# (2S,7R)-2-Benzyloxy-7-bromomethyl-1,2,7-trimethylbicyclo[2.2.1]heptane

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The title compound, $C_{18}H_{25}BrO$, is a chiral bicyclo[2.2.1]-heptane derivative with the benzyloxy group oriented *endo* with respect to the ring.

## Comment

The uniqueness of the structure of camphor is illustrated by a wide variety of intriguing structural transformations that frequently involve fascinating rearrangement processes (Money, 1985). Studies on these transformations have produced much chemical knowledge on theoretical and mechanistic aspects of organic chemistry over the past century and have offered synthetically useful chiral building blocks from readily available natural camphor.



(I)
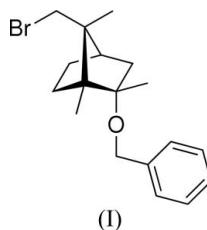
Starting from 9-bromocamphor (Cachia *et al.*, 1976), a series of routine transformations including Wittig olefination by $Ph_3P{=}CH_2$ (Greenwald *et al.*, 1963), epoxidation by *m*-CPBA (3-chloroperoxybenzoic acid) and reduction by $LiAlH_4$, were performed. The resulting *endo*-tertiary alcohol (*A*) was protected by conversion into its benzyl derivative (I) in order to determine the hydroxyl configuration.

The molecular structure of the title compound, (I), is illustrated in Fig. 1. The chiral bicyclo[2.2.1]heptane group is not symmetrical due to the influence of the substituents. For example, the C8—C9—C10 angle is larger than the corresponding C10—C11—C12 angle. The benzyloxy group is oriented *endo* with respect to the ring.

## Experimental

To a stirred solution of the tertiary alcohol (*A*) (see *Comment*) (169 mg, 0.5 mmol) in THF (4 ml) was added NaH (20 mg, 60% dispersion in mineral oil) followed by the addition of $Bu_4NI$ (20 mg) and benzyl bromide (105 mg, 0.6 mmol). The mixture was stirred for 1 h and quenched with sat. $NaHCO_3$ (2 ml) and extracted with $Et_2O$ (50 ml). The organic phase was washed with water (5 ml) and brine (5 ml), dried over $MgSO_4$ and concentrated. The crude residue was purified by flash chromatography on silica gel (petroleum ether/AcOEt = 30:1) to give 135 mg (80%) of the benzyl ether derivative (I) as colorless crystals. Single crystals suitable for X-ray determination were obtained by slow evaporation of a hexane solution over a period of several days [m.p. 345–346 (*n*-hexane)].

# organic papers

## Crystal data

C$_{18}$H$_{25}$BrO
$M_r = 337.29$
Monoclinic, $P2_1$
$a = 7.1721\ (3)$ Å
$b = 7.9624\ (3)$ Å
$c = 14.5849\ (6)$ Å
$\beta = 95.719\ (2)°$
$V = 828.76\ (6)$ Å$^3$

$Z = 2$
$D_x = 1.352$ Mg m$^{-3}$
Mo $K\alpha$ radiation
$\mu = 2.48$ mm$^{-1}$
$T = 294\ (2)$ K
Block, colorless
$0.43 \times 0.27 \times 0.26$ mm

## Data collection

Bruker APEX CCD area-detector
   diffractometer
$\varphi$ and $\omega$ scans
Absorption correction: none
5095 measured reflections

3480 independent reflections
2336 reflections with $I > 2\sigma(I)$
$R_{int} = 0.025$
$\theta_{max} = 27.5°$

## Refinement

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)] = 0.038$
$wR(F^2) = 0.096$
$S = 0.97$
3480 reflections
185 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0411P)^2]$
   where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.32$ e Å$^{-3}$
$\Delta\rho_{min} = -0.37$ e Å$^{-3}$
Extinction correction: SHELXL97
Extinction coefficient: 0.060 (4)
Absolute structure: Flack (1983),
   1440 Friedel pairs
Flack parameter: 0.030 (12)



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

## Table 1
Selected geometric parameters (Å, °).

| | | | |
|---|---|---|---|
| Br1—C18 | 1.978 (3) | | |
| C14—C18—Br1 | 112.7 (2) | C12—C11—C10 | 102.8 (3) |
| C10—C9—C8 | 105.8 (4) | C7—O1—C8 | 117.3 (3) |

All H atoms were positioned geometrically and refined using a riding model [C—H = 0.98 (methine), 0.97 (methylene), 0.96 (methyl) and 0.93 Å (aromatic)], with $U_{iso}$(H) = 1.2 or 1.5 times $U_{eq}$(C).

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 2000); software used to prepare material for publication: *SHELXTL*.
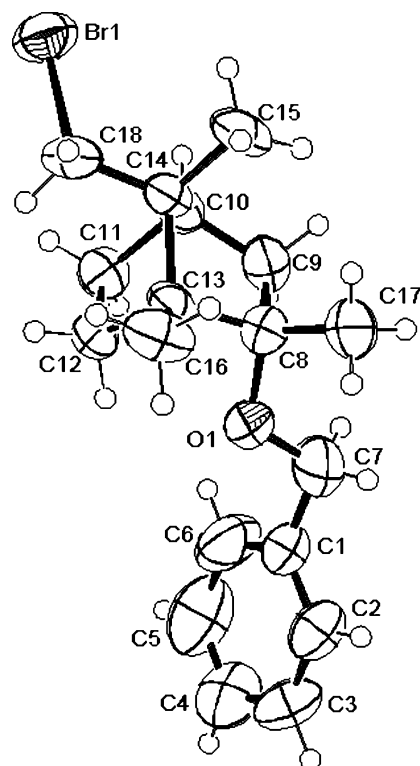
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