organic papers

2-[2'-(Phenylsulfonyl)ethyl]cyclopentanone

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Key indicators

Single-crystal X-ray study
$T = 295$ K
Mean σ(C–C) = 0.003 Å
R factor = 0.042
wR factor = 0.130
Data-to-parameter ratio = 19.1

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

The structure of the title compound, $C_{13}H_{16}O_3S$, prepared by the reaction of the lithium enolate of cyclopentanone with phenylvinyl sulfoxide and subsequent oxidation with *m*-chloroperoxybenzoic acid (*m*-CPBA), shows the phenylsulfonylethyl side chain to be bonded to the cyclopentanone ring in a pseudo-equatorial orientation.

Comment

The structure of the title compound, (I), has been determined as part of an investigation into the reaction of lithium enolates of cycloalkanones with phenyl vinyl sulfoxide. The alkylation of various enolates with vinyl sulfoxides to produce keto sulfoxides has been described (Bienayme & Guicher, 1997; Montgomery & Overman, 1993; Ono *et al.*, 1985; Brown *et al.*, 1983; Seki *et al.*, 1975). In addition, we reported recently the structural characterization of the 2,6-dimethyl-2-[2-(phenylvinylsulfonyl)ethyl]cyclohexanone, (II), in which the substituents were orientated such that the largest alkyl group was placed in an equatorial position (Loughlin *et al.*, 2002). Herein we report the synthesis, isolation and structural characterization of the novel monoalkylated product, (I), arising from the reaction of the lithium enolate of cyclopentanone (obtained from lithium diisopropylamide, LDA) with phenyl vinyl sulfoxide and subsequent oxidation with *m*-chloroperoxybenzoic acid (*m*-CPBA). Compound (I) represents a simple substituted ketone with different internal steric demands to those of the highly substituted cyclohexanone (II).
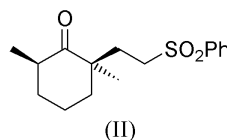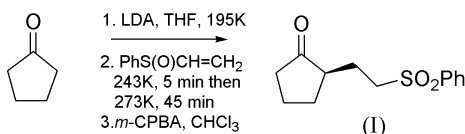
Compound (I) crystallizes in space group $P2_1/n$ with one molecule in the asymmetric unit (Fig. 1). The molecules are separated by normal van der Waals distances (Fig. 2), with the bond lengths in accord with conventional values (Allen *et al.*, 1987). The planes of the SO_2 group and the phenyl ring lie approximately normal to the plane of the alkyl chain. The cyclopentanone ring is planar about carbonyl atom C1, with
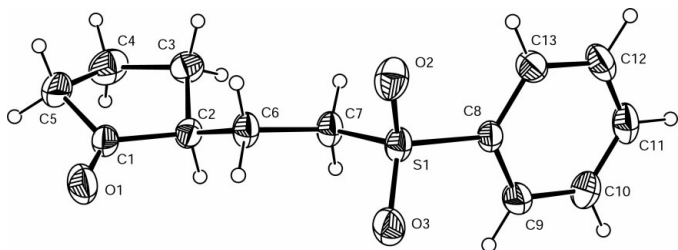
Figure 1
ORTEP-3 (Farrugia, 1997) plot, showing the atomic numbering scheme for the molecule in the asymmetric unit of (I). Displacement ellipsoids for non-H atoms are drawn at the 30% probability level.
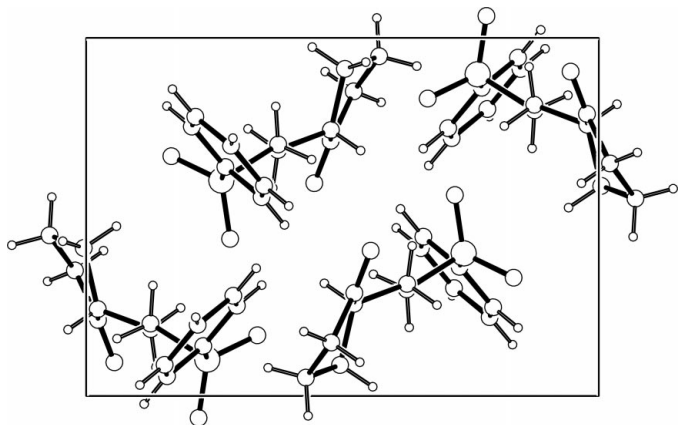

Figure 2
Unit-cell diagram of (I), projected down the *a* axis. The *b* axis is horizontal and the *c* axis is vertical.

C3 located above and C4 located below the plane, giving a puckered conformational structure for the ring. The structure shows that the cyclopentanone ring is alkylated at atom C2 by phenylvinyl sulfoxide, such that the alkyl substituent is placed in a pseudo-equatorial orientation. This corresponds to the equatorial phenylsulfonylethyl side chain in the derivative obtained from oxidation, *viz.* compound (I), where the O1—C1—C2—C6 torsion angle is found to be −42.4 (3)°. The alkyl group is in the expected, more stable, pseudo-equatorial orientation as it is eclipsed by the carbonyl group, corresponding to the more stable conformation of open-chain ketones. This conformation also avoids diaxial interactions (Eliel *et al.*, 1965).

Experimental

Cyclopentanone (0.55 ml, 6.220 mmol) was reacted with lithium diisopropylamide (1.95 *M*, 3.2 ml, 6.220 mmol) in THF (35.5 ml), at 195 K under nitrogen for 5 min. The reaction was warmed to 243 K and phenyl vinyl sulfoxide (0.83 ml, 6.220 mmol) was added over 5 min. The reaction mixture was warmed to 273 K and stirred for 45 min. Upon work-up as described elsewhere (Loughlin *et al.*, 2002), the crude sulfoxide mixture was obtained as a yellow oil (1.365 g) and oxidized to the corresponding sulfone mixture, using the crude sulfoxide mixture (1.365 g, 5.775 mmol) in chloroform (20 ml) and *m*-CPBA (5.775 mmol) in chloroform (30 ml). Work-up of the reaction mixture was followed by silica column chromatography (hexane–ethyl acetate, 60:40). Compound (I) was obtained in conjunction with a mixture of other minor products. An analytically pure sample of compound (I) was obtained by semi-preparative HPLC (hexane–ethyl acetate, 60:40). Colourless crystals of (I) (m.p. 348–349 K) were isolated by slow evaporation of a hexane–ethyl acetate (60:20) solution. Analysis found: C 61.98, H 6.43%; calculated for $C_{13}H_{16}O_3S$: C 61.87, H 6.39%. ν_{max}(KBr)/cm^{-1} 1733, (CO), 1299, (SO$_2$), 1143, (SO$_2$). δ_H(400 MHz,CDCl$_3$, p.p.m.) 7.85–7.93 (2H, *m*, *o*-C$_6$H$_5$), 7.60–7.68 (1H, *m*, *p*-C$_6$H$_5$), 7.50–7.60 (2H, *m*, *m*-C$_6$H$_5$), 3.31 (1H, *ddd*, *J*2′2′ = 7, *J*2′1′ = 3 Hz, 2′-H), 3.16 (1H, *ddd*, *J*2′2′ = 7, *J*2′1′ = 5.5, *J*2′1′ = 3 Hz, 2′-H), 2.00–2.15 (4H, *m*, 2-H, 3-H, 2 × 5-H), 1.93–2.00 (2H, *m*, 4-H, 1′-H), 1.67–1.83 (2H, *m*, 4-H, 1′-H), 1.42–1.52 (1H, *m*, 3-H). δ_C (50 MHz, CDCl$_3$) 219.7 (C-1), 139.3 (*i*-C$_6$H$_5$), 133.7 (*p*-C$_6$H$_5$), 129.7 (*m*-C$_6$H$_5$), 128.3 (*o*-C$_6$H$_5$), 54.0 (C-2′), 47.5 (C-2), 37.4 (C-5), 29.3 (C-3), 22.8 (C-1′), 20.5 (C-4′). ESMS+ 259 (*M*Li$^+$ 94%), 275 (*M*Na$^+$, 100%). HRMS found 253.08884, $C_{13}H_{17}SO_3$ requires 253.0898.

Crystal data

$C_{13}H_{16}O_3S$	$D_x = 1.306$ Mg m^{-3}
$M_r = 252.33$	MoKα radiation
Monoclinic, $P2_1/n$	Cell parameters from 25
$a = 11.986$ (2) Å	reflections
$b = 12.387$ (6) Å	$\theta = 12.8$–$17.3°$
$c = 9.2183$ (13) Å	$\mu = 0.25$ mm^{-1}
$\beta = 110.293$ (14)°	$T = 295$ K
$V = 1283.7$ (7) Å^3	Prismatic, colorless
$Z = 4$	$0.40 \times 0.30 \times 0.30$ mm

Data collection

Rigaku AFC-7*R* diffractometer	$\theta_{max} = 27.5°$
ω–2θ scans	$h = -5 \rightarrow 15$
Absorption correction: none	$k = 0 \rightarrow 16$
3202 measured reflections	$l = -11 \rightarrow 11$
2943 independent reflections	3 standard reflections
2167 reflections with $I > 2\sigma(I)$	every 150 reflections
$R_{int} = 0.041$	intensity decay: 0.2%

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0693P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.042$	$+ 0.2568P]$
$wR(F^2) = 0.130$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.03$	$(\Delta/\sigma)_{max} = 0.001$
2943 reflections	$\Delta\rho_{max} = 0.27$ e Å^{-3}
154 parameters	$\Delta\rho_{min} = -0.35$ e Å^{-3}
H-atom parameters constrained	

Table 1
Selected geometric parameters (Å, °).

S1—O2	1.4323 (18)	S1—C8	1.764 (2)
S1—O3	1.4402 (17)	O1—C1	1.209 (3)
S1—C7	1.767 (2)		
O2—S1—O3	118.14 (10)	O1—C1—C2	124.19 (18)
O2—S1—C7	108.51 (10)	O1—C1—C5	126.6 (2)
O2—S1—C8	108.21 (10)	C2—C1—C5	109.19 (16)
O3—S1—C7	107.91 (10)	S1—C7—C6	110.13 (14)
O3—S1—C8	108.71 (9)	S1—C8—C9	119.64 (15)
C7—S1—C8	104.53 (9)	S1—C8—C13	119.09 (15)

H atoms were constrained as riding atoms, fixed to their parent C atoms at a C—H distance of 0.95 Å. U_{iso}(H) values were set to 1.2U_{eq} for the parent atom.

Data collection: *AFC-7 Diffractometer Control Software* (Molecular Structure Corporation, 1999); cell refinement: *MSC/AFC-7 Diffractometer Control Software*; 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, 1980–2001) and *ORTEP*-3 (Farrugia, 1997); software used to prepare material for publication: *TEXSAN* for Windows and *PLATON*.

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