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The 2-*exo*,7-*exo*,9-*exo*,10-*exo* isomer of 11-oxatricyclo[6.2.1.0^{2,7}]undec-4-ene-9,10-diyl diacetate

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The title compound, (2-*exo*,7-*exo*,9-*exo*,10-*exo*)-11-oxatricyclo[6.2.1.0^{2,7}]undec-4-ene-9,10-diyl diacetate, $C_{14}H_{18}O_5$, was synthesized in the same way as its 9-*endo*,10-*endo* isomer. The X-ray study showed that the Diels–Alder reaction of 5-*exo*,6-*exo*-diacetato-7-oxabicylclo[2.2.1]hepta-2-ene with 3-sulfolene, a protected 1,3-butadiene, yields the 2-*exo*,7-*exo* product, *i.e.* reacts in the same way as the 5-*endo*,6-*endo* isomer of the starting compound. Intermolecular C—H$\cdots$O interactions link the molecules into infinite chains extending along the *b* axis of the monoclinic crystal structure.

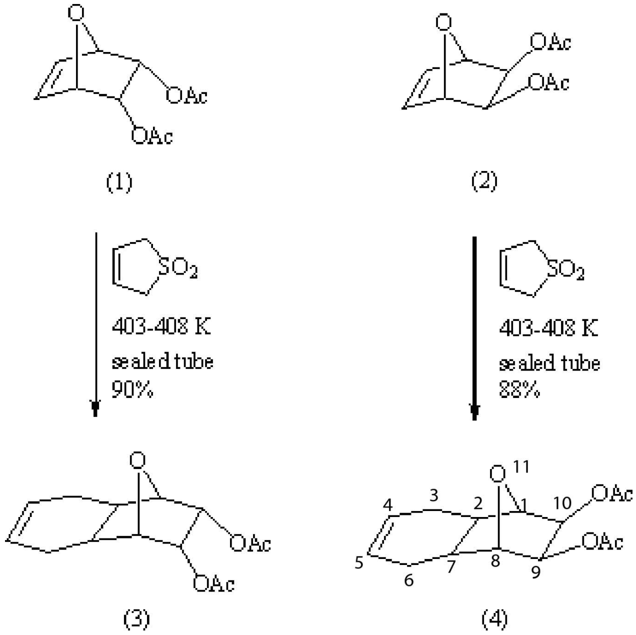
Key indicators

Single-crystal X-ray study
T = 150 K
Mean σ(C–C) = 0.002 Å
R factor = 0.045
wR factor = 0.127
Data-to-parameter ratio = 11.4

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

Comment

The preparation of the *endo*,*endo*-diacetate, (1), or the *exo*,*exo*-diacetate, (2), based on furan–vinylene carbonate cycloaddition followed by hydrolysis and acetylation, has been well documented (Baran *et al.*, 2003). As both compounds (1) and (2) have alkene groups, they may participate in Diels–Alder cycloaddition with a diene to give a new ring-fused system. In our previous study, we reported the reaction of 5-*endo*,6-*endo*-diacetate (1) with 3-sulfolene, a protected 1,3-butadiene, to afford cycloadduct (3), and determined its structure (Akkurt *et al.*, 2005). In this study, we present the reaction of the 5-*exo*,6-*exo*-diacetate, (2), with 3-sulfolene.



The reaction of (2) with 1,3-butadiene formed by thermolysis of 3-sulfolene in a sealed tube proceeded in an analogous fashion to its *endo*,*endo* isomer and produced the title cyclo-

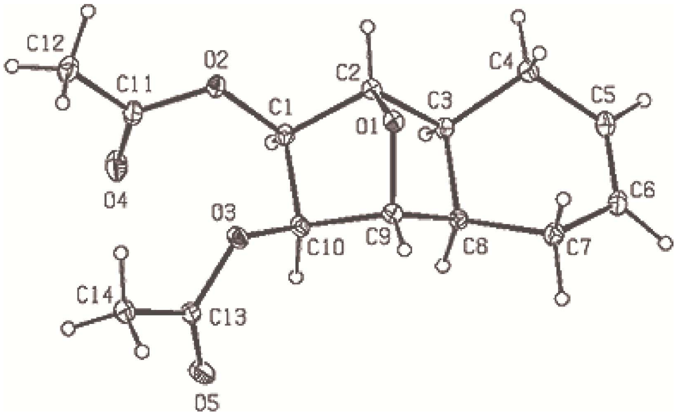


Figure 1
A view of (4), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 20% probability level.

adduct, (4), as the sole product in high yield (88%). Compound (4) shows seven signals in ^{13}C NMR spectrum. As Diels–Alder reactions proceed in a stereospecific manner, one would expect compound (4) to have mirror symmetry. Nevertheless, substitution at positions 2 and 3 of the starting molecule may occur in one of two ways, in either an *endo*- or an *exo*-orientation. Therefore, in order to determine unambiguously the stereochemistry of product (4), its X-ray diffraction study was undertaken.

The present X-ray study of compound (4) confirms that cycloaddition of butadiene to 5-*exo*,6-*exo*-diacetato-7-oxabicylclo[2.2.1]hepta-2-ene proceeds at the *exo* side and yields the 2-*exo*,7-*exo* product. The molecular structure of (4) is shown in Fig. 1.

The bond lengths and angles in (4) are in accordance with the results of Akkurt *et al.* (2004, 2005) and are also within the normal ranges for corresponding bonds (Allen *et al.*, 1987). For the 9-*endo*,10-*endo*-isomer, the C9—C10—O3—C13 and C2—C1—O2—C11 torsion angles are 170.77 (8) and −94.10 (10)°, respectively (Akkurt *et al.*, 2005); the corresponding torsion angles in the title compound are −120.62 (13) and 173.23 (11)°, respectively.

In contrast with the 9-*endo*,10-*endo* isomer, the structure of which did not show any important intermolecular contacts, the crystal packing of the title compound suggests the existence of a some C—H···O interactions (Table 2), which link the molecules into infinite chains extending along the *b* axis of the crystal structure. The molecular packing of the crystal of (4) is shown in Fig. 2.

Experimental

The synthesis of the title compound and preparation of the crystals for X-ray study were carried out in the same way as for the 9-*endo*,10-*endo* analogue (Akkurt *et al.*, 2005). The yield of colourless crystals of compound (4) was 88% (m.p. 389–391 K). Elemental analysis, found: C 62.66, H 6.74%; calculated for $C_{14}H_{18}O_5$: C 63.15, H 6.81%. Spectroscopic analysis: ^{1}H NMR (200 MHz, CDCl$_3$, δ, p.p.m.): 5.85–5.81 (*m*, 2H), 4.89 (*bs*, 2H), 4.09 (*bs*, 2H), 2.31–1.65 (*m*, 6H), 2.03 (*s*, 6H); ^{13}C NMR (50 MHz, CDCl$_3$, δ, p.p.m.): 170.0, 128.3, 85.0, 75.4, 39.2, 25.8, 20.4.

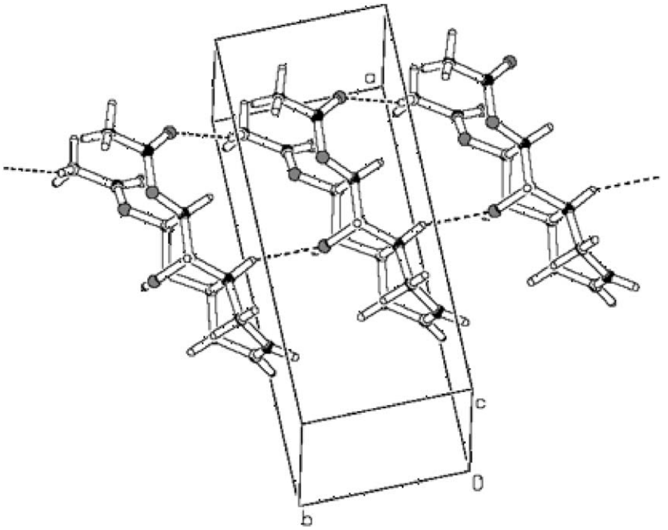


Figure 2
A packing diagram for (4). The C—H···O interactions are shown as dashed lines.

Crystal data

$C_{14}H_{18}O_5$
$M_r = 266.28$
Monoclinic, $P2_1/n$
$a = 13.9144$ (13) Å
$b = 5.5055$ (4) Å
$c = 17.8016$ (17) Å
$\beta = 107.858$ (8)°
$V = 1298.0$ (2) Å^3
$Z = 4$
$D_x = 1.363$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 9643 reflections
$\theta = 1.5$–27.6°
$\mu = 0.10$ mm^{-1}
$T = 150$ K
Prism, colourless
0.55 × 0.50 × 0.44 mm

Data collection

Stoe IPDS-II diffractometer
ω scans
9038 measured reflections
2534 independent reflections
2247 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.075$
$\theta_{\rm max} = 26.0°$
$h = -17 \rightarrow 17$
$k = -6 \rightarrow 6$
$l = -21 \rightarrow 21$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.045$
$wR(F^2) = 0.127$
$S = 1.05$
2534 reflections
222 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0754P)^2 + 0.3715P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.012$
$\Delta\rho_{\rm max} = 0.33$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.37$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

O1—C2	1.4394 (15)	O3—C10	1.4379 (16)
O1—C9	1.4444 (17)	O3—C13	1.3536 (18)
O2—C1	1.4394 (16)	O4—C11	1.198 (2)
O2—C11	1.3558 (19)	O5—C13	1.2029 (19)
C2—O1—C9	96.07 (9)	O3—C10—C1	109.61 (10)
C1—O2—C11	115.35 (11)	O3—C10—C9	110.43 (10)
C10—O3—C13	117.43 (11)	O2—C11—O4	123.02 (15)
O2—C1—C2	107.66 (10)	O2—C11—C12	111.07 (13)
O2—C1—C10	111.49 (10)	O4—C11—C12	125.90 (15)
O1—C2—C1	102.72 (10)	O3—C13—O5	123.68 (14)
O1—C2—C3	102.95 (10)	O3—C13—C14	110.65 (13)
O1—C9—C8	103.67 (11)	O5—C13—C14	125.67 (14)
O1—C9—C10	102.75 (11)		

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Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C3—H3···O1^{i}	0.97 (2)	2.35 (2)	3.2468 (15)	153 (2)
C14—H14A···O4^{ii}	0.96	2.59	3.460 (2)	151

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

The H atoms of the methyl groups were placed geometrically and included in the refinement in the riding-model approximation, with C—H = 0.96 Å and $U_{\rm iso}$(H) = 1.5$U_{\rm eq}$(C). Other H atoms were located in a difference Fourier map and refined isotropically, with C—H distances in the range 0.95–1.02 Å.

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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