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## Key indicators

Single-crystal X-ray study
$T=295 \mathrm{~K}$
Mean $\sigma(\mathrm{C}-\mathrm{C})=0.006 \AA$
$R$ factor $=0.042$
$w R$ 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.
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## 2,6-Dimethyl-2-[2'-(phenylsulfonyl)ethyl]cyclohexanone

The structure of the title compound, $\mathrm{C}_{16} \mathrm{H}_{22} \mathrm{O}_{3} \mathrm{~S}$, shows the phenylsulfonylethyl side chain to be in the 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 direct introduction of a two-carbon side chain bearing a sulfur functionality $\alpha$ 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).

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Compound (I) crystallizes in space group $P 2_{1} 2_{1} 2_{1}$, 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 C 2 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).


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 ( $0.55 \mathrm{ml}, 3.96 \mathrm{mmol}$ ) was reacted with lithium diisopropylamide $(1.55 \mathrm{M}, 2.56 \mathrm{ml}, 3.96 \mathrm{mmol})$ in THF $(25 \mathrm{ml})$ 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) ( $577 \mathrm{mg}, 53 \%$ ), 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 $\mathrm{C}_{16} \mathrm{H}_{22} \mathrm{SO}_{3}: \mathrm{C} 65.27, \mathrm{H} 7.53, \mathrm{~S} 10.89 \%$; $v_{\text {max }}(\mathrm{KBr}) / \mathrm{cm}^{-1}: 1695(\mathrm{CO})$, $1299\left(\mathrm{SO}_{2}\right), 1148\left(\mathrm{SO}_{2}\right) ; \delta_{\mathrm{H}}\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right.$, p.p.m.): 7.86-7.95 ( 2 H , $\left.m, o-\mathrm{C}_{6} \mathrm{H}_{5}\right), 7.60-7.66\left(1 \mathrm{H}, m, p-\mathrm{C}_{6} \mathrm{H}_{5}\right), 7.52-7.60\left(2 \mathrm{H}, m, m-\mathrm{C}_{6} \mathrm{H}_{5}\right)$, $3.28\left(1 \mathrm{H}, d d d, J_{2^{\prime}, 2^{\prime}}=14, J_{2^{\prime}, 1^{\prime}}=11.5, J_{2^{\prime}, 1^{\prime}}=5.5 \mathrm{~Hz}, 2^{\prime}-\mathrm{H}\right), 3.13(1 \mathrm{H}$, $\left.d d d, J_{2^{\prime}, 2^{\prime}}=13.5, J_{2^{\prime}, 1^{\prime}}=11.5, J_{2^{\prime}, 2^{\prime}}=5.5 \mathrm{~Hz}, 2^{\prime}-\mathrm{H}\right), 2.52-2.63(1 \mathrm{H}, m, 6-$ H), $1.96-2.04(1 \mathrm{H}, m, 5-\mathrm{H}), 1.47-1.90(6 \mathrm{H}, m, 2 \times 3-\mathrm{H}, 2 \times 4-\mathrm{H}, 2 \times$ $\left.1^{\prime}-\mathrm{H}\right), 1.24\left(1 \mathrm{H}, d d d d, J_{5,5}=13, J_{5,6}=13, J_{5,4}=13, J_{5,4}=4 \mathrm{~Hz}, 5-\mathrm{H}\right)$, $1.15(3 \mathrm{H}, s, 2-\mathrm{Me}), 0.91\left(3 \mathrm{H}, d, J_{6-\mathrm{Me}, 6}=6.5 \mathrm{~Hz}, 6-\mathrm{Me}\right) ; \delta_{\mathrm{C}}(50 \mathrm{MHz}$, $\mathrm{CDCl}_{3}$, p.p.m.): 215.6, C-1; 148.3, $i-\mathrm{C}_{6} \mathrm{H}_{5} ; 133.5, p-\mathrm{C}_{6} \mathrm{H}_{5} ; 129.2$, $m-\mathrm{C}_{6} \mathrm{H}_{5} ; 127.9, o-\mathrm{C}_{6} \mathrm{H}_{5} ; 52.2, \mathrm{C}-2^{\prime} ; 47.4, \mathrm{C}-2 ; 41.1, \mathrm{C}-6 ; 39.4, \mathrm{C}-3 ; 36.5$, C-5; 31.5, C-1'; 23.9, 2-Me; 21.1, C-4; 14.8, 6-Me; ESMS+: 317 ( $\mathrm{MNa}^{+}$, 100\%); ESMS-: 293 ( $M-\mathrm{H}, 21 \%$ ).

## Crystal data

$\mathrm{C}_{16} \mathrm{H}_{22} \mathrm{O}_{3} \mathrm{~S}$
$M_{r}=294.41$
Orthorhombic, $P 2_{1} 2_{1} 2_{1}$
$a=12.641$ (3) $\AA$
$b=20.240(5) \AA$
$c=6.051$ (2) $\AA$
$V=1548.2(7) \AA^{3}$
$Z=4$
$D_{x}=1.263 \mathrm{Mg} \mathrm{m}^{-3}$
Mo $\mathrm{K} \alpha$ radiation
Cell parameters from 25 reflections
$\theta=13.0-16.5^{\circ}$
$\mu=0.21 \mathrm{~mm}^{-1}$
$T=295 \mathrm{~K}$
Prism, colourless
$0.60 \times 0.40 \times 0.20 \mathrm{~mm}$

## Data collection

Rigaku AFC-7R diffractometer $\omega$ scans
Absorption correction: none
2193 measured reflections
2094 independent reflections
1316 reflections with $I>2 \sigma(I)$
$R_{\text {int }}=0.034$

$$
\begin{aligned}
& \theta_{\max }=27.6^{\circ} \\
& h=-6 \rightarrow 16 \\
& k=0 \rightarrow 26 \\
& l=-3 \rightarrow 7 \\
& 3 \text { standard reflections } \\
& \quad \text { every } 150 \text { reflections } \\
& \quad \text { intensity decay: } 2.2 \%
\end{aligned}
$$

## Refinement

Refinement on $F^{2}$
$R\left[F^{2}>2 \sigma\left(F^{2}\right)\right]=0.042$
$w R\left(F^{2}\right)=0.125$
$S=0.99$
2094 reflections
181 parameters
H -atom parameters constrained

$$
\begin{aligned}
& w=1 /\left[\sigma^{2}\left(F_{o}{ }^{2}\right)+(0.0606 P)^{2}\right] \\
& \text { where } P=\left(F_{o}^{2}+2 F_{c}^{2}\right) / 3 \\
& (\Delta / \sigma)_{\max }<0.001 \\
& \Delta \rho_{\max }=0.23 \mathrm{e}^{-3} \\
& \Delta \rho_{\min }=-0.20 \mathrm{e} \AA^{-3} \\
& \text { Flack parameter }=0.41(17)
\end{aligned}
$$

## Table 1

Selected geometric parameters $\left(\AA^{\circ},{ }^{\circ}\right)$.

| 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-C | $113.6(2)$ |
| 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 $0.95 \AA . U_{\text {iso }}(\mathrm{H})$ values were set to $1.2 U_{\text {eq }}$ 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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