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(1*R*,8*R*,11*R*)-3,3,11-Trimethyl-6,6-ethylenedioxybicyclo[6.3.0]undecan-2-one and (1*R*,2*R*,8*R*,11*R*)-3,3,11-trimethyl-6,6-ethylenedioxybicyclo[6.3.0]undecan-2-ol

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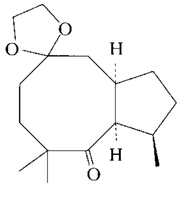
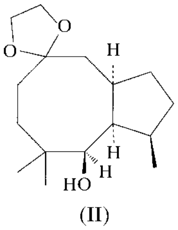
The reduction of (1*R*,8*R*,11*R*)-3,3,11-trimethyl-6,6-ethylenedioxybicyclo[6.3.0]undecan-2-one, $C_{16}H_{26}O_3$, (I), gave exclusively an alcohol, $C_{16}H_{28}O_3$, (II). The stereochemistry of the hydroxyl group in (II) was shown as *R*. The conformation around the eight-membered carbocycle in (I) differs markedly from that in (II).

Comment

During the course of our synthetic studies on precapnelladiene, one of the terpenoids having an eight-membered carbocycle, we prepared a chiral (1*R*,8*R*,11*R*)-3,3,11-trimethylbicyclo[6.3.0]undeca-2,6-dione (Maeda & Inouye, 1994) as the synthetic intermediate. Because of the flexible nature of an eight-membered ring, it is worthwhile clarifying the conformational change of the eight-membered ring during the reaction. We report here the crystal structures of (1*R*,8*R*,11*R*)-3,3,11-trimethyl-6,6-ethylenedioxybicyclo[6.3.0]-undecan-2-one, (I), which was synthesized from the dione, and the corresponding alcohol, (II).



(I)



(II)

The stereochemistry of the hydroxyl group in (II) was unequivocally confirmed as *R*, as deduced from its NMR spectrum; the H atom attached at the alcoholic C atom absorbs at δ 3.56 with J = 3.1 Hz. Two independent molecules were found in (II) and these differ only in their conformations around an acetal moiety. On the other hand, the conformation of the eight-membered carbocycle differs markedly in (I) and (II). Torsion angles indicate major differences being found at C atoms 4 and 5. The crystal structure of (I) reveals that the *Re*-side of the carbonyl carbon is protected by the C6-methylene group from an incoming reagent to give an *R* alcohol exclusively. The resulting alcoholic O atom in (II) interacts with the C6-methylene group, giving a conformational change at C atoms 4 and 5.

Experimental

(1*R*,8*R*,11*R*)-3,11,11-Trimethylbicyclo[6.3.0]undecane-2,6-dione (Maeda & Inouye, 1994) was treated with *tert*-butyldimethylsilyl trifluoromethanesulfonate and 1,2-bis(trimethylsilyloxy)ethane at 203 K for 2 h, followed by a further 2 h at room temperature. The solution was filtered through a short silica-gel column with chloroform. After evaporating the solvent, the residue was chromatographed on alumina (benzene) to give (I) in 94% yield. (I) was reduced with $LiAlH_4$ in dry tetrahydrofuran at 273 K to afford (II) in 96% yield. Compound (I): m.p. 361–362 K (from hexane); found: C 72.35, H 9.67%; calculated for $C_{16}H_{26}O_3$: C 72.14, H 9.84%. Compound (II): m.p. 418–420 K (from hexane); found: C 71.76, H 10.66%; calculated for $C_{16}H_{28}O_3$: C 71.60, H 10.52%.

Compound (I)

Crystal data

$C_{16}H_{26}O_3$
M_r = 266.37
Orthorhombic, $P2_12_12_1$
a = 15.594 (3) Å
b = 16.837 (2) Å
c = 5.6919 (8) Å
V = 1494.4 (4) Å^3
Z = 4
D_x = 1.184 Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 25 reflections
θ = 10.01–13.57°
μ = 0.080 mm^{-1}
T = 293 (2) K
Needle, colourless
0.50 × 0.20 × 0.20 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
2616 measured reflections
2616 independent reflections
1316 reflections with $I > 2\sigma(I)$
$\theta_{\max}$ = 30.51°

$h = 0 \rightarrow 22$
$k = 0 \rightarrow 24$
$l = 0 \rightarrow 8$
3 standard reflections
frequency: 120 min
intensity decay: 5.1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.068
$wR(F^2)$ = 0.168
S = 1.038
2616 reflections
243 parameters

H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.1375P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max}$ = 0.005
$\Delta\rho_{\max}$ = 0.44 e Å^{-3}
$\Delta\rho_{\min}$ = −0.42 e Å^{-3}

Table 1
Selected torsion angles (°) for (I).

C8—C1—C2—C3	114.4 (4)	C4—C5—C6—C7	−76.8 (7)
C1—C2—C3—C4	−41.1 (5)	C5—C6—C7—C8	93.2 (6)
C2—C3—C4—C5	−60.3 (6)	C6—C7—C8—C1	−58.1 (6)
C3—C4—C5—C6	90.5 (7)	C2—C1—C8—C7	−42.0 (5)

Compound (II)

Crystal data

$C_{16}H_{28}O_3$
$M_r = 268.38$
Monoclinic, $P2_1$
$a = 10.368$ (3) Å
$b = 16.3349$ (14) Å
$c = 10.211$ (3) Å
$\beta = 116.614$ (12)°
$V = 1546.1$ (7) Å^3
$Z = 4$

$D_x = 1.153$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 11.58$–13.98°
$\mu = 0.077$ mm^{-1}
$T = 293$ (2) K
Needle, colourless
0.70 × 0.30 × 0.20 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
4876 measured reflections
4647 independent reflections
3562 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.0128$

$\theta_{\rm max} = 29.98°$
$h = -14 \rightarrow 13$
$k = 0 \rightarrow 22$
$l = 0 \rightarrow 14$
3 standard reflections
frequency: 120 min
intensity decay: 3.0%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.045$
$wR(F^2) = 0.111$
$S = 1.064$
4647 reflections
503 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0713P)^2 + 0.0858P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = -0.001$
$\Delta\rho_{\rm max} = 0.22$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.15$ e Å^{-3}

Table 2
Selected torsion angles (°) for (II).

C8*A*—C1*A*—C2*A*—C3*A*	95.1 (3)	C8*B*—C1*B*—C2*B*—C3*B*	95.9 (2)
C1*A*—C2*A*—C3*A*—C4*A*	−63.0 (3)	C1*B*—C2*B*—C3*B*—C4*B*	−62.8 (3)
C2*A*—C3*A*—C4*A*—C5*A*	65.1 (3)	C2*B*—C3*B*—C4*B*—C5*B*	65.1 (3)
C3*A*—C4*A*—C5*A*—C6*A*	−106.6 (3)	C3*B*—C4*B*—C5*B*—C6*B*	−106.9 (3)
C4*A*—C5*A*—C6*A*—C7*A*	49.8 (3)	C4*B*—C5*B*—C6*B*—C7*B*	49.7 (3)
C5*A*—C6*A*—C7*A*—C8*A*	58.5 (3)	C5*B*—C6*B*—C7*B*—C8*B*	58.7 (3)
C6*A*—C7*A*—C8*A*—C1*A*	−68.6 (3)	C6*B*—C7*B*—C8*B*—C1*B*	−68.0 (3)
C2*A*—C1*A*—C8*A*—C7*A*	−36.9 (3)	C2*B*—C1*B*—C8*B*—C7*B*	−38.0 (3)

Table 3
Hydrogen-bonding geometry (Å, °) for (II).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O12*A*—H12*A*···O15*B*$^{\rm i}$	0.79 (4)	2.25 (4)	2.937 (3)	146 (4)
O12*B*—H12*B*···O15*A*$^{\rm ii}$	0.82 (4)	2.19 (4)	2.912 (3)	148 (3)

Symmetry codes: (i) $x - 1, y, z$; (ii) $x, y, z - 1$.

In (II), atoms C17*B* and C17*C* (0.50:0.50) were disordered. The positions of all the H atoms, except methyl H and disordered methylene H atoms, were refined in the final calculations. The methyl and the methylene H atoms were calculated geometrically. Friedel pairs were not measured for (I) and a few (229) for (II). Refinement of the absolute structure parameter is meaningless for this combination of chemical composition and X-ray wavelength; the absolute configurations are deduced from those of the chemical precursors.

For both compounds, data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989); cell refinement: *CAD*-4 *Software* (Enraf–Nonius, 1989); data reduction: *MolEN* (Fair, 1990); program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993); software used to prepare material for publication: *SHELXL*93 (Sheldrick, 1993).

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