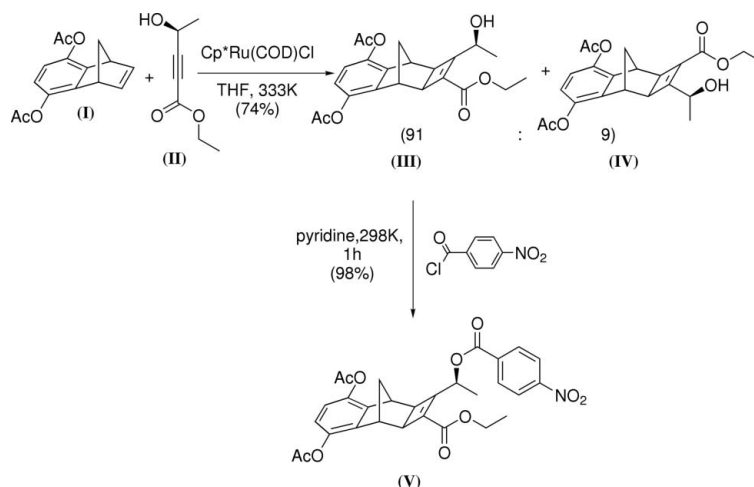


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Key indicators

Single-crystal X-ray study
T = 150 K
Mean $\sigma(\text{C}-\text{C}) = 0.006 \text{ \AA}$
R factor = 0.045
wR factor = 0.125
Data-to-parameter ratio = 8.7For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.Absolute configuration of the *p*-nitrobenzoate
ester of the cycloadduct of (*S*)-4-hydroxy-2-
pentynoate and acetic acid 8-acetoxy-1,4-
dihydro-1,4-methanonaphthalen-5-yl esterThe regio- and absolute stereochemistry of the title
compound, ethyl 3,6-diacetoxy-11-[1-(4-nitrobenzoyloxy)ethyl]
tetracyclo[6.4.1.0^{2,7}.0^{9,12}]trideca-2,4,6,10-tetraene-10-carboxylate,
C₂₉H₂₇O₁₀, has been established. In the crystal
structure, weak intermolecular hydrogen bonds link mol-
ecules into a three-dimensional network.Received 7 June 2006
Accepted 9 June 2006

Comment

Recently, we studied the ruthenium-catalysed [2 + 2]-cyclo-
additions between bicyclic alkenes and propargyl alcohols
(Villeneuve *et al.*, 2003). Two different diastereoisomers could
be formed in the cycloadditions. When dihydro-1,4-
methanonaphthalene-5,8-dioldiacetate, (I), was used as the
bicyclic alkene component and ethyl (*S*)-4-hydroxy-2-
pentynoate, (II), was used as the alkyne component, two
diastereoisomers, (III) and (IV), were obtained in a 91:9 ratio.
These diastereoisomers were derivatized to the corresponding
p-nitrobenzoyl esters and were separated by fractional
recrystallization. The absolute stereochemistry of the major
isomer, (V), was established by single-crystal X-ray diffraction
analysis.The molecular structure of (V) (Fig. 1) shows that the
dihedral angle between the two aromatic rings (C4–C9 and
C17–C22) is 55.61 (12)°. In the crystal structure, weak
intermolecular hydrogen bonds link molecules into a three-
dimensional network, as detailed in Table 1.

Experimental

Addition of dihydro-1,4-methanonaphthalene-5,8-dioldiacetate, (I)
(90.1 mg, 0.349 mmol), and ethyl (*S*)-4-hydroxy-2-pentynoate, (II)

(35.1 mg, 0.246 mmol), to Cp*Ru(COD)Cl (5.6 mg, 0.015 mmol) (Cp* = 1,2,3,4,5-pentamethylcyclopentadienyl and COD = 1,5-cyclooctadiene) in tetrahydrofuran (0.6 ml) at 358 K provided two diastereoisomers, (III) and (IV), in 74% yield (73.2 mg, 0.183 mmol) in a 91:9 ratio. The mixture of diastereoisomers (42.1 mg, 0.105 mmol), was esterified with *p*-nitrobenzoyl chloride (38.4 mg, 0.207 mmol) in pyridine (0.3 ml) at 298 K. Fractional recrystallization from diethyl ether/hexanes (1:1) provided the major diastereoisomer, (V) (56.3 mg, 0.102 mmol, 98%). Suitable crystals were grown from a diethyl ether/hexanes solution of (V).

Crystal data

C₂₉H₂₇NO₁₀
M_r = 549.52
 Monoclinic, *P*2₁
a = 13.5862 (6) Å
b = 7.3020 (3) Å
c = 14.3462 (7) Å
 β = 114.709 (2)°
V = 1292.93 (10) Å³

Z = 2
D_x = 1.412 Mg m⁻³
 Mo *K*α radiation
 μ = 0.11 mm⁻¹
T = 150 (1) K
 Block, colourless
 0.40 × 0.40 × 0.34 mm

Data collection

Bruker–Nonius KappaCCD
 diffractometer
 φ and ω scans with κ offsets
 Absorption correction: multi-scan
 (SORTAV; Blessing, 1995)
T_{min} = 0.869, *T_{max}* = 0.962

8306 measured reflections
 3175 independent reflections
 2230 reflections with *I* > 2σ(*I*)
R_{int} = 0.055
 θ_{\max} = 27.5°

Refinement

Refinement on *F*²
R [*F*² > 2σ(*F*²)] = 0.045
wR (*F*²) = 0.125
S = 1.03
 3175 reflections
 366 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0697P)^2 + 0.0871P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.30 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.26 \text{ e \AA}^{-3}$
 Extinction correction:
 SHELXTL/PC
 Extinction coefficient: 0.037 (5)

Table 1

Hydrogen-bond geometry (Å, °).

<i>D</i> –H... <i>A</i>	<i>D</i> –H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> –H... <i>A</i>
C13–H13B...O5 ⁱ	0.99	2.38	3.189 (4)	139
C15–H15C...O5 ⁱⁱ	0.98	2.58	3.513 (4)	159
C25–H25A...O4 ⁱⁱⁱ	0.98	2.58	3.345 (6)	135

Symmetry codes: (i) *x*, *y* – 1, *z*; (ii) –*x* + 1, *y* – ½, –*z* + 2; (iii) *x* + 1, *y* + 1, *z* + 1.

H atoms were placed in calculated positions, with C–H distances in the range 0.95–1.00 Å, and included in the refinement in the riding-model approximation, with *U*_{iso}(H) = 1.2*U*_{eq}(C) or 1.5*U*_{eq}(methyl C). In the absence of significant anomalous dispersion effects, 1942 Friedel pairs were merged. The absolute configuration was determined by reference to the unchanging chiral centre throughout the synthesis based on (*S*)-4-hydroxy-2-pentynoate, (II).

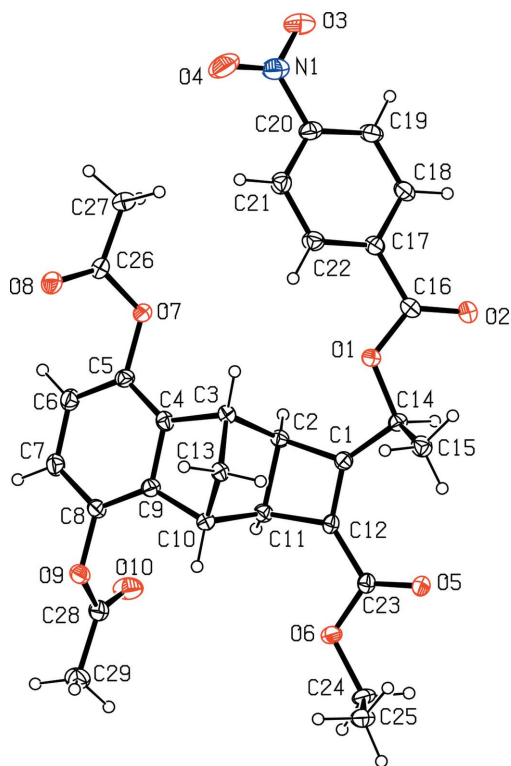


Figure 1

The molecular structure of (V), showing 30% probability displacement ellipsoids.

Data collection: COLLECT (Nonius, 2002); cell refinement: DENZO-SMN (Otwinowski & Minor, 1997); data reduction: DENZO-SMN; program(s) used to solve structure: SIR92 (Altomare *et al.*, 1994); program(s) used to refine structure: SHELXTL/PC (Sheldrick, 2001); molecular graphics: PLATON (Spek, 2003); software used to prepare material for publication: SHELXTL/PC.

The authors acknowledge NSERC and the University of Toronto for funding.

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