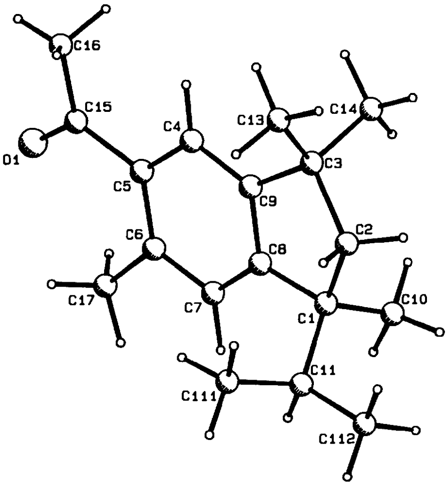

Fig. 2. The numbering system of 6-acetyl-3-isopropyl-1,1,3,5-tetramethylindan (II). The H atoms are shown but not labelled.

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trans-4-*tert*-Butyl-3-hydroxy-5-cyclohepten-1-one (2) and *trans*-6-*tert*-Butyl-3-hydroxy-2,7-dimethyl-4-cyclohepten-1-one (5)

By Alaa S. Abd-El-Aziz,* Mark Lautens and Alan J. Lough†

Department of Chemistry, University of Toronto, Toronto, Ontario, Canada M5S 1A1

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Abstract. (2) $C_{11}H_{18}O_2$, $M_r = 182{\cdot}3$, monoclinic, $P2_1/a$, $a = 7{\cdot}463\ (3)$, $b = 9{\cdot}776\ (3)$, $c = 14{\cdot}955\ (5)$ Å, $\beta = 97{\cdot}33°$, $V = 1082{\cdot}2$ Å^3, $Z = 4$, $D_x = 1{\cdot}12$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 0{\cdot}70$ cm^{-1}, $F(000) = 400$, room temperature, $R = 0{\cdot}041$ for 480 observed reflections. (5) $C_{13}H_{22}O_2$, $M_r = 210{\cdot}3$, orthorhombic, *Pnab*, $a = 9{\cdot}747\ (1)$, $b = 10{\cdot}724\ (2)$, $c = 24{\cdot}365\ (4)$ Å, $V = 2546{\cdot}8$ Å^3, $Z = 8$, $D_x = 1{\cdot}10$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 0{\cdot}67$ cm^{-1}, $F(000) = 928$, room temperature, $R = 0{\cdot}037$ for 521 observed reflections. In both (2) and (5) the hydroxyl group is *trans* with respect to the *tert*-butyl group. In (2) pairs of molecules are linked *via* hydrogen bonds [O···O $(1-x,\ 1-y,\ 1-z)$ 2·809 (7) Å] to form centrosymmetric dimers, while in (5) molecules are hydrogen bonded [O···O$(x,\ -0{\cdot}5+y,\ 1{\cdot}5-z)$ 2·847 (7) Å] through 2_1 screw axes to form infinite chains. The highly strained seven-membered ring in (2) has a boat-type conformation and in (5) it has a sofa-type conformation.

Introduction. We have recently investigated the ring opening reaction of 8-oxabicyclo[3.2.1]oct-6-en-3-one (1) and 2,4-dimethyl-8-oxabicyclo[3.2.1]oct-6-en-3-one (4) with organocuprate reagents (Lautens, Di Felice & Huboux, 1989). These types of reaction provide an extremely efficient route to seven-membered rings where two or four contiguous stereocentres are created in two steps. The syntheses of the starting oxabicyclic compounds (1) and (4) were carried out according to a literature procedure (Fohlisch, Gottstein, Herter & Wanner, 1981; Hoffmann, 1984). Treatment of compound (1) with five equivalents of ^{t}BuLi/CuCN (1·6/1) in tetrahydrofuran with ageing the cuprate for 3 h led to the formation of the regioisomers (2) and (3) in 3/1 ratio with total yield of 95%. Under the same experi-

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* Current address: Department of Chemistry, University of Winnipeg, Winnipeg, Manitoba, Canada R3B 2E9.

† To whom correspondence should be addressed. E-mail address: ALOUGH@ALCHEMY.CHEM.UTORONTO.CA

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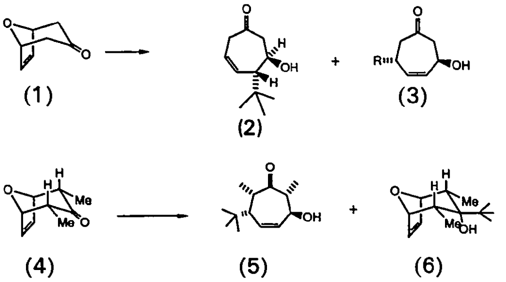
mental conditions compound (4) gave (5) and (6) in 9/1 ratio with overall yield of 71%.



Compounds (2), (3) and (5), (6) were separated using column chromatography. The stereochemistries of these compounds were tentatively assigned on the basis of ^{1}H NMR. Owing to the uncertainty of the NMR assignments in the seven-membered ring we have examined compounds (2) and (5) by X-ray crystallographic analysis.

Experimental. Compound (2). Crystals were grown from pentane. Accurate cell dimensions and crystal orientation matrix were determined on a CAD-4 diffractometer by a least-squares treatment of the setting angles of 25 reflections in the range $8 < \theta < 12°$. Crystal dimensions 0·10 × 0·20 × 0·20 mm; intensities of reflections with indices h 0 to 7, k 0 to 10, l −15 to 15, with $2 < 2\theta < 44°$ measured, ω–2θ scans, ω-scan width $(0{\cdot}6 + 0{\cdot}35\tan\theta)°$; graphite-monochromatized Mo $K\alpha$ radiation; intensities of two reflections measured every 2 h indicated linear intensity fall-off to a maximum of 20%, which was subsequently corrected for (correction factors ranged from 1·00 to 1·37). 1532 reflections measured, 1014 unique ($R_{\rm int} = 0{\cdot}025$) and only 480 with $I > 3\sigma(I)$ labelled observed and used in the structure solution and refinement. Data corrected for Lorentz and polarization effects. Space group $P2_1/a$ was determined uniquely by the systenatic absences ($0k0$ absent if $k = 2n + 1$, $h0l$ absent if $h = 2n + 1$). The structure was solved by direct methods using *SHELXS*86 (Sheldrick, 1986). Refinement was by full-matrix least-squares calculations, initially with isotropic and then with anisotropic thermal parameters. A difference map showed maxima in positions consistent with the expected locations of H atoms. The hydroxyl H atom was refined with an individual isotropic thermal parameter. In the final rounds of calculations the other H atoms were positioned on geometric grounds (C—H 0·95 Å) and included (as riding atoms) in the structure-factor calculation. These atoms were assigned general isotropic thermal parameters; $U_{\rm iso}$ 0·106 Å^2 for methyl H atoms and 0·050 (7) Å^2 for the rest. The final cycle of refinement included 124 variable parameters, $R = 0{\cdot}041$, $wR = 0{\cdot}038$, goodness of fit 1·40, $w = 1/[\sigma^2(F_o) + 0{\cdot}00022(F_o)^2]$. Max. shift/e.s.d. in final refinement cycle 0·009; density in final difference map in range −0·13 to 0·13 e Å^{-3}; there were no chemically significant features. No correction for secondary extinction.

Table 1. *Positional and thermal parameters and their e.s.d.'s for compound* (2)

$U_{\rm eq} = (U_{11} + U_{22} + U_{33})/3.$

	x	y	z	$U_{\rm eq}/U_{\rm iso}$(Å^2)
C(1)	0·1825 (9)	0·4409 (7)	0·4429 (5)	0·050 (5)
C(2)	0·2430 (8)	0·5712 (7)	0·4051 (4)	0·053 (5)
C(3)	0·3429 (8)	0·5532 (6)	0·3227 (4)	0·048 (4)
C(4)	0·2394 (7)	0·4722 (6)	0·2447 (4)	0·039 (4)
C(5)	0·0393 (7)	0·4802 (6)	0·2418 (4)	0·055 (5)
C(6)	−0·0486 (8)	0·4272 (7)	0·3040 (4)	0·063 (5)
C(7)	0·0420 (7)	0·3581 (6)	0·3872 (4)	0·059 (5)
O(8)	0·2436 (6)	0·4000 (5)	0·5167 (3)	0·082 (4)
O(9)	0·5062 (6)	0·4809 (6)	0·3495 (3)	0·066 (4)
C(10)	0·3015 (5)	0·4997 (4)	0·1515 (3)	0·049 (4)
C(11)	0·50565 (22)	0·48379 (9)	0·15364 (6)	0·079 (6)
C(12)	0·21109 (14)	0·39650 (13)	0·08371 (8)	0·087 (6)
C(13)	0·24964 (13)	0·64345 (16)	0·11683 (7)	0·087 (6)
HO	0·566 (9)	0·521 (8)	0·386 (5)	0·12 (4)

Table 2. *Positional and thermal parameters and their e.s.d.'s for compound* (5)

$U_{\rm eq} = (U_{11} + U_{22} + U_{33})/3.$

	x	y	z	$U_{\rm eq}/U_{\rm iso}$(Å^2)
C(1)	0·1052 (6)	−0·0411 (6)	0·68407 (26)	0·053 (5)
C(2)	0·1379 (6)	−0·1271 (5)	0·73053 (17)	0·049 (4)
C(3)	0·2818 (6)	−0·1817 (6)	0·71997 (26)	0·057 (5)
C(4)	0·3021 (6)	−0·2365 (6)	0·66479 (25)	0·067 (5)
C(5)	0·2124 (7)	−0·2556 (6)	0·62539 (24)	0·065 (5)
C(6)	0·0603 (6)	−0·2307 (5)	0·62487 (20)	0·046 (4)
C(7)	0·0343 (6)	−0·0900 (5)	0·63360 (19)	0·054 (4)
O(8)	0·1342 (5)	0·0689 (5)	0·68745 (18)	0·083 (3)
O(9)	0·3228 (5)	−0·2645 (6)	0·76166 (21)	0·080 (4)
C(10)	−0·0174 (4)	−0·2941 (4)	0·57650 (16)	0·060 (4)
C(11)	−0·16870 (17)	−0·25622 (9)	0·57761 (4)	0·093 (5)
C(12)	0·04160 (10)	−0·27000 (8)	0·51917 (6)	0·085 (5)
C(13)	−0·01207 (19)	−0·4352 (5)	0·58662 (19)	0·116 (6)
C(14)	0·06087 (9)	−0·00579 (11)	0·58438 (6)	0·096 (5)
C(15)	0·13201 (9)	−0·06290 (10)	0·78656 (6)	0·077 (5)
HO	0·267 (8)	−0·317 (7)	0·770 (3)	0·14 (4)

Compound (5). Diffractometer measurements and structure determination as for compound (2) except: crystal size 0·35 × 0·15 × 0·15 mm, θ range for cell refinement 9–13°. 1416 reflections measured, 1189 not systematically absent and 521 with $I > 3\sigma(I)$ labelled observed. Index range h 0 to 9, k 0 to 10 and l 0 to 23; space group $Pnab$ (non-standard setting of $Pbcn$) determined from systematic absences ($0kl$ absent if $k + l = 2n + 1$, $h0l$ absent if $h = 2n + 1$, $hk0$ absent if $k = 2n + 1$). All non-H atoms refined anisotropically, hydroxyl H atom refined with isotropic thermal parameter. Other H atoms positioned on geometric grounds [C—H 0·95 Å, $U_{\rm iso}$ for methyl H atoms 0·113, $U_{\rm iso}$ for other H atoms 0·049 (7) Å^2]. Final cycle of refinement included 142 parameters, $R = 0{\cdot}0373$, $wR = 0{\cdot}0384$, goodness of fit 1·33, $w = 1/[\sigma^2(F_o) + 0{\cdot}00050(F_o)^2]$, max. shift/e.s.d. = 0·003;

Table 3. *Molecular distances* (Å), *angles* (°) *and torsion angles* (°) *for compounds* (2) *and* (5)

Compound (2)		Compound (5)	
C(1)—C(2)	1·487 (9)	C(1)—C(2)	1·494 (8)
C(1)—C(7)	1·492 (9)	C(1)—C(7)	1·505 (8)
C(1)—O(8)	1·207 (8)	C(1)—O(8)	1·216 (8)
C(2)—C(3)	1·530 (8)	C(2)—C(3)	1·541 (8)
C(3)—C(4)	1·534 (8)	C(2)—C(15)	1·530 (5)
C(3)—O(9)	1·421 (8)	C(3)—C(4)	1·481 (9)
C(4)—C(5)	1·490 (7)	C(3)—O(9)	1·407 (9)
C(4)—C(10)	1·547 (7)	C(4)—C(5)	1·314 (9)
C(5)—C(6)	1·312 (9)	C(5)—C(6)	1·507 (9)
C(6)—C(7)	1·499 (9)	C(6)—C(7)	1·545 (8)
C(10)—C(11)	1·528 (4)	C(6)—C(10)	1·557 (7)
C(10)—C(12)	1·526 (4)	C(7)—C(14)	1·523 (5)
C(10)—C(13)	1·530 (4)	C(10)—C(11)	1·530 (4)
O(9)—HO	0·77 (7)	C(10)—C(12)	1·533 (4)
OH···O(8^{i})	2·05 (7)	C(10)—C(13)	1·533 (7)
O(9)···O(8^{i})	2·809 (7)	O(8^{i})···O(9)	2·847 (7)
		O(8^{i})···HO	2·05 (8)
		O(9)—HO	0·81 (8)

C(7)—C(1)—C(2)	118·6 (5)	C(7)—C(1)—C(2)	120·1 (5)
O(8)—C(1)—C(2)	122·2 (6)	O(8)—C(1)—C(2)	119·8 (5)
C(3)—C(2)—C(1)	114·2 (5)	C(3)—C(2)—C(1)	107·6 (4)
O(8)—C(1)—C(7)	119·2 (6)	C(15)—C(2)—C(1)	113·0 (4)
C(6)—C(7)—C(1)	115·4 (5)	O(8)—C(1)—C(7)	120·0 (6)
C(4)—C(3)—C(2)	115·0 (5)	C(6)—C(7)—C(1)	112·2 (5)
O(9)—C(3)—C(2)	108·5 (5)	C(14)—C(7)—C(1)	111·0 (4)
O(9)—C(3)—C(4)	106·8 (5)	C(15)—C(2)—C(3)	110·7 (4)
C(5)—C(4)—C(3)	113·6 (5)	C(4)—C(3)—C(2)	115·1 (5)
C(10)—C(4)—C(3)	114·5 (4)	O(9)—C(3)—C(2)	112·2 (5)
C(10)—C(4)—C(5)	112·3 (4)	O(9)—C(3)—C(4)	111·5 (6)
C(6)—C(5)—C(4)	123·3 (5)	C(5)—C(4)—C(3)	129·5 (6)
C(11)—C(10)—C(4)	112·1 (3)	C(6)—C(5)—C(4)	129·3 (5)
C(12)—C(10)—C(4)	109·0 (3)	C(7)—C(6)—C(5)	109·5 (5)
C(13)—C(10)—C(4)	111·9 (3)	C(10)—C(6)—C(5)	114·0 (4)
C(7)—C(6)—C(5)	123·5 (5)	C(10)—C(6)—C(7)	116·8 (4)
C(12)—C(10)—C(11)	107·6 (3)	C(14)—C(7)—C(6)	116·3 (4)
C(13)—C(10)—C(11)	108·0 (2)	C(11)—C(10)—C(6)	109·8 (3)
C(13)—C(10)—C(12)	108·1 (3)	C(12)—C(10)—C(6)	115·7 (3)
O(9)—HO···O(8^{i})	170 (7)	C(13)—C(10)—C(6)	107·0 (3)
		C(12)—C(10)—C(11)	109·4 (3)
		C(13)—C(10)—C(11)	107·0 (3)
		C(13)—C(10)—C(12)	107·5 (3)
		O(9)—HO···O(8^{i})	164 (8)

	Compound (2)	Compound (5)
C(7)—C(1)—C(2)—C(3)	− 65·7 (7)	89·8 (6)
C(2)—C(1)—C(7)—C(6)	− 10·4 (8)	25·5 (7)
C(1)—C(2)—C(3)—C(4)	− 55·0 (7)	51·1 (7)
C(2)—C(3)—C(4)—C(5)	− 26·9 (7)	6·9 (10)
C(3)—C(4)—C(5)—C(6)	− 66·4 (7)	1·9 (11)
C(4)—C(5)—C(6)—C(7)	− 2·8 (10)	60·9 (8)
C(5)—C(6)—C(7)—C(1)	54·7 (8)	− 53·2 (6)

Symmetry code: (i) x, $0·5 - y$, $1·5 - z$.

residual electron density in range −0·11 to 0·11 e Å^{-3}. The atomic coordinates for molecules (2) and (5) are given in Tables 1 and 2,* respectively.

Scattering factors as embedded in software. All calculations carried out on a PDP 11/23 computer using *SDP* (B. A. Frenz & Associates Inc., 1982) and an Apollo computer using *SHELX76* and *SHELXS86* (Sheldrick, 1976, 1986).

Discussion. Bond lengths, bond angles and selected torsion angles for (2) and (5) are listed in Table 3. Figs. 1 and 2 are views of the molecules prepared using *ORTEPII* (Johnson, 1976).

The crystallographic analyses establish the stereochemistries of compound (2) and compound (5). The configuration at asymmetric centres C(3) and C(4) is *RS* (or *SR*) in compound (2) and in compound (5)

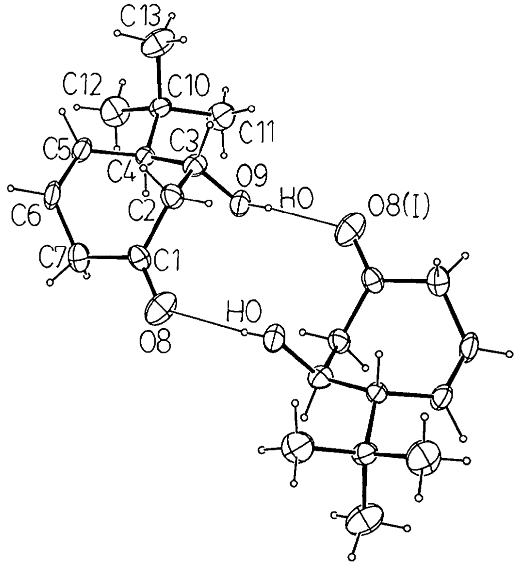


Fig. 1. View of hydrogen-bonded dimer of (2) indicating atomic labelling scheme. The thermal ellipsoids of the C and O atoms are drawn at the 25% probability level. H atoms are represented by spheres of arbitrary radius.

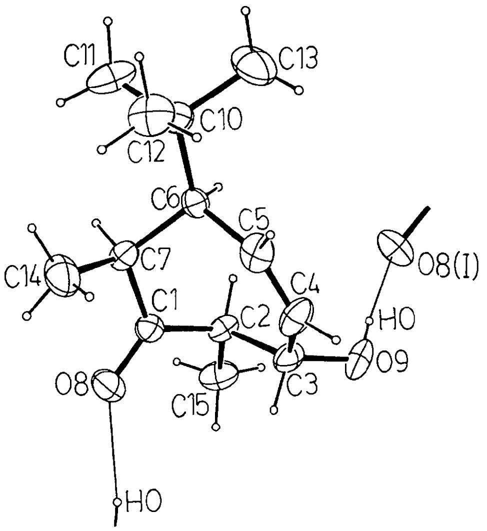


Fig. 2. View of (5) indicating atomic labelling scheme and hydrogen-bonded atoms. Atoms are represented as in Fig. 1.

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* Lists of structure factors, thermal parameters, calculated H-atom coordinates, mean-plane data and torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53600 (15 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

the configuration at atoms C(2), C(3), C(6) and C(7) is *RSSS* (or *SRRR*). This gives rise to a *trans* arrangement in both compounds of the *tert*-butyl and hydroxyl substituents at chiral centres. In (2) pairs of molecules are linked through crystallographic symmetry centres by hydrogen bonds [O(9)···O(8)($1-x$, $1-y$, $1-z$) 2·809 (7) Å] to form dimers. Molecules of (5) are linked by hydrogen bonds [O(9)···O(8)(x, $-0·5+y$, $1·5-z$) 2·847 (7) Å] into infinite chains through crystallographic 2_1 screw axes. In (2) the hydroxyl group and the carbonyl group have a *cis* arrangement which facilitates dimer formation. Molecule (5) has an unfavourable arrangement for dimerization (the hydroxyl group and the carbonyl group are *trans* to each other) and hence chains are formed.

The geometry of the seven-membered ring in compound (2) is significantly different from that in compound (5) (see Table 3 for values of ring torsion angles). The seven-membered ring in compound (2) can best be described as a boat conformation with the atoms C(1), C(7), C(3) and C(4) defining the base plane [maximum deviation 0·042 (6) Å for C(3)], C(5) and C(6) defining the stern and C(2) the bow. Compound (5) has a sofa-type conformation with atoms C(2), C(3), C(4), C(5) and C(6) defining one plane [maximum deviation −0·060 (7) Å for C(3)] and C(6), C(7), C(1) and C(2) defining another [maximum deviation 0·126 (6) Å for C(1)], with interplanar angle 65 (2)°. In compound (2) all the interior angles of the ring [except for the angle at C(1)] are larger than would be expected on the basis of hybridization principles. Steric repulsions of substituent groups could only cause a reduction of the magnitude of the ring angles, therefore the angles in (2) probably indicate a highly strained system. The compound dimethyl 3-bromo-7-oxo-1-cyclohepten-1,2-dicarboxylate (Atwood, Williams, Garner & Cone, 1974) adopts a similar conformation to that of (2) and displays a similar pattern of interior angles. The argument for a strained system can also be presented in the case of (5) although the angle widening effect appears to be concentrated at the angles at C(4) and C(5). Steric repulsions (due to two extra methyl substituents) may also affect the interior bond angles in (5) and hence may account for the conformational differences from (2).

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Structure of 4-Deoxyphenobarbital

By Donald Mastropaolo and Arthur Camerman

Departments of Medicine (*Neurology*) *and Pharmacology, University of Washington, Seattle, WA* 98195, *USA*

and Norman Camerman

*Department of Biochemistry, University of Toronto, Toronto, Ontario M*5*S* 1*A*8, *Canada*

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Abstract. 5-Ethyl-5-phenyl-4,5-dihydro-2,6(1*H*,3*H*)-pyrimidinedione 1,4-dioxane solvate, $C_{12}H_{14}N_2O_2.0{\cdot}5C_4H_8O_2$, $M_r = 262{\cdot}29$, monoclinic, $P2_1/c$, $a = 6{\cdot}8256$ (5), $b = 27{\cdot}078$ (3), $c = 8{\cdot}5647$ (7) Å, $\beta = 116{\cdot}47$ (1)°, $V = 1417{\cdot}0$ Å^3, $Z = 4$, D_m (flotation in KI/H_2O) = 1·24 (1), $D_x = 1{\cdot}229$ Mg m^{-3}, λ(Cu $K\alpha$) = 1·5418 Å, $\mu = 0{\cdot}723$ mm^{-1}, $F(000) = 560$, $T = 282$ K, $R = 0{\cdot}046$ for 1720 observations, $wR = 0{\cdot}045$