

4-Ethoxycarbonyl-3-hydroxy-3-phenylcyclohexanone

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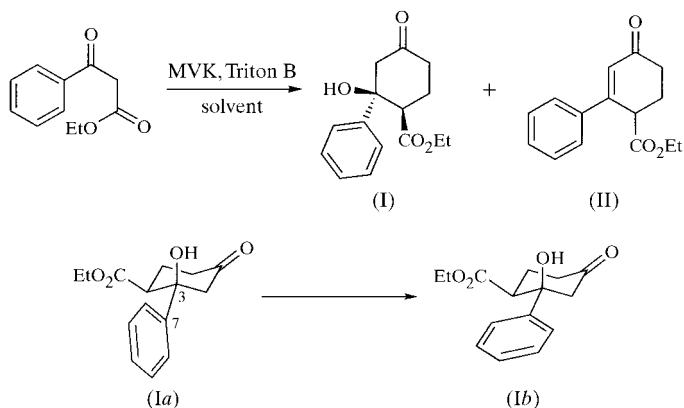
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The title compound, ethyl 2-hydroxy-4-oxo-2-phenylcyclohexanecarboxylate, $C_{15}H_{18}O_4$, was obtained by a Michael–Aldol condensation and has the cyclohexanone in a chair conformation. The attached hydroxy, ethoxycarbonyl and phenyl groups are disposed in β -axial, β -equatorial and α -equatorial configurations, respectively. An intermolecular hydrogen bond, with an $O \cdots O$ distance of 2.874 (2) Å, links the OH group and the ring carbonyl. Weak intermolecular $C-H \cdots O=C$ (ester and ketone), $O-H \cdots O=C$ (ketone) and $C-H \cdots OH$ hydrogen bonds exist.

Comment

In our current research into the 1,5- to 1,3-diketone rearrangement (Jiménez-Cruz *et al.*, 1998, 2000) *versus* the consecutive Michael addition–Aldol dehydration, the title compound, (I), was obtained in 68% yield by the reaction of ethyl benzoylacetate and methyl vinyl ketone, using Triton B in anhydrous tetrahydrofuran as the solvent.



Previously, this conversion was reported by Walker (1955) to give a mixture of products using aqueous *tert*-butyl alcohol as solvent: (I) as a white powder (21% yield) and the oily compound (II) (55% yield). Structural studies of (I) have not previously been reported. We describe here the X-ray struc-

ture analysis of (I) in order to observe the configuration of the groups attached to the cyclohexanone ring.

A molecular perspective drawing of (I) is shown in Fig. 1. The crystal structure, with the hydrogen-bonded chains along **b**, is shown in Fig. 2, and selected bond distances and angles are given in Table 1. The molecule consists of a cyclohexanone ring, which displays the chair conformation, and hydroxy, phenyl and ethoxycarbonyl groups, which adopt β -axial, α -equatorial and β -equatorial configurations, respectively.

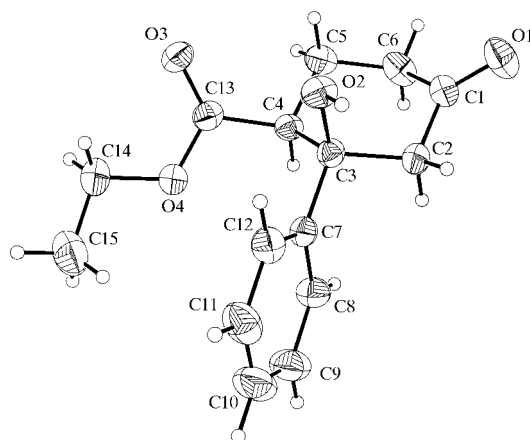


Figure 1

A molecular view of (I) with the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

By comparing (I) with similar 4-substituted 3-phenylcyclohexanones described in the Cambridge Structural Database (*CONQUEST*, Version 1.0; Cambridge Structural Database, 2000), we found that 4-ethoxycarbonyl-3-ethoxypropanoyl-3-phenylcyclohexanone, (III) (Brunner & Maas, 1995), showed a phenyl group in a β -axial position and an ethoxycarbonyl group in an α -axial position, but in 4-cyano-4-*tert*-butoxycarbonyl-3,5-diphenylcyclohexanone, (IV) (Rowland *et al.*, 1998), and 5-hydroxy-5-methyl-2,4-bis(methylcarbamoyl)-3-(3-nitrophenyl)cyclohexanone, (V) (Ravikumar & Mehdi, 1993), the phenyl groups are disposed in α -equatorial positions.

The $C1(=O1)-C2-C6$ fragment in the cyclohexanone ring is practically planar [mean deviation 0.0038 (6) Å] and the $C1=O1$ bond distance [1.220 (3) Å] is within the normal range, similar results being found in (III) and (IV).

The phenyl group at C3 is planar [mean deviation 0.0017 (6) Å] and it is inclined at an angle of 86.09 (8)° to the best plane described by C1, C2, C4 and C5 [mean deviation 0.0138 (6) Å]. This value is larger than those described in the other 3-phenylcyclohexanones cited above [81.4° in (III), 61.6° in (IV) and 77° in (V)]. The deviation from a right angle in (I) is caused by both steric and electronic repulsion between the phenyl group and the carboxy group ($C13/O3/O4$) in the 4 β -equatorial position, which have an angle of 54.52 (9)° between them. This is similar to the values in (IV) (58.3°) and (V) (53.6°). The plane described by C1, C2, C4 and C5 forms an angle of 39.21 (13)° with the ethoxycarbonyl group, which is smaller than in (III) (79.6°), (IV) (90°) or (V) (76.1°).

This orientation of the phenyl group in the cyclohexanone ring, shown in (Ia), can be understood by comparison with the other space-orientated structure, (Ib), derived from the concerted rotation of the phenyl group around the C3—C7 bond by 90°. *PM3* (Dewar *et al.*, 1985) and *AM1* (Stewart, 1989) semi-empirical calculations of the optimized geometries using *SPARTAN* (Wavefunction, 1995) indicated that the orientation found, (Ia), is more stable than (Ib) by 14.8 and 17.8 kJ mol⁻¹, respectively, for these methods.

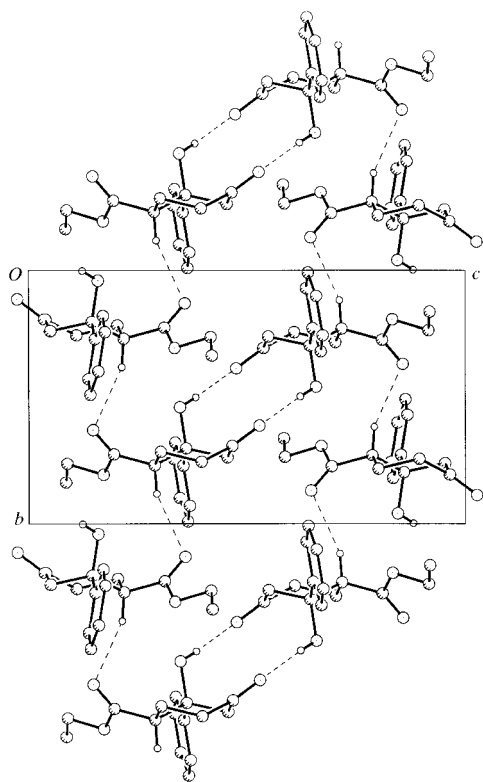


Figure 2
The packing diagram of (I) showing the hydrogen-bonded chains of the molecules along *b*.

The molecules in the crystal of (I) are linked by intermolecular O2—H2...O1 hydrogen bonds (Table 2) and are stacked as dimers along the [010] direction. These dimers are joined by different weak C—H...O intermolecular bonds involving the ester and hydroxy groups. These hydrogen bonds contribute to stabilizing the crystal structure (Fig. 2).

Experimental

Compound (I) was prepared by the slow addition of freshly distilled methyl vinyl ketone (0.17 mol) to a solution of ethyl benzoylacetate (0.13 mol) and Triton B (0.1 mol) in anhydrous tetrahydrofuran (60 ml) under a nitrogen atmosphere at 283 K. After stirring for 6 h (thin-layer chromatography control), the mixture was added to cold water (30 ml). After extraction with dichloromethane (3 × 100 ml) and washing with water (2 × 100 ml), the solid crude product was recrystallized from ethanol–water in 68% yield. White crystals of (I) were grown by slow evaporation from an ethanol–water solution (70:30) at room temperature (m.p. 392–394 K).

Crystal data

C ₁₅ H ₁₈ O ₄	$D_x = 1.274 \text{ Mg m}^{-3}$
$M_r = 262.29$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 40 reflections
$a = 10.601(2) \text{ \AA}$	$\theta = 5.42\text{--}24.60^\circ$
$b = 8.673(2) \text{ \AA}$	$\mu = 0.092 \text{ mm}^{-1}$
$c = 15.322(5) \text{ \AA}$	$T = 293(2) \text{ K}$
$\beta = 103.81(2)^\circ$	Prism, colourless
$V = 1368.0(6) \text{ \AA}^3$	$0.38 \times 0.24 \times 0.10 \text{ mm}$
$Z = 4$	

Data collection

Siemens <i>P4/PC</i> diffractometer	$h = 0 \rightarrow 14$
$\omega/2\theta$ scans	$k = 0 \rightarrow 12$
4191 measured reflections	$l = -21 \rightarrow 20$
3996 independent reflections	3 standard reflections
1517 reflections with $I > 2\sigma(I)$	every 97 reflections
$R_{\text{int}} = 0.033$	intensity decay: <2%
$\theta_{\text{max}} = 30^\circ$	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0481P)^2]$
$R(F) = 0.048$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.128$	$(\Delta/\sigma)_{\text{max}} = 0.007$
$S = 0.765$	$\Delta\rho_{\text{max}} = 0.18 \text{ e \AA}^{-3}$
3996 reflections	$\Delta\rho_{\text{min}} = -0.17 \text{ e \AA}^{-3}$
176 parameters	Extinction correction: <i>SHELXL97</i>
H atoms treated by a mixture of independent and constrained refinement	(Sheldrick, 1997)
	Extinction coefficient: 0.0071 (11)

Table 1

Selected geometric parameters (\AA , $^\circ$).

O1—C1	1.220 (3)	C1—C6	1.497 (3)
O2—C3	1.427 (3)	C3—C7	1.536 (3)
O3—C13	1.203 (3)	C4—C13	1.524 (3)
O4—C13	1.337 (3)	C7—C12	1.386 (3)
C1—C2	1.496 (3)	C7—C8	1.401 (3)
C13—O4—C14	116.98 (19)	O2—C3—C4	104.75 (17)
O1—C1—C2	122.5 (2)	C7—C3—C4	112.49 (16)
O1—C1—C6	122.9 (2)	C12—C7—C8	118.5 (2)
C2—C1—C6	114.64 (18)	C12—C7—C3	121.7 (2)
O2—C3—C7	112.64 (18)	C8—C7—C3	119.8 (2)
O2—C3—C2	108.97 (17)		

Table 2

Hydrogen-bonding and short-contact geometry (\AA , $^\circ$).

$D\text{—}H\cdots A$	$D\text{—}H$	$H\cdots A$	$D\cdots A$	$D\text{—}H\cdots A$
O2—H2...O1 ⁱ	0.82 (3)	2.06 (3)	2.874 (2)	174 (2)
C6—H6A...O3 ⁱⁱ	0.97	2.78	3.569 (3)	139
C8—H8...O3 ⁱⁱ	0.93	2.74	3.619 (3)	158
C5—H5A...O2 ⁱⁱ	0.97	2.84	3.535 (3)	129
C4—H4...O3 ⁱⁱ	0.98	2.44	3.351 (3)	155

Symmetry codes: (i) $1-x, 1-y, 1-z$; (ii) $1-x, y-\frac{1}{2}, \frac{3}{2}-z$.

The positional parameters of the hydroxy H atom were refined, with a fixed $U_{\text{iso}}(\text{H2}) = 1.2U_{\text{eq}}(\text{O2})$; those of the other H atoms were calculated geometrically and they were refined as riding, with a fixed $U_{\text{iso}} = 1.2U_{\text{eq}}$ of the parent atom and with C—H distances in the range 0.93–0.97 \AA .

Data collection: *XSCANS* (Siemens, 1994); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine

structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL/PC* (Sheldrick, 1990); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1318). Services for accessing these data are described at the back of the journal.

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