LS shift/error $= 0.00$; Digital Equipment Corp. PDP 11/45 computer.

Discussion. Atomic coordinates and equivalent isotropic thermal parameters are given in Table 1,* bond distances and angles in Table 2.

The molecular structure of the title compound (3) is shown in Fig. 1, and a perspective view of the unit cell in Fig. 2. The tetrahydropyran-2-one ring adopts a chair conformation while the dihydropyran-4-one has a half-chair conformation which is twisted toward di-planar sofa conformation (Valente, Santarsiero & Schomaker, 1979). Atoms C(7) and C(8) lie on opposite sides of the least-squares plane defined by O(3), C(9), C(10) and C(11) by 0.56 and 0.17 Å respectively.

The substituents on C(7) and C(8) contain a *cis-erythro* stereochemistry in pseudo-equatorial and axial positions, respectively. The C—C and C—O bond distances and angles compare favorably with those

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* Lists of structure-factor amplitudes, anisotropic thermal parameters, and H-atom coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38410 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Atomic coordinates* ($\times 10^4$) *and equivalent isotropic thermal parameters for the non-H atoms with e.s.d.'s in parentheses*

$$B_{eq} = \tfrac{4}{3} \sum_i \sum_j \beta_{ij} \mathbf{a}_i \cdot \mathbf{a}_j.$$

	x	y	z	$B_{eq}(\text{Å}^2)$
O(1)	2770 (3)	65 (4)	1667 (1)	4.50 (8)
O(2)	873 (2)	1463 (4)	1621 (1)	3.52 (7)
O(3)	−3207 (3)	874 (4)	1320 (1)	4.03 (8)
O(4)	−1714 (3)	−2158 (4)	−93 (1)	5.23 (9)
C(1)	2219 (4)	1476 (6)	1694 (2)	3.5 (1)
C(2)	2891 (4)	3201 (6)	1856 (2)	3.5 (1)
C(3)	2155 (4)	4779 (6)	1548 (2)	3.7 (1)
C(4)	714 (4)	4716 (6)	1691 (2)	3.3 (1)
C(5)	111 (4)	3033 (6)	1397 (2)	3.3 (1)
C(6)	−1311 (4)	2651 (5)	1533 (2)	3.2 (1)
C(7)	−1802 (4)	894 (6)	1242 (2)	3.3 (1)
C(8)	−1558 (4)	525 (6)	523 (2)	3.2 (1)
C(9)	−2161 (4)	−1223 (6)	329 (2)	3.6 (1)
C(10)	−3363 (4)	−1692 (6)	640 (2)	3.5 (1)
C(11)	−3839 (4)	−566 (6)	1066 (2)	4.0 (1)
C(12)	−4329 (4)	3135 (7)	1722 (2)	5.7 (1)
C(13)	−23 (5)	6340 (6)	1409 (2)	5.4 (1)
C(14)	−1534 (4)	2726 (6)	2269 (2)	5.0 (1)
C(15)	−2127 (5)	1925 (7)	40 (2)	5.2 (1)
C(16)	−4095 (5)	−3321 (7)	426 (2)	5.8 (1)

Table 2. *Bond distances* (Å) *and angles* (°)

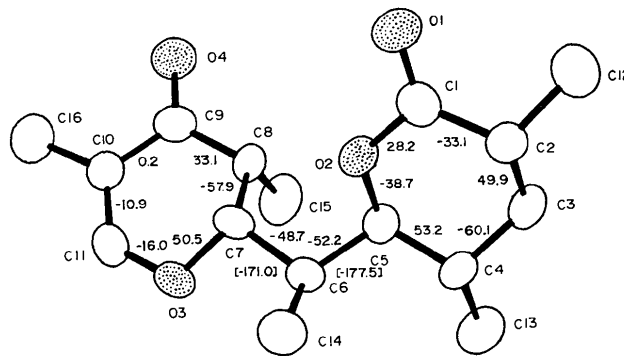|			
O(1)—C(1)	1.217 (4)	C(6)—C(7)	1.532 (4)
O(2)—C(1)	1.368 (4)	C(7)—C(8)	1.529 (4)
O(2)—C(5)	1.479 (4)	C(8)—C(9)	1.507 (5)
O(3)—C(7)	1.454 (4)	C(9)—C(10)	1.467 (5)
O(3)—C(11)	1.354 (4)	C(10)—C(11)	1.337 (5)
O(4)—C(9)	1.229 (4)	C(2)—C(12)	1.512 (5)
C(1)—C(2)	1.507 (5)	C(4)—C(13)	1.535 (5)
C(2)—C(3)	1.526 (5)	C(6)—C(14)	1.535 (4)
C(3)—C(4)	1.519 (4)	C(8)—C(15)	1.533 (5)
C(4)—C(5)	1.525 (4)	C(10)—C(16)	1.496 (5)
C(5)—C(6)	1.525 (5)		
O(1)—C(1)—C(2)	125.2 (4)	O(2)—C(5)—C(6)	105.9 (3)
O(1)—C(1)—O(2)	116.9 (4)	C(5)—C(6)—C(7)	112.5 (3)
C(1)—O(2)—C(5)	121.7 (3)	C(5)—C(6)—C(14)	112.6 (3)
C(1)—O(2)—C(3)	113.4 (3)	C(7)—C(6)—C(14)	110.0 (3)
C(1)—C(2)—C(12)	111.2 (4)	C(6)—C(7)—O(3)	105.2 (3)
C(3)—C(2)—C(12)	113.8 (4)	C(6)—C(7)—C(8)	117.3 (3)
C(7)—O(3)—C(11)	114.2 (3)	O(3)—C(7)—C(8)	109.8 (3)
O(4)—C(9)—C(8)	122.0 (4)	C(7)—C(8)—C(9)	108.7 (3)
O(4)—C(9)—C(10)	121.9 (4)	C(7)—C(8)—C(15)	113.8 (3)
O(2)—C(1)—C(2)	117.7 (4)	C(9)—C(8)—C(15)	108.7 (3)
C(2)—C(3)—C(4)	110.4 (3)	C(8)—C(9)—C(10)	116.0 (4)
C(3)—C(4)—C(5)	108.6 (3)	C(9)—C(10)—C(11)	118.8 (4)
C(3)—C(4)—C(13)	110.8 (4)	C(9)—C(10)—C(16)	119.3 (4)
C(5)—C(4)—C(13)	111.2 (3)	C(11)—C(10)—C(16)	121.6 (4)
C(4)—C(5)—O(2)	111.9 (3)	O(3)—C(11)—C(10)	125.6 (4)
C(4)—C(5)—C(6)	116.7 (3)		

Fig. 1. A perspective *ORTEP* drawing (Johnson, 1976) of (3) with 50% probability thermal-motion ellipsoids, and selected torsion angles for *cis* and [*trans*] related atoms in degrees.
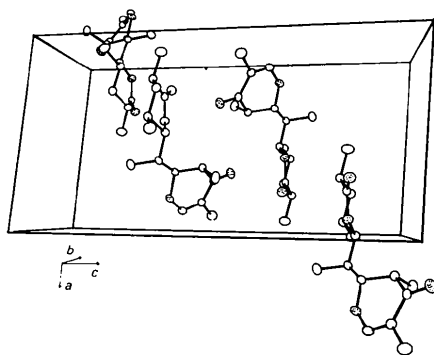
$C_{16}H_{24}O_4$

Fig. 2. A perspective view of the unit cell of (3).

found in 2,6-dimethylpyran-4-one (Brown, Norment & Levy, 1957).

The shortest intermolecular contact is between O(3) and C(12) at 3·203 (5) Å.

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Acta Cryst. (1983). C**39**, 782–784

7-Hydroxy-1,2,3,5,6,8-hexamethyltetracyclo[4.2.1.1^{2,5}.0^{3,7}]dec-4-yl Methanesulphonate, $C_{17}H_{28}O_4S$
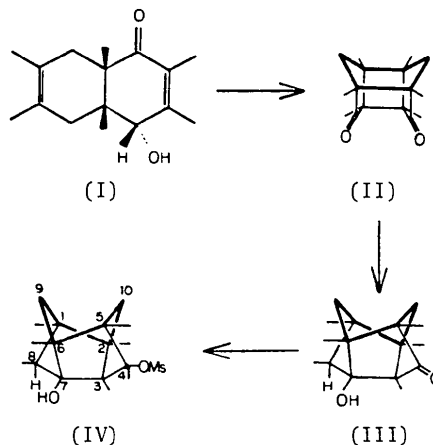
By ANTHONY S. SECCO AND JAMES TROTTER

Department of Chemistry, University of British Columbia, Vancouver, BC, Canada V6T 1Y6

Abstract. $M_r = 328·48$, $F(000) = 712$, monoclinic, $P2_1/c$, $a = 9·246$ (2), $b = 10·938$ (1), $c = 17·335$ (4) Å, $\beta = 102·11$ (1)°, $V = 1714·1$ (6) Å^3, $Z = 4$, $D_x = 1·273$ g cm^{-3}, $\mu(\text{Mo } K\alpha) = 1·94$ cm^{-1}, $\lambda = 0·71073$ Å, $T = 294$ K, $R = 0·042$ for 2997 reflexions. The ring skeleton has approximate 2 (C_2) symmetry, with a twist-boat six-membered ring and envelope five-membered rings. Steric strain is evident in an intramolecular H···H distance of 2·03 Å, long C—C bonds (1·584–1·614 Å), and deviations from tetrahedral angles. Molecules are linked by an O—H···O hydrogen bond, H···O = 2·07 Å, O—H···O = 177°.

Introduction. Photoirradiation of the hexamethyltetrahydronaphthoquinol (I), followed by oxidation of the resulting photoproduct, produces the diketone (II) (Appel, Greenhough, Scheffer, Trotter & Walsh, 1980). An attempted intramolecular pinacolization of (II) resulted in formation of an unexpected product (Herbert, Scheffer, Secco & Trotter, 1981); crystals suitable for X-ray analysis could not be obtained. Sodium borohydride reduction of the product, followed by treatment of one of the resultant diols with methanesulphonyl chloride yielded a crystalline meth-

anesulphonate. Crystal structure analysis of this derivative now shows it to have structure (IV), containing a tetracyclo[4.2.1.1^{2,5}.0^{3,7}]decane ring system; the unexpected precursor is therefore (III).

(I) (II)

(IV) (III)

Experimental. After several attempts at recrystallization of (IV), a crystal of fair quality was obtained from a hexane–acetone solution; 0·45 × 0·43 × 1·03 mm, not