The title compound, C$_{15}$H$_{20}$O$_3$S, shows a conformational arrangement of the phenyl ring that permits hydrogen-bonded dimers to be disposed about a centre of symmetry.

Comment

The preparation of fused carbo cyclic ring systems bearing a bridgehead hydroxyl group has been achieved by the reaction between the lithium enolates of simple unfunctionalized ketones and phenyl vinyl sulfoxide (Loughlin et al., 2002; Loughlin & McCleary, 2003; Healy et al., 2002; Loughlin et al., 2003). In the current study, reaction of the lithium enolate of 2-methylcyclohexan-1-one (obtained from lithium diisopropylamide, LDA) with phenyl vinyl sulfoxide and subsequent oxidation with m-chloroperoxybenzoic acid (m-CPBA) generated a novel methylbicyclo[4.2.0]octan-1-ol, compound (I).

Bicyclo[4.2.0]octan-1-ols with a methyl substituent proximal to the bridgehead have been observed as key intermediates in synthetic and mechanistic studies (Blanchard & Burnell, 2001; Syah & Ghisalberti, 1998; Jamart-Gregoire et al., 1995). Under the present unoptimized reaction conditions, (I) was formed as the major bicyclo[4.2.0]octan-1-ol isomer in a 21:14:65 ratio of (I):(II):(III) and (IV) from 2-methylcyclohexan-1-one and phenyl vinyl sulfoxide (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—O3 bond in conjunction with the phenyl group is directed away from the bicyclo[4.2.0]alkan-1-ol ring, whereas the S—O2 bond is oriented towards this ring. The structure of (I) is stabilized by three-centred bifurcated intra- and intermolecular hydrogen bonds between the hydroxyl H and sulfone O atoms, forming a dimeric structure disposed about a crystallographic centre of symmetry (Table 2, Fig. 2). This differs from the chain-like intermolecular hydrogen-bonding pattern previously observed in the analogues of (I) that lack the C2 methyl group (Healy et al., 2002; Loughlin et al., 2003).
Experimental

2-Methylcyclohexanone (0.5 ml, 4.119 mmole) was reacted with lithium diisopropylamide (1.4 M, 2.95 ml, 4.119 mmol) in THF (44.5 ml) at 273 K under nitrogen over a period of 1 h. The reaction vessel was shielded from light. Rapid addition of phenyl vinyl sulf oxide (0.55 ml, 3.119 mmol) at 263 K with a 10 min reaction time and work-up as described elsewhere (Loughlin et al., 2002) gave the crude sulfoxide mixture (1.074 g). This was subsequently oxidized with m-CPBA (1 equiv) in chloroform (50 ml). Work-up of the reaction mixture as described elsewhere (Loughlin et al., 2002) was followed by silica chromatography (hexane:ethyl acetate, 60:40). A mixture of compounds (I)-(IV) (658 mg, 57%) was obtained. An analytically pure sample of compound (I) was obtained by semi-preparative HPLC (hexane–ethyl acetate, 80:20, retention time 11.8 min, 3 ml min⁻¹). Colourless crystals of compound (I) (m.p. 383.2–384.6 K) were isolated by slow evaporation of a hexane–ethyl acetate (80:20) solution of the compound. Analysis found: C 64.52, H 7.36, S 11.32%; calculated for C₁₅H₂₀SO₃: C 64.25, H 7.19, S 11.43%.

Crystal data

C₁₅H₂₀O₃S
M_r = 280.38
Monoclinic, P₂₁/n
a = 12.328 (6) Å
b = 10.362 (4) Å
c = 12.149 (2) Å
 β = 99.60 (3)°
V = 1530.2 (10) Å³
Z = 4
D_x = 1.217 Mg m⁻³
Mo Kα radiation

Cell parameters from 24 reflections
θ = 12.8–16.0°
μ = 0.21 mm⁻¹
T = 295 K

Prism, colourless

0.30 x 0.20 x 0.10 mm

Data collection

Rigaku AFC-7R diffractometer
ω-2θ scans
Absorption correction: none
3987 measured reflections
3516 independent reflections
1717 reflections with I > 2σ(I)

R(int) = 0.067

max = 27.5°
h = -7 to 16
k = 0 to 13
l = -15 to 15
3 standard reflections every 150 reflections
Intensity decay: none

Refinement

Refinement on F²
R[F² > 2σ(F²)] = 0.053
wR(F²) = 0.174
S = 0.98
3516 reflections
173 parameters

H-atoms were positioned geometrically (C–H = 0.95 and O–H = 0.96 Å) and refined as riding, with U_H = 1.2U_eq(parent atom).

Table 1

Selected geometric parameters (Å, °).

<table>
<thead>
<tr>
<th></th>
<th>S1—O₂</th>
<th>1.441 (2)</th>
<th>S1—O₃</th>
<th>1.442 (2)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>S1—C₈</td>
<td>1.765 (4)</td>
<td>S1—C₉</td>
<td>1.764 (4)</td>
</tr>
<tr>
<td>O₂—S₁—O₃</td>
<td>118.05 (14)</td>
<td>O₁—C₁—C₆</td>
<td>117.3 (2)</td>
<td></td>
</tr>
<tr>
<td>O₂—S₁—C₈</td>
<td>106.36 (15)</td>
<td>S₁—C₆—C₁</td>
<td>119.4 (3)</td>
<td></td>
</tr>
<tr>
<td>O₃—S₁—C₈</td>
<td>106.78 (15)</td>
<td>S₁—C₈—C₇</td>
<td>117.5 (3)</td>
<td></td>
</tr>
<tr>
<td>O₃—S₁—C₉</td>
<td>107.55 (15)</td>
<td>S₁—C₉—C₁₀</td>
<td>120.2 (3)</td>
<td></td>
</tr>
<tr>
<td>C₈—S₁—C₉</td>
<td>105.74 (18)</td>
<td>S₁—C₉—C₁₄</td>
<td>119.2 (3)</td>
<td></td>
</tr>
<tr>
<td>O₁—C₁—C₂</td>
<td>107.6 (3)</td>
<td>O₁—C₁—C₂</td>
<td>117.1 (3)</td>
<td></td>
</tr>
</tbody>
</table>

Table 2

Hydrogen-bonding geometry (Å, °).

<table>
<thead>
<tr>
<th>D—H···A</th>
<th>D—H</th>
<th>H···A</th>
<th>D···A</th>
<th>D—H···A</th>
</tr>
</thead>
<tbody>
<tr>
<td>O₁—H₁···O₂</td>
<td>0.96</td>
<td>2.44</td>
<td>3.036 (4)</td>
<td>120</td>
</tr>
<tr>
<td>O₁—H₁···O₂'</td>
<td>0.96</td>
<td>2.02</td>
<td>2.918 (3)</td>
<td>154</td>
</tr>
</tbody>
</table>

Symmetry code: (i) 2–x, 1–y, 2–z.

H atoms were positioned geometrically (C–H = 0.95 and O–H = 0.96 Å) and refined asriding, with U_H = 1.2U_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.

The authors thank Griffith University and the Australian Research Council for financial assistance.

References