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rac-(1*S*,6*S*)-Methyl 6-methyl-2-oxobicyclo[4.1.0]-heptane-1-carboxylate

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Key indicators

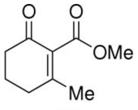
Single-crystal X-ray study
T = 120 K
Mean σ(C–C) = 0.002 Å
R factor = 0.040
wR factor = 0.109
Data-to-parameter ratio = 19.3

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

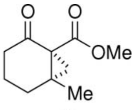
The crystal structure of the title compound, $C_{10}H_{14}O_3$, was investigated as part of a study of the chemistry of nucleophilic 1,4-additions to highly electrophilic C═C double bonds. The cyclohexane ring adopts a half-chair conformation. The crystal packing is stabilized by van der Waals forces.

Comment

As part of a study investigating the chemistry of nucleophilic 1,4-additions to highly electrophilic C═C double bonds, α,β-unsaturated ketoester (II) was prepared (Belmont *et al.*, 1985). It is known that enones with enolizable α-protons often undergo deprotonation instead of addition when subjected to dimethylsulfoxonium methylide in a Corey–Chaykovsky cyclopropanation reaction, although not in all cases (Thompson *et al.*, 1992). Utilizing freshly prepared dimethylsulfoxonium methylide as the nucleophile no deprotonation was observed and cyclopropane (I) (Yang *et al.*, 2002) was obtained in an impressive 89% yield as a white solid.



(II)



(I)

The crystal structure of (I) shows the expected bicyclo[4.1.0]heptane skeleton (Fig. 1). The space group is centrosymmetic and therefore equal numbers of the enantiomers are present. The bond lengths and angles are as expected for this type of compound (Allen *et al.*, 1987). The cyclohexane ring adopts a half-chair conformation and the ester group is oriented perpendicular to the cyclohexane ring to minimize steric interactions with the oxygen of the ketone and the C9 methyl group, while the π orbitals of the ester overlap to some extent with the Walsh orbitals of the cyclopropane ring. The crystal packing is stabilized by van der Waals forces.

Experimental

To a suspension of KH (413 mg, 10.3 mmol, rinsed twice with pentane) in tetrahydrofuran (10 ml) was added trimethylsulfoxonium chloride (0.882 g, 6.86 mmol) and the reaction mixture was stirred at reflux under argon for 4 h. The mixture was vacuum-filtered and the concentration determined to be 0.71 *M*. To a flask containing ketoester (II) (250 mg, 1.49 mmol) was added a solution of freshly prepared dimethylsulfoxonium methylide (2.3 ml, c = 0.71 *M*) and the reaction was stirred for 45 min, then quenched with H_2O (7 ml). Et_2O (7 ml) was added and the aqueous phase was extracted with Et_2O

(2 × 10 ml) and the combined organic phases were dried (Na_2SO_4), filtered, and evaporated to dryness *in vacuo*. The residue was purified by flash column chromatography on silica gel (Et_2O–*n*-pentane, 1:9–1:2), affording cyclopropane (I) (242 mg, 89%) as a white solid, which was recrystallized from diethyl Et_2O/*n*-pentane (1:4), yielding single crystals suitable for X-ray measurements.

Crystal data

$C_{10}H_{14}O_3$
$M_r = 182.21$
Monoclinic, $P2_1/c$
$a = 7.3651$ (6) Å
$b = 7.2746$ (6) Å
$c = 17.5576$ (14) Å
$\beta = 92.204$ (2)°
$V = 940.01$ (13) Å^3

$Z = 4$
$D_x = 1.288$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 0.09$ mm^{-1}
$T = 120$ (2) K
Block, colourless
0.48 × 0.30 × 0.17 mm

Data collection

Bruker SMART 1K CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2001*a*)
$T_{min} = 0.846$, $T_{max} = 1.000$

12246 measured reflections
2274 independent reflections
2035 reflections with $I > 2/s(I)$
$R_{int} = 0.021$
$\theta_{max} = 28.0°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.040$
$wR(F^2) = 0.109$
$S = 1.09$
2274 reflections
118 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0601P)^2 + 0.246P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.39$ e Å^{-3}
$\Delta\rho_{min} = -0.18$ e Å^{-3}

All H atoms were positioned geometrically and refined using a riding model, with C—H = 0.98 Å and $U_{iso}(H) = 1.5U_{eq}(C)$ for methyl H atoms, and C—H = 0.99 Å and $U_{iso}(H) = 1.2U_{eq}(C)$ for the remaining H atoms.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 1998); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2001*b*); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

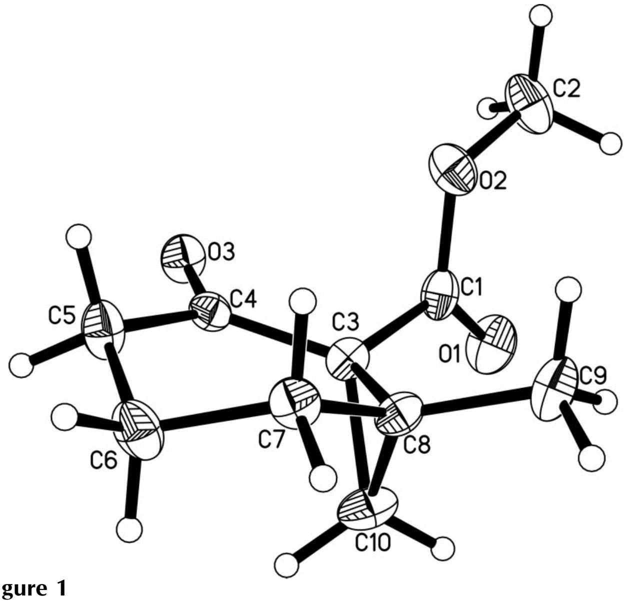


Figure 1
The molecular structure and the atom-labelling scheme of (I). Displacement ellipsoids are drawn at the 50% probability level.

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