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(1*R*,2*S*,5*R*)-5-Methyl-2-(1-methyl-1-phenylethyl)cyclohexyl chloroacetate

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Key indicators

Single-crystal X-ray study
T = 100 K
Mean σ(C–C) = 0.002 Å
R factor = 0.033
wR factor = 0.085
Data-to-parameter ratio = 25.2

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

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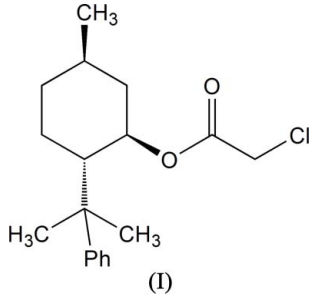
The title compound, $C_{18}H_{25}ClO_2$, is an intermediate for the chiral auxiliary (−)-8-phenylmenthol *en route* from (*R*)-(+)-pulegone. Its crystal structure was determined in order to relate the stereochemistry of the compound to that of other 8-arylmenthol esters. The compound crystallizes with an unusually elongated unit cell, *c*:*a* = 42.287:8.8672.

Comment

The chiral auxiliary (−)-8-phenylmenthol has proved to be a superior face-differentiating agent in asymmetric organic synthesis compared with other chiral terpene alcohols such as menthol or borneol. Starting from (*R*)-(+)-pulegone, 8-phenylmenthol is readily available in a three-step synthesis *via* conjugate addition of phenylmagnesiumbromide/CuBr and carbonyl reduction with Na/2-propanol as a 87:13 mixture of diastereomers (Ort, 1987), which are then separated by fractional crystallization of the chloroacetic acid esters from diethyl ether/hexane to give diastereomerically pure (I) as the major product. This well crystallizing and stable ester is used as a storage form because (−)-8-phenylmenthol, available from (I) by saponification, is unstable (Herzog & Scharf, 1986).



(I)

In the solid state, the cyclohexane ring of (I) adopts the usual chair conformation with all substituents in equatorial ring positions (Fig. 1). The stereochemistry of the compound is basically determined by the orientation of the phenyl substituent relative to the cyclohexane ring, defined by the torsion angle *T*1 = C13—C8—C7—C6 = 80.2 (1)° for (I); the value of this angle means that the phenyl ring is *syn* oriented to O1 enabling a substantial contact between this O atom and the phenyl π electrons. This leads to a characteristic short intramolecular contact O1···C6 = 2.897 (2) Å. A search in the Cambridge Structural Database (Version 5.27; Allen, 2002) revealed that 39 of 57 related 8-arylmentholesters prefer this type of conformation, showing the following mean values for the two quantities defined above: *T*1 = 73 (5)° (range 61–83°) and O1···C6 = 2.88 (6) Å (range 2.79–3.02 Å). If the acyl group replacing chloroacetate in (I) becomes bulky, then the

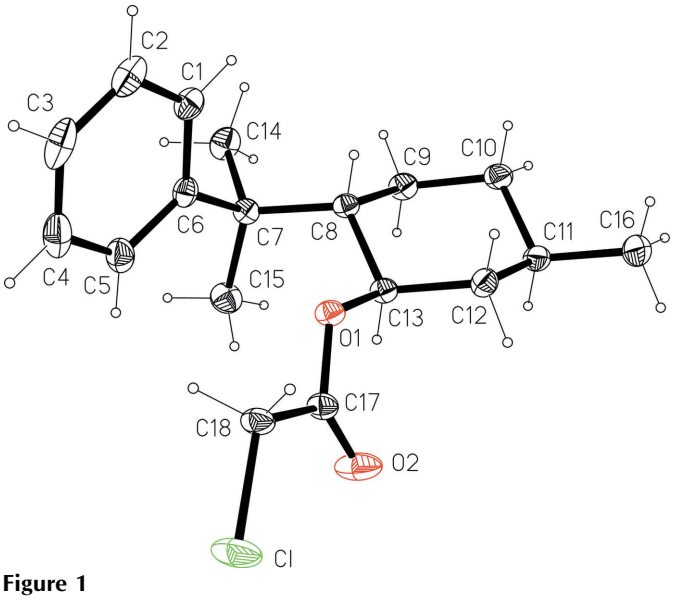


Figure 1
A perspective view of (I). Displacement ellipsoids are shown at the 50% probability level.

phenyl ring may flip about the C8—C7 bond axis by ∼120° in a clockwise direction, thereby moving phenyl C6 to the former C14 position (Fig. 1). 16 out of the 57 compounds show this feature, having a mean value $T1 = -171\,(5)^\circ$. Only two compounds adopt the third possible orientation where phenyl C6 moves into C15 position [$T1 = -67\,(3)^\circ$]. In this case the phenyl ring interferes with two adjacent axial H atoms of the cyclohexyl ring, which is clearly disfavoured. Another feature of interest is the orientation of the acyl group O1—C17═O2 relative to the cyclohexane ring, defined in (I) by $T2$ = C8—C13—O1—C17 = 150.65 (9)°. Interestingly, all 57 related compounds adopt this type of orientation with a mean value of $T2 = 146\,(13)^\circ$. Hence, a moderately inclined pseudo-axial orientation of C17—O2 relative to cyclohexane and a short distance O2···H13 [2.39 Å for (I)] are strongly favoured.

Experimental

Compound (I) was synthesized according to a literature method (Ort, 1987) and crystallized from ethanol (Sieder, 2000). Spectroscopic (NMR and IR) and physical data agreed with the literature (Ort, 1987; Herzog & Scharf, 1986).

Crystal data

$C_{18}H_{25}ClO_2$
$M_r = 308.83$
Tetragonal, $P4_32_12$
$a = 8.8672\,(4)$ Å
$c = 42.287\,(2)$ Å
$V = 3324.9\,(3)$ Å^3
$Z = 8$
$D_x = 1.234$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 0.23$ mm^{-1}
$T = 100\,(2)$ K
Block, colourless
0.48 × 0.36 × 0.28 mm

Data collection

Bruker SMART CCD diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2003)
$T_{min} = 0.862$, $T_{max} = 0.937$
49620 measured reflections
4856 independent reflections
4760 reflections with $I > 2\sigma(I)$
$R_{int} = 0.025$
$\theta_{max} = 30.0^\circ$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.033$
$wR(F^2) = 0.085$
$S = 1.10$
4856 reflections
193 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0481P)^2 + 0.6838P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.34$ e Å^{-3}
$\Delta\rho_{min} = -0.19$ e Å^{-3}
Absolute structure: Flack (1983), 1992 Friedel pairs
Flack parameter: 0.02 (4)

Table 1
Selected geometric parameters (Å, °).

Cl—C18	1.7644 (11)	O2—C17	1.1970 (14)
O1—C17	1.3432 (12)	C17—C18	1.5133 (15)
O1—C13	1.4638 (12)		
C13—O1—C17	116.46 (8)	O2—C17—C18	126.17 (10)
O1—C17—O2	125.30 (10)	C17—C18—Cl	111.38 (8)
O1—C17—C18	108.53 (9)		
C13—C8—C7—C6	80.20 (11)	O1—C17—C18—Cl	176.92 (8)
C8—C13—O1—C17	150.65 (9)		

All H atoms were placed in calculated positions and thereafter treated as riding (C—H = 0.95–1.00 Å). A torsional parameter was refined for each methyl group. The constraints $U_{iso}(H) = 1.2U_{eq}(C_{alkyl,\ aryl})$ and $U_{iso}(H) = 1.5U_{eq}(C_{methyl})$ were used.

Data collection: *SMART* (Bruker, 2003); cell refinement: *SAINT* (Bruker, 2003); data reduction: *SAINT*, *SADABS* (Bruker, 2003) and *XPREP* (Bruker, 2003); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 2003); software used to prepare material for publication: *SHELXTL*.

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