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An enantiopure bicyclic pentasubstituted piperidine

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Key indicators

Single-crystal X-ray study
T = 89 K
Mean σ(C–C) = 0.002 Å
R factor = 0.030
wR factor = 0.071
Data-to-parameter ratio = 21.7

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

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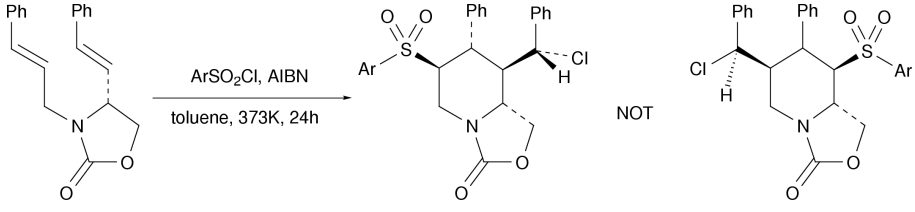
A single addition product has been confirmed in the radical cyclization of a 1,6-diene by a sulfonyl radical. The product, (3*R*,4*S*,5*R*,6*R*)-5-[(1*R*)-1-chloro(phenylmethyl)]-3-[(4-methylphenyl)sulfonyl]-4-phenyl-1-aza-8-oxabicyclo[4.3.0]nonan-9-one, $C_{27}H_{26}ClNO_4S$, results in a highly substituted piperidine.

Comment

Over the past several decades, radical cyclization reactions have been shown to be powerful tools for organic synthesis, enabling carbon–carbon bond formation to be effected in a highly controlled manner (Ellman & Plunkett, 1995). The free-radical cyclization of 1,6-dienes mediated by sulfonyl radicals has been reported by several groups (Kurth & Rodriguez, 1987; Kurth & Rodriguez, 1989; Kurth *et al.*, 1990; Kurth & Kantorowski, 1996). Reaction of diene (I) with *p*-toluenesulfonyl chloride and AIBN (2,2′-azobisisobutyronitrile) in toluene at 373 K for 24 h gives rise to a single addition product in 30% yield. Based upon initial NMR data, it was not immediately obvious which of two possible structures, (II) or (III), could be assigned to this material, although mechanistically (II) appeared the more plausible, based on the expected preference of the sulfonyl radical to add to the less hindered alkene moiety. As a result, we carried out an X-ray crystal structure determination, which confirmed that (II) was indeed the sole product of the reaction.



(I) **(II)** Ar = *p*-Tol **(III)**

The structure determination shows that (II) possesses a piperidine ring fused to the oxazolidinone moiety and all substitutents possess equatorial stereochemistry, thus transmitting with 100% fidelity the original configurational information at the single stereocenter of (I) to the four new stereocenters in the product, including that of the side chain (Beebe *et al.*, 1992, 1995). The conformational characteristics of the system are consistent with those of an early NMR study of the parent bicyclic compound, which concluded that the latter was characterized by a relatively undistorted chair conformation for the piperidine ring (Cahill & Crabb, 1973).

The molecular structure of (II) is presented in Fig. 1. A face-to-face arrangement of one of the phenyl rings and the *p*-tolyl

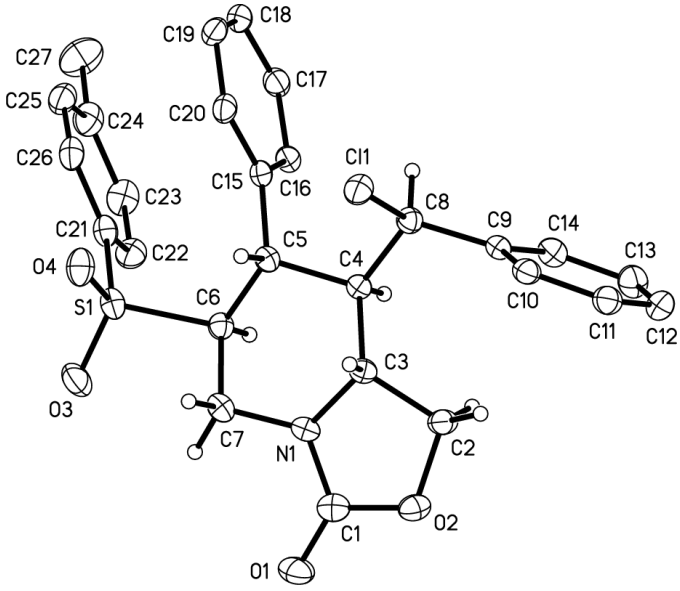


Figure 1
The molecular structure of (II) showing the atom-labeling scheme. Displacement ellipsoids are shown at the 50% probability level.

ring is apparent in the drawing. The distance between the phenyl-ring centroid and the six-membered ring of the *p*-tolyl group is 3.165 Å, and the angle between their normals is 9.43 (10)°. Crystal packing shows that there is a weak hydrogen bond between the primary hydrogen on C4 and the screw-axis-related oxazolidone atom O1.

Experimental

A solution of (4*R*)-*N*-[(*E*)-3-phenyl-2-propenyl]-4-[(*E*)-2-phenyl-1-ethenyl]-2-oxazolidinone (0.050 g, 0.164 mmol) in 3 ml toluene was permitted to react with *p*-toluenesulfonyl chloride (0.031 g, 0.163 mmol) and AIBN (0.005 g) at 373 K for 24 h. The solvent was removed and the residue chromatographed (7:3 EtOAc/hexane) to give 0.024 g (30% yield) of the bicyclic product as a colorless crystalline solid [m.p. 493 K (decomposition)].

Crystal data

$C_{27}H_{26}ClNO_4S$
M_r = 496.00
Monoclinic, $P2_1$
a = 9.5207 (10) Å
b = 9.1141 (10) Å
c = 14.1033 (14) Å
β = 101.957 (8)°
V = 1197.2 (2) Å^3
Z = 2
D_x = 1.376 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 880 reflections
θ = 2.2–31.2°
μ = 0.28 mm^{-1}
T = 89 (2) K
Plate, colorless
0.30 × 0.24 × 0.06 mm

Data collection

Bruker SMART 1000 diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1999)
T_{min} = 0.920, T_{max} = 0.983
16388 measured reflections
6690 independent reflections
5850 reflections with $I > 2\sigma(I)$
R_{int} = 0.024
θ_{max} = 30.0°
$h = -13 \rightarrow 13$
$k = -12 \rightarrow 12$
$l = -19 \rightarrow 19$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.030
$wR(F^2)$ = 0.071
S = 0.97
6690 reflections
308 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0384P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.004
$\Delta\rho_{max}$ = 0.28 e Å^{-3}
$\Delta\rho_{min}$ = −0.21 e Å^{-3}
Absolute structure: Flack (1983)
Flack parameter = −0.03 (4)

Table 1
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C4—H4···O1^{i}	1.00	2.29	3.2237 (19)	155

Symmetry code: (i) $1-x, y-\frac{1}{2}, 1-z$.

Data collection: *SMART* (Bruker, 1999); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1999); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL* (Sheldrick, 1994); software used to prepare material for publication: *SHELXL*97.

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