

2,6-dimethyl-2-[2'(phenylsulfonyl)ethyl]cyclohexanone

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Key indicators

Single-crystal X-ray study

T = 295 K

Mean $\sigma(\text{C}-\text{C}) = 0.006 \text{ \AA}$

R factor = 0.042

wR factor = 0.125

Data-to-parameter ratio = 11.6

For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.2,6-Dimethyl-2-[2'-(phenylsulfonyl)ethyl]-
cyclohexanoneThe structure of the title compound, $\text{C}_{16}\text{H}_{22}\text{O}_3\text{S}$, shows the phenylsulfonylethyl side chain to be in the equatorial orientation.

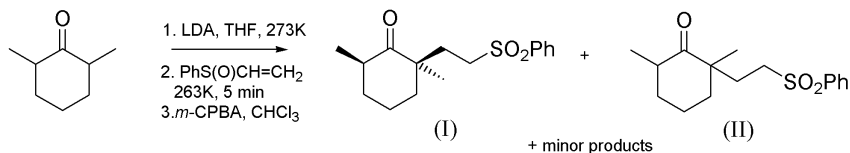
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Comment

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 direct introduction of a two-carbon side chain bearing a sulfur functionality α to a ketone is generally difficult. 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). However, the generality of this approach is evidenced by overalkylation and cyclobutanol formation (Haynes *et al.*, 1991). Herein we report the synthesis, isolation and structural characterization of the novel monoalkylated product, (I), arising from the reaction of the lithium enolate of 2,6-dimethylcyclohexanone (obtained from lithium diisopropylamide, LDA) with phenyl vinyl sulfoxide and subsequent oxidation with *m*-chloroperoxybenzoic acid (*m*-CPBA).



Compound (I) crystallizes in space group $P2_12_12_1$, with one molecule in the asymmetric unit (Fig. 1). The overall conformation of the molecule adopts an approximate *L* shape (Fig. 2). The bond lengths and angles of the molecule are in accord with conventional values (Allen *et al.*, 1987).

2,6-Dimethylcyclohexanone is alkylated at atom C2 by phenyl vinyl sulfoxide, such that the larger substituent is placed in an equatorial orientation. This corresponds to the equatorial phenylsulfonylethyl side chain in the derivative obtained from oxidation, *viz.* compound (I). The methyl groups on C2 and C6 of the cyclohexanone ring are axial and equatorial, respectively. An alkyl group would be expected to be more stable in the 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). Compound (I) was obtained as a diastereomeric mixture with compound (II) (see *Scheme*). At present, it is not possible to determine the relative stereochemistry of compound (II).

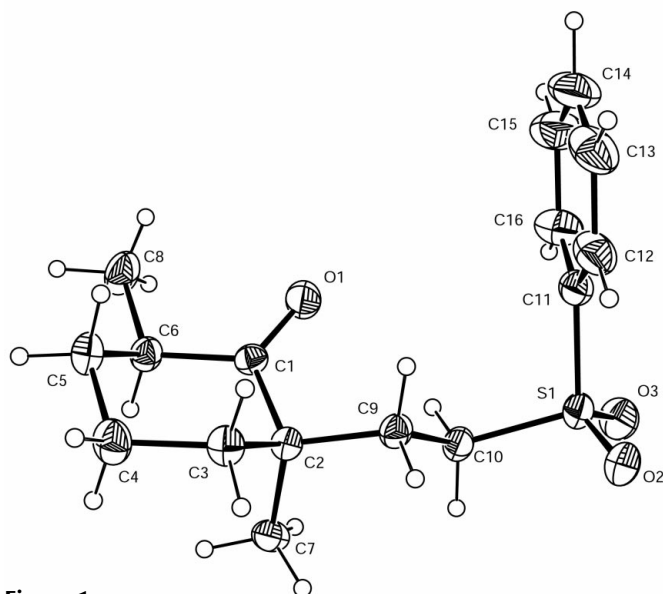


Figure 1
ORTEP-3 (Farrugia, 1997) plot, showing the atomic numbering scheme. Displacement ellipsoids for non-H atoms are drawn at the 30% probability level.

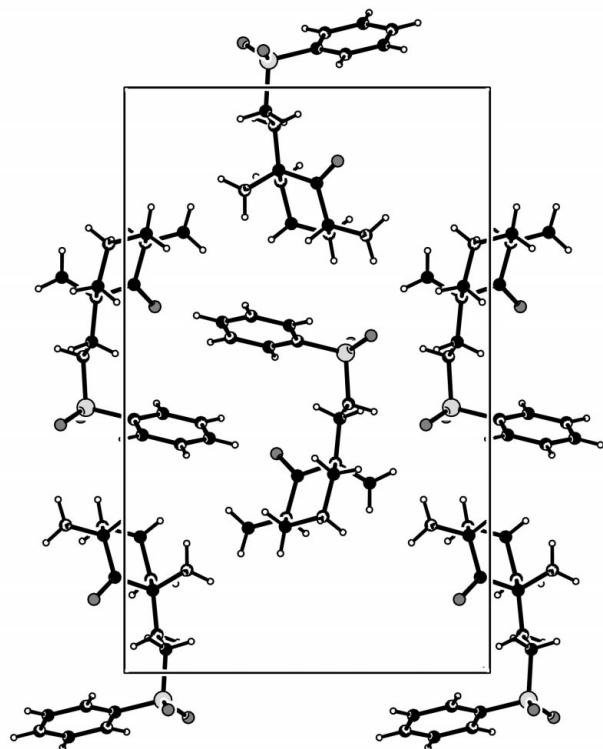


Figure 2
Unit-cell diagram of (I), projected down the *c* axis. The *a* axis is horizontal and the *b* axis is vertical.

Experimental

2,6-Dimethylcyclohexanone (0.55 ml, 3.96 mmol) was reacted with lithium diisopropylamide (1.55 M, 2.56 ml, 3.96 mmol) in THF (25 ml) at 273 K under nitrogen over 1 h. The reaction vessel was shielded from light. Rapid addition of phenyl vinyl sulfoxide (0.55 ml,

3.96 mmol) at 263 K, with a 5 min reaction time and work-up as described elsewhere (Loughlin *et al.*, 2002), gave the crude sulfoxide mixture (1.077 g). This was subsequently oxidized with *m*-CPBA (1 equivalent) 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, 80:20). A mixture of two diastereomers of 2,6-dimethyl-2-[2-(phenylsulfonyl)ethyl]cyclohexanone, compounds (I) and (II) (577 mg, 53%), was obtained in conjunction with mixtures of other minor products. A pure sample of compound (I) was isolated as colourless crystals (m.p. 404.3–405.2 K) by slow evaporation of a hexane–ethyl acetate (80:20) solution of (I) and (II). Analysis found: C 65.45, H 7.71, S 11.03%; calculated for $C_{16}H_{22}O_3S$: C 65.27, H 7.53, S 10.89%; ν_{\max} (KBr)/ cm^{-1} : 1695 (CO), 1299 (SO₂), 1148 (SO₂); δ_H (400 MHz, CDCl₃, p.p.m.): 7.86–7.95 (2H, *m*, *o*-C₆H₅), 7.60–7.66 (1H, *m*, *p*-C₆H₅), 7.52–7.60 (2H, *m*, *m*-C₆H₅), 3.28 (1H, *ddd*, $J_{2,2'} = 14$, $J_{2,1'} = 11.5$, $J_{2,1''} = 5.5$ Hz, 2'-H), 3.13 (1H, *ddd*, $J_{2,2'} = 13.5$, $J_{2,1'} = 11.5$, $J_{2,2''} = 5.5$ Hz, 2'-H), 2.52–2.63 (1H, *m*, 6-H), 1.96–2.04 (1H, *m*, 5-H), 1.47–1.90 (6H, *m*, 2 × 3-H, 2 × 4-H, 2 × 1'-H), 1.24 (1H, *dddd*, $J_{5,5} = 13$, $J_{5,6} = 13$, $J_{5,4} = 13$, $J_{5,4} = 4$ Hz, 5-H), 1.15 (3H, *s*, 2-Me), 0.91 (3H, *d*, $J_{6-Me,6} = 6.5$ Hz, 6-Me); δ_C (50 MHz, CDCl₃, p.p.m.): 215.6, C-1; 148.3, *i*-C₆H₅; 133.5, *p*-C₆H₅; 129.2, *m*-C₆H₅; 127.9, *o*-C₆H₅; 52.2, C-2'; 47.4, C-2; 41.1, C-6; 39.4, C-3; 36.5, C-5; 31.5, C-1'; 23.9, 2-Me; 21.1, C-4; 14.8, 6-Me; ESMS⁺: 317 (MNa⁺, 100%); ESMS⁻: 293 (M–H, 21%).

Crystal data

$C_{16}H_{22}O_3S$	Mo K α radiation
$M_r = 294.41$	Cell parameters from 25 reflections
Orthorhombic, $P2_12_12_1$	$\theta = 13.0$ – 16.5°
$a = 12.641$ (3) Å	$\mu = 0.21$ mm ⁻¹
$b = 20.240$ (5) Å	$T = 295$ K
$c = 6.051$ (2) Å	Prism, colourless
$V = 1548.2$ (7) Å ³	0.60 × 0.40 × 0.20 mm
$Z = 4$	
$D_x = 1.263$ Mg m ⁻³	

Data collection

Rigaku AFC-7R diffractometer	$\theta_{\max} = 27.6^\circ$
ω scans	$h = -6 \rightarrow 16$
Absorption correction: none	$k = 0 \rightarrow 26$
2193 measured reflections	$l = -3 \rightarrow 7$
2094 independent reflections	3 standard reflections
1316 reflections with $I > 2\sigma(I)$	every 150 reflections
$R_{\text{int}} = 0.034$	intensity decay: 2.2%

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0606P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.042$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.125$	$(\Delta/\sigma)_{\max} < 0.001$
$S = 0.99$	$\Delta\rho_{\max} = 0.23$ e Å ⁻³
2094 reflections	$\Delta\rho_{\min} = -0.20$ e Å ⁻³
181 parameters	Flack parameter = 0.41 (17)
H-atom parameters constrained	

Table 1

Selected geometric parameters (Å, °).

S1–O2	1.434 (3)	S1–C11	1.771 (4)
S1–O3	1.443 (3)	O1–C1	1.203 (5)
S1–C10	1.768 (3)		
O2–S1–O3	118.29 (18)	O1–C1–C2	122.2 (3)
O2–S1–C10	108.75 (18)	O1–C1–C6	120.9 (3)
O2–S1–C11	108.15 (18)	S1–C10–C9	113.6 (2)
O3–S1–C10	107.83 (18)	S1–C11–C12	120.5 (3)
O3–S1–C11	107.91 (18)	S1–C11–C16	118.3 (3)
C10–S1–C11	105.16 (18)		

H atoms were constrained as riding atoms, fixed to their parent C atoms at a C—H distance of 0.95 Å. $U_{\text{iso}}(\text{H})$ values were set to $1.2U_{\text{eq}}$ for the parent atom. Determination of the absolute configuration for this structure is ambiguous, with a Flack parameter (Flack, 1983) of 0.4 (2), and the structure may be racemically twinned. Refinement in the inverted structure resulted in no change in the agreement factors, and a Flack parameter greater than 0.5.

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

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