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(2-*exo*,7-*exo*,9-*endo*,10-*endo*)-11-Oxatricyclo-[6.2.1.$0^{2,7}$]undec-4-ene-9,10-diyl diacetate

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The title compound, $C_{14}H_{18}O_5$, shows a non-planar geometry.

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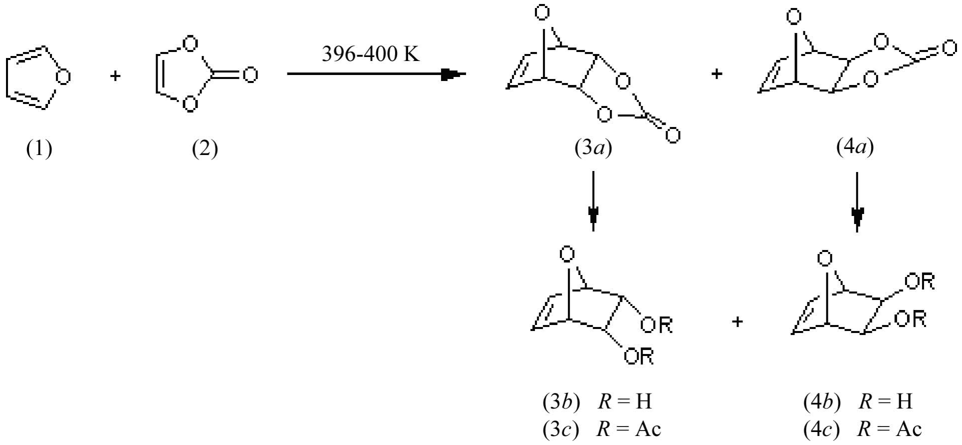
Key indicators

Single-crystal X-ray study
T = 150 K
Mean *σ*(C–C) = 0.002 Å
R factor = 0.032
wR factor = 0.084
Data-to-parameter ratio = 12.2

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

The reaction of furan (1) and vinylene carbonate (2) to give cycloadducts (3*a*) and (4*a*) has been well known for about 50 years (Newman & Addor, 1955). Cycloadducts (3*a*) and (4*a*) can be readily converted to the corresponding diols (3*b*) and (4*b*) and acetate derivatives (3*c*) and (4*c*) with no change of the stereochemistry of oxygen functionalities.

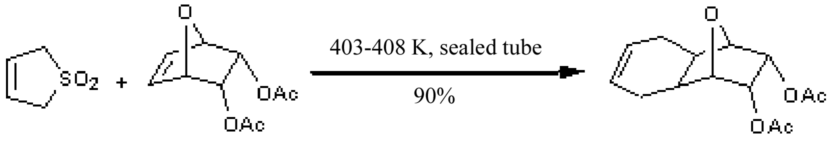


(1) (2) (3*a*) (4*a*)

(3*b*) *R* = H
(3*c*) *R* = Ac

(4*b*) *R* = H
(4*c*) *R* = Ac

Cycloadducts (3) and (4) have been used for many synthetic purposes. Cycloadducts (3*a*) and (4*a*) were used for the preparation of conduritol-C (Yur'ev & Zefirov, 1961), for the stereoselective synthesis of inositols (Kowarski & Sarel, 1973), for the preparation of ribose derivatives (Schmidt & Lieberknecht, 1978) and for the synthesis of muscarone analogs (De Micheli *et al.*, 1993). Cycloadducts (3*b*) and (4*b*) were used for the preparation of 7-oxabicyclo[2.2.1]hepta-2,5-diene, which is benzene-1,4-epoxide (Prinzbach *et al.*, 1986). *endo*-Diacetate (3*c*) was reported to be a ROMP (ring-opening metathesis polymerization) polymerizable material.



(5) (3*c*) (6)

In our recent studies, we used diacetates (3*c*) and (4*c*) for stereoselective preparation of haloconduritols (Baran *et al.*, 2003, 2004). We also reported the formation of two dichloroconduritols from the reaction of diol (3*b*) with BCl_3 (Öztürk *et*

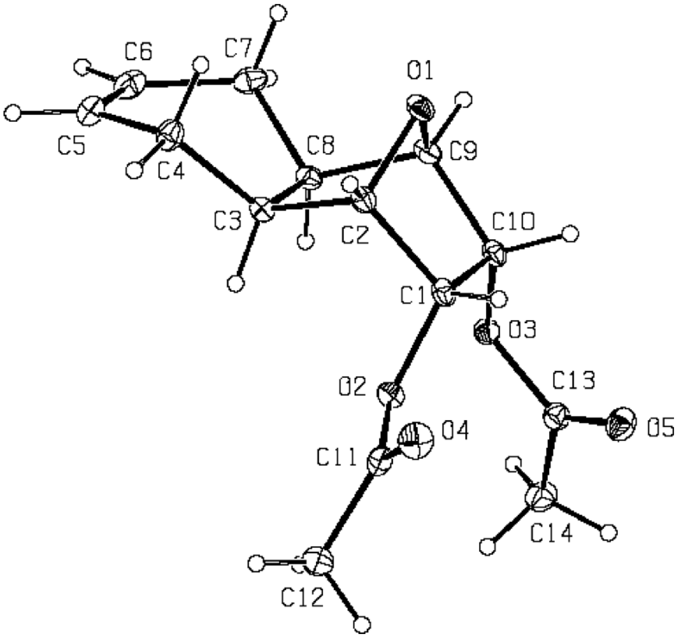


Figure 1
ORTEP-3 view (Farrugia, 1997) of (6), showing the atom-numbering scheme and 20% probability displacement ellipsoids

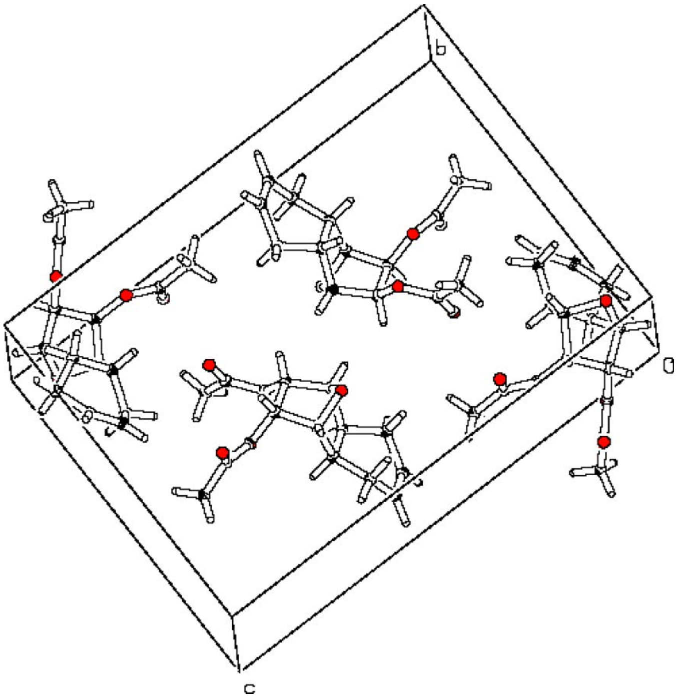


Figure 2
The unit-cell contents of (6).

al., 2004; Akkurt *et al.*, 2004). In this paper, we report the Diels–Alder reaction of *endo*-diacetate (3*c*) and *exo*-diacetate (4*c*) with butadiene. *endo*-Diacetate (3*c*) was reacted with 3-sulfolene (5), a protected 1,3-butadiene, to give the title compound, (6), in a high yield (90%) and as the sole product.

Compound (6) showed seven signals in its ^{13}C NMR spectrum. If one considers that Diels–Alder reactions proceed in a stereospecific manner, compound (6) should have mirror symmetry. However, butadiene may approach (3*c*) and (4*c*) from the *endo*-face or the *exo*-face. Therefore, the stereochemistry of H atoms at C3 and C8 is unknown; accordingly, an X-ray crystallographic analysis was undertaken.

We have shown that 7-oxabicyclo[2.2.1]hept-5-enediyl diacetates (3*c*) and (4*c*) prefer the *exo*-face in the Diels–Alder cycloaddition with butadiene. The conformation of (6), together with the atom-numbering scheme, is shown in Fig. 1. The two tetrahydrofuran junctions link a non-planar cyclohexene ring. Molecule (6) has the *E* configuration at the central C3—C8 bond. The mean C—O1 distance is 1.449 (1) Å, with a bent C2—O1—C9 angle of 96.44 (7)°. The two tetrahydrofuran rings each have an envelope conformation [the ring puckering parameters (Cremer & Pople, 1975) are Q(2) = 0.590 (1) Å and $\varphi(2)$ = 175.63 (11)° for the C1/C2/O1/C9/C10 ring, and Q(2) = 0.545 (1) Å and $\varphi(2)$ = 1.89 (11)° for the C3/C2/O1/C9/C8 ring]. The torsion angles C9—C10—O3—C13 and C2—C1—O2—C11 are 170.77 (8) and −94.10 (10)°, respectively.

We have carried out *CNDO* (complete neglect of differential overlap) quantum mechanical calculations (Allinger *et al.*, 1989) on (6), using their experimental atomic coordinates from the X-ray structure determination, and the charge distribution on the molecule in the gas phase was calculated (C4 0.45, C7 0.33, C11 0.43, C13 0.51, O1 −0.48, O2 −0.26, O3 −0.36, O4 −0.32 and O5 −0.28 e$^-$). The dipole moment of (6) is 6.96 D. The highest occupied and lowest unoccupied molecular orbital energy levels are −5.84 and 1.08 eV.

Experimental

(2-*endo*,3-*endo*)-7-Oxabicyclo[2.2.1]hept-5-ene-2,3-diyl diacetate, (3*c*) (1060 mg, 5 mmol), dissolved in 1,2-dichloroethane (5 ml), and 3-sulfolene (1500 mg, 12.7 mmol) were added to a pressure tube. The top of the tube was tightly closed and the tube was heated at 403–408 K for 24 h. After cooling the pressure tube, the reaction mixture was added to a flask. Removal of the solvent and unreacted 1,3-butadiene and SO$_2$ gave cycloadduct (6) (1200 mg, 90%) as colorless crystals (m.p. 362–363 K, from 1,2-dichloroethane). ^{1}H NMR (200 MHz, CDCl$_3$): δ 5.85–5.82 (*m*, 2H), 4.83–4.80 (*m*, 2H), 4.26–4.23 (*m*, 2H), 2.33–1.75 (*m*, 6H), 1.99 (*s*, 6H). ^{13}C NMR (50 MHz, CDCl$_3$): δ 169.6, 128.5, 83.4, 68.7, 36.8, 25.8, 20.4. Analysis calculated for C$_{14}$H$_{18}$O$_5$: C 63.15, H 6,81%; found: C 63.23, H 6.69%.

Crystal data

$C_{14}H_{18}O_5$
M_r = 266.28
Monoclinic, $P2_1/c$
a = 5.8430 (3) Å
b = 12.8501 (8) Å
c = 17.5767 (11) Å
β = 97.449 (5)°
V = 1308.58 (13) Å^3
Z = 4
D_x = 1.352 Mg m^{-3}
Mo Kα radiation
Cell parameters from 2988 reflections
θ = 1.6–27.6°
μ = 0.10 mm^{-1}
T = 150 K
Prism, colorless
0.57 × 0.40 × 0.27 mm

Data collection

Stoe IPDS-II diffractometer
ω scans
Absorption correction: by integration (*X-RED32*; Stoe & Cie, 2002)
$T_{\min}$ = 0.944, $T_{\max}$ = 0.973
18334 measured reflections
2988 independent reflections
2624 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.027
$\theta_{\max}$ = 27.5°
$h = -7 \rightarrow 7$
$k = -16 \rightarrow 16$
$l = -22 \rightarrow 22$

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Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.032$
$wR(F^2) = 0.084$
$S = 1.03$
2988 reflections
244 parameters
All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0437P)^2 + 0.2964P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.22$ e Å^{-3}
$\Delta\rho_{\min} = -0.18$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

O1—C2	1.450 (1)	O3—C10	1.433 (1)
O1—C9	1.448 (1)	O3—C13	1.355 (1)
O2—C1	1.435 (1)	O4—C11	1.200 (1)
O2—C11	1.347 (1)	O5—C13	1.202 (1)
C2—O1—C9	96.44 (7)	O3—C10—C1	114.07 (8)
C1—O2—C11	117.61 (8)	O3—C10—C9	111.61 (8)
C10—O3—C13	114.35 (8)	O2—C11—O4	123.71 (10)
O2—C1—C2	112.59 (8)	O2—C11—C12	110.56 (9)
O2—C1—C10	109.23 (8)	O4—C11—C12	125.72 (10)
O1—C2—C1	100.95 (8)	O3—C13—O5	122.77 (10)
O1—C2—C3	103.03 (8)	O3—C13—C14	111.77 (9)
O1—C9—C8	103.23 (8)	O5—C13—C14	125.46 (10)
O1—C9—C10	99.16 (8)		

All H atoms were found in a difference Fourier map and refined isotropically.

Data collection: *X-AREA* (Stoe & Cie, 2002); cell refinement: *X-AREA*; data reduction: *X-RED32* (Stoe & Cie, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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