

**(1RS,2SR,6SR,8SR)-2,6-dimethyl-8-
(phenylsulfonyl)bicyclo[4.2.0]octan-1-ol**

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Key indicators

Single-crystal X-ray study
 $T = 295\text{ K}$
Mean $\sigma(\text{C}-\text{C}) = 0.004\text{ \AA}$
 R factor = 0.047
 wR factor = 0.131
Data-to-parameter ratio = 19.3For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.(1*RS*,2*SR*,6*SR*,8*SR*)-2,6-Dimethyl-8-(phenylsulfonyl)bicyclo[4.2.0]octan-1-ol

The title compound, $\text{C}_{16}\text{H}_{22}\text{O}_3\text{S}$, exhibits a conformational arrangement that permits intramolecular $\text{O}-\text{H}\cdots\text{O}-\text{S}$ hydrogen bonds. Intermolecular bifurcated hydrogen bonding between the hydroxyl H and the sulfone O atoms, observed in the unmethylated derivative, is disrupted by the presence of the methyl group at the 6-position.

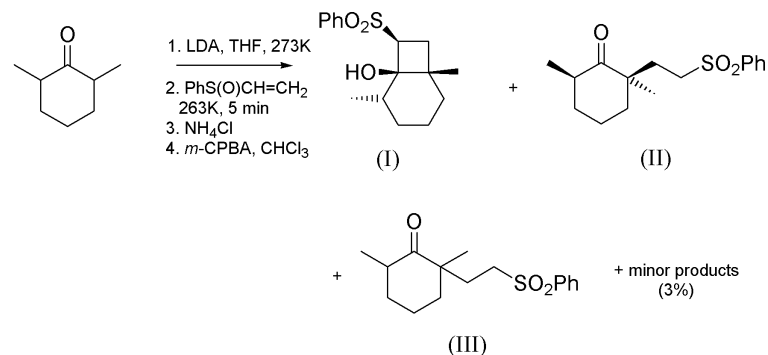
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Comment

We have recently shown that a novel cyclization reaction between the lithium enolates of simple unfunctionalized ketones and phenyl vinyl sulfoxide provides a simple and convenient route to the preparation of fused carbocyclic ring systems bearing a bridgehead hydroxyl group (Loughlin & McCleary, 2003; Loughlin, Rowen & Healy, 2002). In the current study, reaction of the lithium enolate of 2,6-dimethylcyclohexan-1-one (obtained from lithium diisopropylamide, LDA) with phenyl vinyl sulfoxide and subsequent oxidation with *m*-chloroperoxybenzoic acid (*m*-CPBA) generated a novel dimethylbicyclo[4.2.0]octan-1-ol, (I).



A bicyclo[4.2.0]octan-1-ol with a methyl bridgehead substituent can be perceived as a key structural component of, for example, natural products such as melleolide K (Momose *et al.*, 2000) and cyclobutatusin (Zelnik *et al.*, 1977; Wang *et al.*, 1974) and as a synthetic intermediate in natural product synthesis (Morisaki *et al.*, 1985, Ayer *et al.*, 1981). Under the present unoptimized reaction conditions, (I) was formed as the major bicyclo[4.2.0]octan-1-ol isomer in a 22:78 ratio of (I):(II) (Loughlin, McCleary & Healy, 2002) and (III) from 2,6-dimethylcyclohexan-1-one and phenyl vinyl sulfoxide with less than 5 percent of other products observed (see Scheme). Here we report the synthesis, isolation and solid-state structural characterization of the novel bicyclo[4.2.0]octan-1-ol (I), Fig. 1. The S—O2 and S—O3 bonds are directed away from the bicyclo[4.2.0]alkan-1-ol ring, whereas the phenyl group is oriented towards this ring. Intramolecular hydrogen-bonding

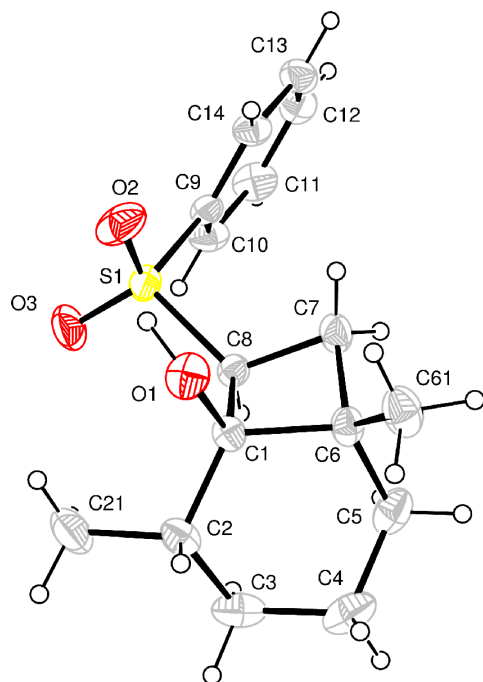


Figure 1
ORTEP-3 (Farrugia, 1997) plot, showing the atomic numbering scheme for the molecule of (I). Displacement ellipsoids for non-H atoms are drawn at the 30% probability level.

interactions are observed between the hydroxyl H atom and the sulfone O atom O2, with an O1...O2 distance of 2.765 (3) Å and an estimated O—H...O angle of 153°. The six-membered ring displays a pseudo-chair conformation. In the previously reported 8-(phenylsulfonyl)bicyclo[4.2.0]octan-1-ol, which lacks the 2,6-dimethyl groups of compound (I), the orientation of the six-membered ring allows intermolecular bifurcated hydrogen bonding between the hydroxyl H atom and the sulfone O atoms (Healy *et al.*, 2002). However, in compound (I) the presence of the methyl group in the C6 position now disrupts this and intermolecular hydrogen bonding is not observed in the solid-state structure of (I).

Experimental

2,6-Dimethylcyclohexanone (0.55 ml, 3.96 mmole), lithium diisopropylamide (1.55 M, 2.56 ml, 3.96 mmole) in THF, and phenyl vinyl sulfoxide (0.55 ml, 3.96 mmol) were reacted at 263 K with a 5 min reaction time, worked up and subsequently oxidized with *m*-CPBA (1 equiv) in chloroform (50 ml) as described elsewhere (Loughlin, Rowen & Healy, 2002). After silica chromatography (hexane:ethyl acetate, 80:20), compound (I) was obtained (197 mg, 17%) in conjunction with monoalkylated 2,6-dimethylcyclohexanone, compounds (II) and (III) (577 mg, 53%) and other minor products (3%). An analytically pure sample of compound (I) was obtained by semi-preparative HPLC (hexane–ethyl acetate, 90:10, retention time 17.4 min, 3 ml min⁻¹). Colourless crystals of compound (I) (m.p. 381.5–382.1 K) were isolated by slow evaporation of a hexane:ethyl acetate (90:10) solution of (I). Analysis found: C 65.34, H 7.64, O 16.36%; calculated for C₁₆H₂₂O₃: C 65.27, H 7.53, O 16.30%.

Crystal data

C₁₆H₂₂O₃S
M_r = 294.41
 Monoclinic, *P*2₁/*c*
a = 11.340 (3) Å
b = 18.026 (6) Å
c = 7.8442 (16) Å
 β = 106.788 (18)°
V = 1535.1 (7) Å³
Z = 4

D_x = 1.274 Mg m⁻³
 Mo K α radiation
 Cell parameters from 25 reflections
 θ = 12.6–17.4°
 μ = 0.22 mm⁻¹
T = 295 K
 Prism, colourless
 0.40 × 0.35 × 0.20 mm

Data collection

Rigaku AFC-7R diffractometer
 ω -2 θ scans
 Absorption correction: none
 4336 measured reflections
 3518 independent reflections
 1904 reflections with *I* > 2 σ (*I*)
*R*_{int} = 0.053

θ_{\max} = 27.5°
h = -6 → 14
k = -23 → 10
l = -10 → 9
 3 standard reflections
 every 150 reflections
 intensity decay: 0.8%

Refinement

Refinement on *F*²
R [*F*² > 2 σ (*F*²)] = 0.047
wR(*F*²) = 0.131
S = 1.00
 3518 reflections
 182 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0382P)^2 + 0.7618P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.23 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.27 \text{ e } \text{Å}^{-3}$

Table 1

Selected geometric parameters (Å, °).

| | | | |
|----------|-------------|-----------|-------------|
| S1—O2 | 1.445 (2) | S1—C9 | 1.768 (3) |
| S1—O3 | 1.432 (3) | O1—C1 | 1.425 (3) |
| S1—C8 | 1.770 (2) | | |
| O2—S1—O3 | 118.11 (14) | O1—C1—C8 | 112.01 (18) |
| O2—S1—C8 | 108.50 (12) | O1—C1—C2 | 108.1 (2) |
| O2—S1—C9 | 107.31 (12) | S1—C8—C1 | 121.69 (16) |
| O3—S1—C8 | 110.16 (13) | S1—C8—C7 | 117.36 (18) |
| O3—S1—C9 | 108.45 (13) | S1—C9—C10 | 119.7 (2) |
| C8—S1—C9 | 103.25 (11) | S1—C9—C14 | 118.67 (19) |
| O1—C1—C6 | 109.7 (2) | | |

H atoms were positioned geometrically (C—H = 0.95, O—H = 0.96 Å) and refined as riding, with *U*_{iso}(H) = 1.2*U*_{eq}(parent atom).

Data collection: *MSC/AFC-7 Diffractometer Control Software for Windows* (Molecular Structure Corporation, 1999); cell refinement: *MSC/AFC-7 Diffractometer Control Software for Windows*; data reduction: *TEXSAN for Windows* (Molecular Structure Corporation, 1997–2001); program(s) used to solve structure: *TEXSAN for Windows*; program(s) used to refine structure: *TEXSAN for Windows* and *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2001) and *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *TEXSAN for Windows* and *PLATON*.

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