Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

(4a*SR*,7*RS*,9a*RS*)-9a-Bromo-7-methyl-5,5-dioxo-1,2,4a,6,7,9a-hexahydro-8-oxa-5λ^6-thia-1,4-benzocyclohepten-9-one

Matthias Zeller,[a] Allen D. Hunter,[a]* Paul Sampson[b] and Nataliya Chumachenko[b]

[a]Department of Chemistry, Youngstown State University, One University Plaza, Youngstown, OH 44555-3663, USA, and [b]Department of Chemistry, Kent State University, PO Box 5190, Kent, OH 44242-0001, USA

Correspondence e-mail: adhunter@ysu.edu

Key indicators

Single-crystal X-ray study
T = 100 K
Mean σ(C–C) = 0.003 Å
R factor = 0.029
wR factor = 0.078
Data-to-parameter ratio = 15.3

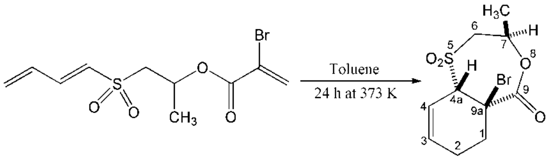
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The title compound, $C_{10}H_{13}BrO_4S$, crystallizes as a racemic mixture in space group $P\overline{1}$. The seven-membered ring exhibits a chair conformation; the methyl group points away from the bromine substituent.

Received 24 March 2004
Accepted 30 March 2004
Online 9 April 2004

Comment

As detailed in the first article in this series (Zeller *et al.*, 2004), two of us (NC and PS) have been exploring the potential utility of sulfone-based tethers in intramolecular Diels–Alder cycloaddition reactions. This has resulted in the preparation of a series of bicyclic β-acyloxy sulfone cycloadducts, several of which have been subjected to analysis using single-crystal X-ray diffraction. In the present paper, the solid-state structure of the title cycloadduct, (I), as established by single-crystal X-ray diffraction methods, is described.



(I)
(major diastereomer)

Compound (I) crystallizes as a racemic mixture of both enantiomers. The six-membered ring exhibits the half-chair conformation expected for cyclohexenes, and the angles at the unsaturated C atoms are 123.62 (17)° (for C4—C3—C2) and 124.12 (17)° (for C3—C4—C4*A*; Fig. 1). The seven-membered ring displays a chair-like conformation. The methyl group on atom C7 is located in the equatorial position, pointing away from the bromine substituent on the bridgehead atom C9*A*.

Experimental

Compound (I) was isolated in 58% yield as the major diastereomer from an intramolecular Diels–Alder cycloaddition reaction of 1-[(*E*)-buta-1,3-dienylsulfonyl]propan-2-yl 2-bromoacrylate in toluene at 373 K. Compound (I) was purified by silica column chromatography (CH_2Cl_2/ether, 40:1) and recrystallized from ethyl acetate/hexane (1:1). Crystals suitable for X-ray diffraction analysis were grown *via* slow evaporation of a CH_2Cl_2 solution.

Crystal data

$C_{10}H_{13}BrO_4S$
$M_r = 309.17$
Triclinic, $P\overline{1}$
$a = 6.0895$ (5) Å
$b = 9.1882$ (7) Å
$c = 10.6027$ (9) Å
$\alpha = 89.383$ (1)°
$\beta = 86.523$ (1)°
$\gamma = 77.697$ (1)°
$V = 578.55$ (8) Å^3
$Z = 2$
$D_x = 1.769$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 5304 reflections
$\theta = 2.3$–28.3°
$\mu = 3.73$ mm^{-1}
$T = 100$ (2) K
Block, colorless
0.5 × 0.5 × 0.5 mm

Data collection

Bruker SMART APEX CCD diffractometer
ω scans
Absorption correction: multi-scan (*SADABS* in *SAINT-Plus*; Bruker, 1997–1999)
$T_{\min} = 0.125$, $T_{\max} = 0.159$
5491 measured reflections

2822 independent reflections
2726 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.030$
$\theta_{\max} = 28.3°$
$h = -8 \rightarrow 8$
$k = -12 \rightarrow 12$
$l = -14 \rightarrow 14$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.029$
$wR(F^2) = 0.078$
$S = 1.06$
2822 reflections
184 parameters
Only coordinates of H atoms refined

$w = 1/[\sigma^2(F_o^2) + (0.0552P)^2 + 0.2933P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 1.12$ e Å^{-3}
$\Delta\rho_{\min} = -1.00$ e Å^{-3}

All H atoms were positioned geometrically. Their coordinates were then refined freely, and their $U_{\rm iso}$ values were defined as 1.2 or 1.5$U_{\rm eq}$ of the parent C atom. The s.u. values of the cell parameters are taken from the software, recognizing that the values are unreasonably small (Herbstein, 2000). The maximum and minimum electron-density peaks are located 0.81 and 0.82 Å, respectively, from atom Br1.

Data collection: *SMART* (Bruker, 1997–2000); cell refinement: *SAINT-Plus* (Bruker, 1997–1999); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 2000); software used to prepare material for publication: *SHELXL*97.

MZ was supported by the NSF (grant No. 0111511), and the diffractometer was funded by the NSF (grant No. 0087210), the Ohio Board of Regents (grant No. CAP-491) and YSU.

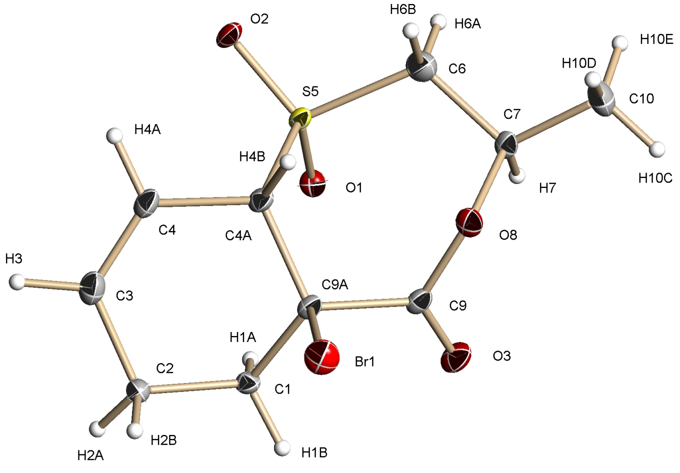


Figure 1
The molecular structure, showing 50% probability displacement ellipsoids.

Funds supporting the synthetic studies (NC and PS) were provided by the Department of Chemistry, Kent State University.

References

Bruker (1997–1999). *SAINT-Plus*. Version 6.02. Bruker AXS Inc., Madison, Wisconsin, USA.
Bruker (1997–2000). *SMART*. Version 5.625 for WNT/2000. Bruker AXS Inc., Madison, Wisconsin, USA.
Bruker (2000). *SHELXTL*. Version 6.10. Bruker AXS Inc., Madison, Wisconsin, USA.
Herbstein, F. H. (2000). *Acta Cryst.* B**56**, 547–557.
Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1997). *SHELXL*97. University of Göttingen, Germany.
Zeller, M., Hunter, A. D., Sampson, P. & Chumachenko, N. (2004). *Acta Cryst.* E**60**, o724–o726.

o728 Matthias Zeller *et al.* • $C_{10}H_{13}BrO_4S$ *Acta Cryst.* (2004). E**60**, o727–o728