

(±)-(1*RS*,2*SR*)-1,2-Bis(2'-methyl-3'-oxocyclohex-1'-enyl)-1,2-diphenylethane

Hasim Ibrahim,^a Thorsten Bach^b
and Klaus Harms^{a*}

^aFachbereich Chemie der Philipps Universität, Hans-Meerwein-Str., D-35032 Marburg, Germany, and ^bLehrstuhl für Organische Chemie I, Technische Universität München, Lichtenbergstr. 4, D-85747 Garching, Germany

Correspondence e-mail:
harms@chemie.uni-marburg.de

Key indicators

Single-crystal X-ray study
T = 213 K
Mean $\sigma(\text{C}-\text{C}) = 0.003 \text{ \AA}$
R factor = 0.058
wR factor = 0.165
Data-to-parameter ratio = 11.3

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

The title compound, $\text{C}_{28}\text{H}_{30}\text{O}_2$, was obtained by an unprecedented osmium tetroxide-mediated dimerization of (2'-methyl-3'-oxocyclohex-1'-enyl)phenylethane. The *trans* stereochemistry was revealed by X-ray crystallography. The molecule exhibits a crystallographic center of inversion.

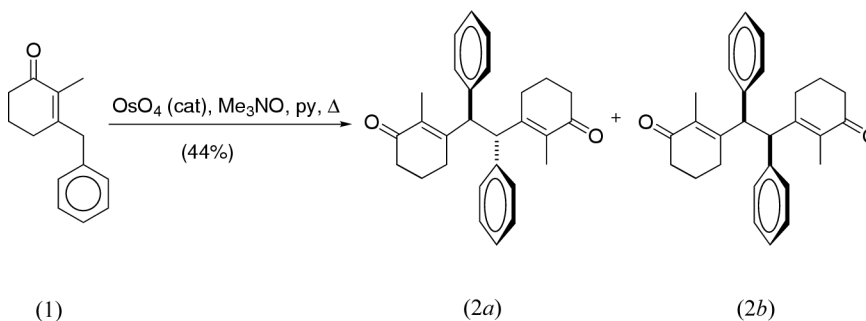
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Comment

The osmium tetroxide-mediated bishydroxylation of alkenes is a well established reaction in organic synthesis. In particular, catalytic versions of this reaction using stoichiometric co-oxidants are routinely used for the conversion of terminal, di- and trisubstituted alkenes to the corresponding diols (Schröder, 1980; Kolb *et al.*, 1994). Tetrasubstituted alkenes and in particular hindered substrates, however, are less suitable and usually require harsh reaction conditions or the use of a stoichiometric amount of the osmium tetroxide (Ogino *et al.*, 1994).



The reaction of enone (1) with a catalytic amount of osmium tetroxide for a period of four days following the conditions described by Ray & Matteson (1980) did not result in the formation of the desired ketodiols. Instead two new compounds were isolated.

The ^1H and ^{13}C NMR spectra of these compounds revealed that the alkene moiety remained intact, suggesting a dimerization of the starting material in the course of this reaction. Examining the mass spectra showed indeed molecular ion peaks at 398 corresponding to the diastereomeric pair (2a) and (2b).

An X-ray analysis of one of the compounds confirmed the dimeric structure and revealed a *trans* relative stereochemistry that corresponds to (2a).

Experimental

Crystals of (2a) were obtained from dichloromethane/pentane. TLC: $R_F = 0.34$ (pentane/EtOAc = 70:30); m.p. 503 K. HRMS (EI): analysis calculated for $\text{C}_{28}\text{H}_{30}\text{O}_2$: 398.2246, found: 398.2252. IR (Film): $\nu =$

3028 cm⁻¹ (w, C_{ar}-H), 2959 (m, C-H), 1656 (vs, C=O), 1616 (m, C_{ar}-C_{ar}), 1449 (m), 1349 (m), 763 (s, C_{ar}-H), 705 (s, C_{ar}-H). ¹H NMR (300 MHz, CDCl₃): δ 1.58–1.73 (m, 4H, CH₂CH₂CH₂), 1.95 (t, ⁵J = 1.4 Hz, 6H, CH₃), 2.14–2.38 (m, 8H, COCH₂CH₂CH₂CBn), 4.80 (s, 2H, PhCHCHPh), 7.20–7.32 (m, 10H, aromatic H). ¹³C NMR (75.5 MHz, CDCl₃): δ 11.5 (CH₃), 22.4 (CH₂CH₂CH₂), 26.5 (CH₂CCPh), 37.7 (CH₂CO), 49.7 (PhCH), 127.4 (C_{ar}H), 127.7 (2C, C_{ar}H), 128.8 (2C, C_{ar}H), 132.6 (PhCHCCCO), 139.4 (C_{ar}), 157.3 (PhCHCCCO), 199.2 (CO). MS (EI), m/z (%): 398 (1) [M⁺], 200 (50) [C₁₄H₁₆O⁺], 199 (100) [M⁺ - C₁₄H₁₅O], 184 (25) [199 - CH₃⁺], 129 (29) [184 - C₃H₅O⁺], 91 (30) [C₇H₇⁺].

Crystal data

C₂₈H₃₀O₂
M_r = 398.52
 Monoclinic, *P*2₁/*n*
a = 10.8658 (7) Å
b = 9.4435 (5) Å
c = 11.7323 (8) Å
 β = 112.740 (6)°
V = 1110.29 (12) Å³
Z = 2
D_x = 1.192 Mg m⁻³
 Cu Kα radiation
 Cell parameters from 25 reflections
 θ = 40.3–46.2°
 μ = 0.57 mm⁻¹
T = 213 (2) K
 Prism, colourless
 0.50 × 0.50 × 0.20 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
 ω scans
 Absorption correction: ψ scan (SHELXTL; Sheldrick, 1996)
T_{min} = 0.765, *T_{max}* = 0.895
 2229 measured reflections
 2116 independent reflections
 1794 reflections with *I* > 2σ(*I*)
R_{int} = 0.039
 θ_{max} = 69.9°
h = 0 → 13
k = -11 → 0
l = -14 → 13
 2 standard reflections
 frequency: 120 min
 intensity decay: 3%

Refinement

Refinement on *F*²
R[*F*² > 2σ(*F*²)] = 0.058
wR(*F*²) = 0.165
S = 1.07
 2116 reflections
 187 parameters
 H atoms treated by a mixture of independent and constrained refinement
w = 1/[σ²(*F_o*²) + (0.0912*P*)² + 0.2417*P*]
 where *P* = (*F_o*² + 2*F_c*²)/3
 (Δ/σ)_{max} < 0.001
 Δρ_{max} = 0.22 e Å⁻³
 Δρ_{min} = -0.18 e Å⁻³
 Extinction correction: SHELXL97
 Extinction coefficient: 0.0092 (16)

Table 1

Selected geometric parameters (Å, °).

C1–C1'	1.525 (3)	C2'–C3'	1.484 (3)
C1–C1 ¹	1.549 (4)	C3'–C4'	1.496 (3)
C1'–C2'	1.350 (3)	C4'–C5'	1.511 (3)
C1'–C6'	1.511 (3)	C5'–C6'	1.516 (3)
C1'–C1–C1 ¹	111.61 (19)	C2'–C3'–C4'	118.82 (17)
C1 ¹ –C1–C1'	113.01 (19)	C3'–C4'–C5'	111.72 (19)
C2'–C1'–C6'	121.83 (17)	C4'–C5'–C6'	109.34 (18)
C1'–C2'–C3'	119.84 (17)	C1'–C6'–C5'	112.56 (17)

Symmetry code: (i) -x, 1 - y, 2 - z.

